EXTRACTION RATES OF OXALIC, NITRIC AND HYDROCHLORIC ACID BY AMBERLITE LA-2 IN A HORIZONTAL RECTANGULAR CHANNEL

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Extraction rates of oxalic acid, nitric acid and hydrochloric acid with Amberlite LA-2 (hereafter called LA-2) in hexane were measured in a horizontal rectangular channel. The experimental results were analyzed by an interfacial reaction model similar to that described in the previous paper4,5) for analyzing the extraction rates of acetic acid and propionic acid with long-chain alkylamines.

1. Extraction of Oxalic Acid

The experimental apparatus and procedures were the same as those described previously.4) The experimental results for oxalic acid are shown in Fig. 1, in which the dimensionless extraction rate of the acid, \( \frac{\Delta C_{A}}{u_1 D_{A} x_{1} C_{A_0}} \), is plotted against \( \frac{u_1}{D_{A}} \) \( \frac{\Delta C_{A}}{u_1 D_{A} x_{1} C_{A_0}} \) at a constant value of \( G_z = \frac{u_1 D_{A} x_{1}}{D_{A} x_{1}} \). Experiments were carried out in the range of low acid concentration \((C_{A_0} \leq 0.011 \text{ kmol/m}^3 \text{ at } C_{W} = 0.013 \text{ kmol/m}^3, \) \( C_{A_0} \leq 0.020 \text{ kmol/m}^3 \text{ at } C_{W} = 0.025 \text{ kmol/m}^3 \) and \( C_{A_0} \leq 0.023 \text{ kmol/m}^3 \text{ at } C_{W} = 0.050 \text{ kmol/m}^3 \)), because it was found that solid products formed at the interface in the high acid concentration ranges.

Oxalic acid (A) reacts with LA-2 (B) to form AB and AB\(_2\) species.2) The amine and products are insoluble in water, while oxalic acid is practically insoluble in hexane. Thus it can be assumed that reaction between A and B proceeds at the interface of the two liquid phases, and the reaction is composed of adsorption step of amine (B), reaction steps between adsorbed species (B\(^*\) or AB\(^*\)) and A or B in the bulk phases at the interface and desorption steps of the products from the interface as shown in Fig. 2, where \( K_{AB1} \), \( K_{AB2} \), and \( K_{AB} \) are the equilibrium constants for each step.\(^*3\) If the rates of all steps in Fig. 2 are assumed to be very rapid, that is, all steps are instantaneously equilibrated at the interface, the relation between \( \frac{\Delta C_{A}}{u_1 D_{A} x_{1} C_{A_0}} \) and \( \frac{u_1}{D_{A}} \) is given by the broken lines in Fig. 1. The differences between the broken lines and experimental results indicate that the extraction rate is influenced by the interfacial reaction rate.

To explain these differences, the following cases are assumed, that is: the rate-controlling steps in Fig. 2 are (1) step 1, (2) step 2, (3) steps 2 and 4, and (4) steps 3 and 5, respectively. For each case, the relation

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\(^*3\) Since the value of \( K_{AB1} \) could not be settled, as shown in the previous paper,\(^3\) the value of \( K_{AB1} \) was assumed to be equal to the value of \( K_{AB2} \).
between $\bar{S}h$ and $\alpha/\beta$ was calculated by the method described in the previous paper.\textsuperscript{3)} In comparison with the standard deviation, $\bar{s}$, between the calculated and experimental results for each case, case (3) gives the best agreement with the experimental results. For this case, interfacial reaction rate equations are written as follows:

\begin{align*}
R_{n1} &= k_{s11}^* K_{s01}^* (C_A^3 C_B - C_{n1}/K_{n1}) \cdot (1 - \theta) - R_{12} \quad (1) \\
R_{12} &= k_{s12}^* K_{s11}^* (C_{n1} + C_{s1}/K_{s1}) \cdot (1 - \theta) \quad (2) \\
(1 - \theta) &= 1.0/(1.0 + K_{s01}^* C_B + K_{s11}^* C_{n1} + K_{s12}^* C_{s1}) \quad (3)
\end{align*}

where $k_{s11}^*$ and $k_{s12}^*$ are the rate constants for steps 2 and 4, respectively, as shown in Table 1. The solid lines in Fig. 1 show the results calculated using Eqs. (1) to (3).

2. Extractions of Nitric and Hydrochloric Acids

The experimental results for the extraction of nitric acid and hydrochloric acid with LA-2 are shown in Figs. 3 and 4. In these systems, acids (A) react with LA-2 (B) to form AB, AB$_2$ and A$_2$B$_2$ species.\textsuperscript{3)} However, in the range of low acid concentration, the concentration of A$_2$B$_2$ species can be assumed to be negligibly small as compared with those of other species. The products are insoluble in water, and nitric acid and hydrochloric acid also insoluble in hexane. Thus, the reaction between A and B is assumed to proceed at the interface, and the reaction scheme can be written as shown in Fig. 2. The equilibrium constants for each step are given in Table 2.\textsuperscript{4)} The broken lines in Figs. 3 and 4 are the results calculated by assuming that all steps in Fig. 2 instantaneously equilibrate at the interface. Some differences between the broken lines and experimental results are found, although the differences are smaller than those shown in Fig. 1. In the same way, four cases were considered to explain these differences. As a result, it was found that in both experimental systems the smallest $\bar{s}$ value among the four cases was obtained for case (3), where the interfacial reaction rate equations are written by Eqs. (1) to (3), and the values of $k_{s11}^*$ and $k_{s12}^*$ are shown in Table 1. The calculated results agree well with the experimental results as shown in Figs. 3 and 4.

Thus, we can conclude that the extraction rates of oxalic, nitric and hydrochloric acid with LA-2 are interpreted by the interfacial reaction model controlled by the reaction steps at the interface.

\textbf{Nomenclature}

$\Delta C_A$ = difference of concentration of acid in aqueous phase between inlet and outlet of extraction cell [kmol/m$^3$]

\textsuperscript{4)} In these cases, $K_{s11} = C_{s1}/(C_A^3 \cdot C_B)$, although $K_{s11} = C_{s1}/(C_A^3 \cdot C_B)$ in the case of oxalic acid.

\begin{table}[h]
\centering
\caption{Reaction rate constants for steps 2 and 4}
\begin{tabular}{|c|c|c|}
\hline
 & (COOH)$_2$ & HNO$_3$ & HCl \\
\hline
$k_{s11}$ [m$^3$/kmol$^2$.s] & 1.5 \times 10$^3$ & - & - \\
$k_{s12}$ [m$^3$/kmol.s] & - & 2.5 \times 10$^2$ & 2.5 \times 10$^2$ \\
$k_{s12}$ [m/s] & 10$^{-6}$ & 3.1 \times 10$^{-3}$ & 5.2 \times 10$^{-3}$ \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{Experimental result for extraction of nitric acid with LA-2 in hexane.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4}
\caption{Experimental result for extraction of hydrochloric acid with LA-2 in hexane.}
\end{figure}

\begin{table}[h]
\centering
\caption{Extraction equilibrium constants and interfacial adsorption constants for LA-2 in hexane and nitric acid and hydrochloric acid system}
\begin{tabular}{|c|c|c|}
\hline
 & HNO$_3$ & HCl \\
\hline
$K_{s1}$ [m$^3$/kmol$^2$] & 3.8 \times 10$^4$ & 2.5 \times 10$^3$ \\
$K_{s2}$ [m$^3$/kmol] & 2.4 \times 10$^5$ & 7.1 \times 10$^2$ \\
$K_{s12}$ [m$^3$/kmol] & 2.7 \times 10$^4$ & 5.7 \times 10$^4$ \\
$K_{s12}$ [m$^3$/kmol] & 2.9 \times 10$^7$ & 9.5 \times 10$^2$ \\
$K_{s22}$ [m$^3$/kmol] & 1.7 \times 10$^8$ & 5.4 \times 10$^3$ \\
$K_{s22}$ [m$^3$/kmol] & 2.6 \times 10$^7$ & 7.1 \times 10$^4$ \\
\hline
\end{tabular}
\end{table}

\textbf{Nomenclature}

$C$ = concentration [kmol/m$^3$]

$D$ = diffusion coefficient [m$^3$/s]

$G_z$ = Graetz number (= $h_\eta^2/D_\eta x_\eta$) [$-$]

$h$ = height of liquid phase [m]
Letter to the Editor

COMMENTS ON THE PAPER “PREDICTION AND STABILITY ANALYSIS OF CHOKING IN VERTICAL PNEUMATIC CONVEYING”

Dear Sir:

Recently, Matsumoto, Sato, Suzuki and Maeda\(^9\) (hereafter referred to as MSSM) expressed their view on the necessity of global consideration of pressure drop characteristics of blower, air distribution piping system and of vertical pneumatic conveying line. This thesis changes essentially the previous point of view on the phenomenon of choking in vertical pneumatic conveying. \textit{An identical thesis and conclusions have been presented by us in ref. 1 and in an earlier Polish publication.}\(^2\) The method proposed by us is also mentioned by Leung.\(^8\)

The results of our experiments, carried out in an installation equipped with a transport line of a diameter almost 3 times larger (0.0585 m) than in ref. 9 have confirmed the validity of the hypothesis that the critical velocity of the gas conveying a granular material corresponds to the point of tangency of the characteristic of the vertical transport and of the effective characteristic of the blower.

MSSM\(^9\) did not mention that the pneumatic transport system is quite rarely as simple as presented in their Fig. 1; more often it is equipped with systems for separation of the granular material and—many a time—with an extended piping system for air (gas) after realization of the pneumatic conveying (e.g. system with closed gas circulation). Also, these elements have their own pressure drop characteristic, which must allowed for in the analysis of the stability of operation. Disregarding them may lead often to serious errors. Of course, the way of carrying out the analysis does not change, for one can abstractly, in an arbitrary manner, displace the elements, situated beyond transport, before the feeding point (since all the resistances on the air flow lines are connected in series). The pressure drop characteristics at the feeding point of granular material will evidently be different in the two cases (i.e. of taking into account or not taking into account the hydraulic resistance concerning the elements situated beyond the pneumatic conveying). Hence in both cases two different critical velocities of pneumatic transport can be determined. The velocity obtained in the case of the allowance for all the resistances will be, of course, correspondingly lower.

In the papers ref. 3, 4 we have presented, on the basis of obtained results, the practically important problems of selection of optimal parameters of operation of vertical pneumatic conveying of granular materials as well as an analysis of operation of vertical pneumatic conveying from the viewpoint of selection of the blower and of the elements of transport piping system.

In view of the great practical significance of pneumatic conveying we would like to make known our own observations, which to a higher extent render more practical the proposal concerning prediction of choking and which have not been allowed for by MSSM.\(^9\)

These observations concern the following problems:

1) validity of the proposal as above in the case of polydisperse materials, which are more important from the point of view of technology.

Literature Cited