Ion Exchange Accompanied by Neutralization Reaction: Removal of Dilute Acids by Anion Exchange

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ABSTRACT

The kinetics of exchange between an anion resin in the OH\(^-\) form with dilute acids was studied in a batch system. The resin used was Dowex 1-X8 and the acids prepared for the experimental work were 0.005 to 0.01 N HCl and H\(_2\)SO\(_4\). The results of study showed that a film diffusion model with a constant rate parameter fits all experimental data very well. The experimental results also showed that the rate is inversely proportional to the resin radius as predicted by the film diffusion model. It was found that the rate for Cl\(^-\)-OH\(^-\) exchange is higher than that for the SO\(_4\)^{2-}-OH\(^-\) exchange. This higher rate of exchange is attributed to the higher effective diffusivity for the HCl-OH\(^-\) system as compared to that for the H\(_2\)SO\(_4\)-OH\(^-\) system.

INTRODUCTION

In an ordinary ion-exchange process, the counterions of different species exchange with each other. In this case the co-ions in the system do not undergo any changes. As a result, the total concentration of counterions and co-ions remains constant before and after exchange. Most of the studies on ion exchange are confined to this type of process in which the result of the exchange is an alteration of the composition of counterions in both the solution and resin phases. There are a number of processes in which chemical reactions are involved in the ion exchange. Helfferich (1, 2) and Helfferich and Hwang (3) have examined some of these processes. The chemical reactions involved may deal with neutralization, complex formation, precipitation, or reaction of weak acid and base. Of these types of reactions, the neutralization and complex formation are of practical importance as they are related to many useful
industrial applications. For instance, the deionization of water by ion exchange is achieved by the neutralization of \( \text{OH}^- \) ion released from the anion resin. In the case of complex formation, many processes have been developed to capitalize on the enhancement of rate and selectivity due to the accompanied complex formation in the exchange process.

At present the demand for superpure water is increasing due to the rapid expansion of the electronic and microelectronic industries (4). The production of deionized water by ion exchange can be carried out by using separate cation and anion beds in series or by using mixed beds (5–10). For the two-bed system, the exchange in the anion bed is between the \( \text{OH}^- \) form of resin and \( \text{Cl}^- \) and \( \text{SO}_4^{2-} \) ions in the feedwater. The design and operation of the anion bed requires ample understanding of the kinetics of exchange which is accompanied by the neutralization reaction. For ease of experimental work and to be able to use simple models for data analysis, most kinetics studies on ion exchange are carried out in a batch system. In this study we also employed the batch method to examine the kinetics of an ion-exchange process accompanied by the neutralization reaction. The experimental work covered anion exchange of both dilute \( \text{HCl} \) and \( \text{H}_2\text{SO}_4 \) and a strong anion exchanger in the \( \text{OH}^- \) form. It is hoped that the results of this study can be utilized for the design and operation of industrial applications of deionization by ion exchange.

**ION EXCHANGE ACCOMPANIED BY CHEMICAL REACTIONS**

Helfferich (1, 2) initiated the theoretical study of ion exchange accompanied by chemical reactions. He classified these reactions into several categories including neutralization, complex formations, and reactions involving weak acid or base (or salts of weak acid and base). A recent study (11) on the removal of acidic substances by weak anion-exchange resins can also be considered as an exchange process accompanied by chemical reaction. Since most ion-exchange processes are conducted in fixed beds, precipitation as a result of chemical reaction will not be of any practical use except possibly with a well-agitated batch system. Ion exchange accompanied by neutralization involves reactions between strong acids and \( \text{OH}^- \) ions released by an anion exchanger or reactions between strong bases and \( \text{H}^+ \) ions released by a cation exchanger. Typical reactions dealing with strong acidic cation resins or strong base anion resins are

\[
\text{RH} + \text{MOH} \leftrightarrow \text{RM} + \text{H}_2\text{O} \quad (1)
\]
\[
\text{ROH} + \text{HA} \leftrightarrow \text{RA} + \text{H}_2\text{O} \quad (2)
\]

where \( R \) represents the matrix group, and \( \text{MOH} \) and \( \text{HA} \) are a strong base and a strong acid, respectively. For the case in which weak acidic or weak base
resins are involved, a typical reaction is (2)

\[ \text{RNa} + \text{HCl} \leftrightarrow \text{RH} + \text{NaCl} \]  

(3)

The kinetics for this type of reaction is more complex compared to the case where reactions deal with strong acidic or base resins.

**KINETICS OF ION EXCHANGE WITH NEUTRALIZATION REACTION**

In general, the rate of ion exchange accompanied by chemical reaction is faster than those due solely to mass transfer or a diffusion step. In the case of the reactions represented by Eqs. (1) and (2), since the co-ions in the solutions are excluded from entering the resin bead due to the Donnan effect, the reaction occurs at the resin bead surface. Thus the rate is either determined by the diffusion of the co-ion and the counterion from the solution bulk to the bead surface or by interdiffusion between the two exchange counterions in the resin.

**Film Diffusion Rate Control**

In the case of film diffusion rate control and for a batch system with a finite solution volume, the following rate equation is formulated for a binary exchange:

\[ \frac{dq}{dt} = K_f (C - C^*) \]  

(4)

where \( q \) and \( C \) are the concentration of one of the species of the two counterions in the resin and in the solution, respectively, \( K_f \) is the mass transfer rate parameter, \( C^* \) is the equilibrium solution concentration at the solid–liquid film interface, and \( t \) is the absolute time.

At the resin bead surface the counterion from the solution is neutralized by either \( \text{OH}^- \) or \( \text{H}^+ \) ions released from the resin. Because of the electroneutrality of ions at the resin–liquid surface, and since the dissociation constant for water is \( 10^{-14} \), the value of \( C^* \) is small and can be neglected in the rate equation. A mass balance for one species of the two counter ions is

\[ V(C_0 - C) = V_r(q - q_0) \]  

(5)

where \( V \) and \( V_r \) are the volume of the solution and the volume of the resin, respectively, and \( C \) and \( q \) are the concentration of one the species of the two counterions in the solution and in the resin, respectively. Subscript “0” denotes the initial condition.

Combining Eqs. (4) and (5) and neglecting \( C^* \):

\[ \frac{dq}{dt} = K_f [C_0 - (V_r/V)(q - q_0)] \]  

(6)
integrating with initial condition \( t = 0, q = q_0 = 0 \):

\[
\frac{V_t q}{VC_0} = 1 - \exp\left(- \frac{K_f V_r t}{V}\right)
\]  

(7)

From the mass balance of Eq. (5),

\[
x = \frac{C}{C_0} = \exp\left(- \frac{K_f V_r t}{V}\right)
\]  

(8)

Let \( y = q/Q_c \), where \( Q_c \) is the exchanger capacity in meq/mL and \( y \) is the equivalent fraction of one of the two counterions in the resin.

\[
y(t) = \frac{1}{R} \left[ 1 - \exp\left(- \frac{K_f V_r t}{V}\right) \right]
\]  

where \( R \) is the stoichiometric ratio defined by

\[
R = \frac{V_t Q_c}{(VC_0)} = \frac{WQ_c'}{(VC_0)}
\]

here \( W \) is the weight of resin in grams and \( Q_c' \) is the resin capacity on a dry basis and the unit is expressed in meq/g.

In the case of \( R < 1 \):

\[
y(t) = \frac{1}{R} \left[ 1 - \exp\left(- \frac{K_f V_r t}{V}\right) \right] \text{ for } 0 < t < t_c
\]  

(10)

\[
y(t) = 1 \text{ for } t > t_c
\]

where

\[
t_c = \frac{(V/V_r)}{K_f} \ln \frac{1}{1 - R}
\]

In the case of \( R > 1 \) the fractional attainment of final steady state is defined by

\[
F(t) = \frac{y(t)}{y(\infty)} = 1 - \exp\left(- \frac{V_t K_f t}{V}\right)
\]  

(11)

Particle Diffusion Rate Control

The equations derived by Helfferich (1) made use of the analytic solution obtained from Fick’s second law or numerical solution from the Nernst–Planck equations (12). If \( G(t) \) represents the fractional attainment of equilibrium for an ordinary ion exchange, then for the case of \( R < 1 \):

\[
F(t) = G(t)
\]  

(12)
For the case of $R > 1$:

\[ F(t) = RG(t) \text{ for } 0 < t < t_c \]
\[ F(t) = 1 \text{ for } t > t_c \]  

(13)

where the value of $t_c$ is determined from $RG(t_c) = 1$, and $G(t_c)$ is obtained from Fick’s second law of solution or numerical solution of the Nernst–Planck equations.

### Other Kinetic Models

The above discussion deals primarily with a strong acidic or base resin. In the case of chemical reactions involving weak resins or weak electrolytes present in solution, various kinetics models have been attempted. For example, Helfferich (2) proposed the use of a shell–core model (13, 14). A slightly more complex model (15) was used in the study of the reaction between a strong acidic exchanger and a weak base in the form of an ammonia solution.

### EXPERIMENTAL

#### Experimental Systems

A strong anion resin, Dowex 1-X8, was used in the experimental work. Three commercially available resin sizes, 20–50 mesh, 50–100 mesh, and 100–200 mesh, were employed. Most of the experiments were conducted with the 20–50 mesh resins. Dilute HCl and H$_2$SO$_4$ with concentrations of about 0.005 to 0.01 N were prepared for the kinetics study of HCl–OH$^-$ and H$_2$SO$_4$–OH$^-$ exchange. The reacting vessel was a rectangular glass container of 400 cm$^2$ cross-section area and had a maximum capacity of 6 L. A total of 12 experimental runs were performed with the experimental conditions listed in Table 1.

#### Resin Capacity Determination and Analytical Methods

The resin was originally in chloride form and was converted to OH$^-$ form by a standard procedure for the kinetics study of HCl–OH$^-$ and H$_2$SO$_4$–OH$^-$ exchange. The capacity of the resin in chloride form was determined to be 3.985 meq/g for the 20–50 mesh. Similarly, the capacities for 50–100 mesh and 100–200 mesh resins were found to be 4.028 and 4.113 meq/g, respectively. For the analytical work, aliquot samples were diluted by a factor of 20 before analyzing for Cl$^-$ or SO$_4^{2-}$ concentration by a Hach DR/2000 spectrophotometer.
Experimental Procedure

A typical run started with a predetermined amount of the OH$^-$ form of resin placed in a cubical glass vessel (20 cm $\times$ 20 cm $\times$ 15 cm) containing a fixed volume of the prepared HCl or H$_2$SO$_4$ solution. A magnetic stirrer was activated when the experiment commenced. Samples of solution were withdrawn periodically from the reaction vessel and the corresponding time for these withdrawals were recorded. These samples were later analyzed for Cl$^-\,$ or SO$_4^{2-}$ concentration. Since most of the rate processes start at a very high initial rate, sampling was more frequent during the early period of an experimental run. The analyses for the Cl$^-$ or SO$_4^{2-}$ concentrations for these samples were performed with the aid of a Hach DR/2000 spectrophotometer. During the experimental run the pH of the solution in the reaction vessel was measured and recorded at frequent intervals. The experiment was terminated when the pH measurements showed no substantial changes. Four experimental runs for the HCl–OH$^-$ system and three experimental runs for the H$_2$SO$_4$–OH$^-$ system were conducted. In addition, the effect of resin size and the degree of agitation were also studied by performing five additional batch experiments. These additional experiments were for the exchange between chloride and hydroxide ions.

RESULT AND DISCUSSIONS

HCl–OH$^-$ System

Four experimental runs were conducted employing different values of $R$. Except for one run, the initial HCl concentration in each run was about 0.005
N. The results of these four runs were fitted with a film diffusion rate control model. As pointed out by Helfferich (1, 2), for an ion-exchange process accompanied by neutralization, the rate is actually controlled by the film diffusion of the counterion Cl\(^-\) and the co-ion H\(^+\). In contrast, the rate could have been controlled by the diffusion of the two counterions in an ordinary ion exchange. This argument can be explained by considering a charge balance at the liquid–solid interface:

\[ [H^+] = [OH^-] + [Cl^-] \]

Thus [Cl\(^-\)] or [OH\(^-\)] is less than [H\(^+\)]. Since the dissociation constant of water is \(10^{-14}\), that of [OH\(^-\)] is less than \(10^{-7}\). This means that any OH\(^-\) ion released by the exchanger will be consumed at the solid–liquid interface provided the HCl solution concentration is greater than \(10^{-7}\). Since the consumption of OH\(^-\) is rapid at the interface, any amount of Cl\(^-\) present at the interface will be immediately exchanged with the OH\(^-\) ion from the exchanger. For this reason the assumption of a negligible value of \(C^*\) (chloride concentration at the liquid–solid surface) is justified, and Eqs. (8) and (9) are applicable. Equation (8) suggests that a plot of \(\ln[C_0/C(t)]\) against \(t\) should yield a straight line with the slope equal to \(K_f V_f/V\) or \(K_f R C_0/Q_c\). The rate parameter, \(K_f\), can then be determined from the value of the slope. Alternatively, individual value of \(K_f\) can be calculated from experimental \(C(t)\) by

\[ K_f(t) = \frac{Q_c \ln[C_0/C(t)]}{RC_0 t} \]

In all four runs it was found that the fit of data with the film diffusion model was very good. Calculation for individual values of \(K_f\) also showed that \(K_f\) is fairly constant, at least for times up to about 30 minutes.

In most of the kinetics studies on ion exchange, the data are usually reported in terms of \(F(t)\), conventional known as fractional attainment of equilibrium. In this work, only a single type of counterion of a binary system was present initially in the solution and in the resin. The term \(F(t)\) can thus be more appropriately interpreted as fractional conversion of one species of counterion to another. To calculate \(F(t)\), it is necessary to know the variation of \(q\) with time. A direct measurement of \(q(t)\) is not easy to perform. However, \(q(t)\) can be determined from a mass balance using the measured \(C(t)\) data. Figures 1 and 2 show the experimental \(C(t)/C_0\) data together with the fitted theoretical curve based on the film diffusion model. The calculated values of \(q(t)/Q_c\) from mass balance for Run 2 are also shown Fig. 2. Similarly, a plot of \(F(t)\) versus time from the data for Run 1 is also shown in Fig. 1. Both Runs 1 and 2 were conducted with \(R\) greater than unity. For these two runs, the total resin capacity available is more than the total counterions initially present in the solution. With the zero \(C^*\) assumption, the value of \(q/Q_c\) approaches the value of \(1/R\)
at the final steady state. Thus, the final equilibrium value for $q/Q_c$ is 0.476 for Run 1 and 0.744 for Run 2. In terms of $F$, a value of unity is reached for both runs at the final steady state. Experimental and calculated results of $x(t)$ and $y(t)$ for Runs 3 are shown in Fig. 3. Both Runs 3 and 4 were conducted by em-

FIG. 1  Experimental and calculated $C(t)/C_0$ and $F(t)$ versus time for HCl–OH$^-$ exchange, $C_0 = 0.00476$ N HCl, $R = 2.101$.

FIG. 2  Experimental and calculated $C(t)/C_0$ and $q(t)/Q_c$ versus time for HCl–OH$^-$ exchange, $C_0 = 0.00558$ N HCl, $R = 1.344$. 

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ploying $R$ values of less than unity. For $R$ less than unity, the solutions in exponential form for $x(t)$ and $y(t)$ are valid only up to a critical time value because of the mass balance consideration. This critical time is obtained by substituting the value of $y$ equal to unity in Eq. (9) and solving for $t$. In the case of Run 3, the calculated $t_c$ is 27.5 minutes and for Run 4 the calculated $t_c$ is 10.2 minutes. When time approaches $t_c$, the resin is nearly exhausted of any $\text{OH}^-$ ions. The assumption of negligible $C^*$ is not quite justified, and the quality of the fit with Eq. (8) is affected. In practical application, it is never economical to operate the resin close to exhaustion. Thus, the rate equation based on negligible surface concentration compared to the bulk solution concentration is still very useful. It is interested to note that the diffusion rate control equation based on this assumption is identical in form to the equation formulated for a first-order irreversible reaction. However, each equation arises from a different physical interpretation of the rate mechanism.

In conjunction with use of the diffusion model, the quantity $K_f$ is equal to $3D/(r_0\delta)$ as derived from Fick’s law. From experimental data for Runs 1 to 4, the values of $K_f$ were determined from the quantity $K_fRC_0/Q_c$, which is the slope of the plot of $\ln(1/x)$ versus $t$. Table 2 summarizes the values of $K_fRC_0/Q_c$ obtained. The corresponding calculated $K_f$ and $D/(r_0\delta)$ are also shown in the same table. The film thickness can be estimated if the effective diffusivity, $D$, and the resin bead size, $r_0$, are known. Runs 1 to 4 were conducted with a resin size of 20–50 mesh; an average value of $r_0$ is assumed to be 0.035 cm. The value of $D_{\text{HCl}}$ can be derived by equating the net flux of $\text{H}^+$...
and Cl\(^-\) ions and eliminating the electric potential flux term to obtain the following expression (1):

\[
\frac{1}{D_{\text{HCl}}} = \frac{1}{2} \left( \frac{1}{D_{\text{H}^+}} + \frac{1}{D_{\text{Cl}^-}} \right) \quad \text{or} \quad D_{\text{HCl}} = \frac{2D_{\text{H}^+}D_{\text{Cl}^-}}{D_{\text{H}^+} + D_{\text{Cl}^-}}
\]

Based on the calculated results of Robinson and Stokes (16), the self-diffusion coefficients for hydrogen and chloride ions at 25 °C were \(D_{\text{H}^+} = 9.31 \times 10^{-5}\) cm\(^2\)/s and \(D_{\text{Cl}^-} = 2.03 \times 10^{-5}\) cm\(^2\)/s. The value of \(D\) calculated is 3.33 \(\times 10^{-5}\) cm\(^2\)/s. The film thickness estimated for Run 1 to 4 is about 0.006 to 0.007 cm. Helfferich (17) stated that film thickness estimated from hydrodynamics consideration or kinetics measurements is about 0.001 to 0.01 cm. The calculated film thickness value based on the kinetics experiments of this work appears to be reasonable. It is to be noted that the values of \(D/\(r_0\delta\)\) for Runs 1 to 4 as listed in Table 2 are very close to each other. This is to be expected since these four runs were all conducted using the same size of resin and with the same degree of stirring in the reaction vessel.

### H\(_2\)SO\(_4\)–OH\(^-\) System

The most common anions present in tap water or brackish water are chlorides and sulfates. For application in the deionization of water by ion exchange, the kinetics of exchange between resins in OH\(^-\) form and dilute sulfuric acid were also investigated in this study. Three experimental runs were conducted. The H\(_2\)SO\(_4\) solution concentration employed for the studies was about 0.005 to 0.01 N. Batch Runs 5 and 6 were performed with \(R\) equal to 1.98 and 1.56, respectively. The experimental data of Run 5 and the fitted curves for \(x(t)\), \(y(t)\) or \(F(t)\) are shown in Fig. 4. Again, a plot of \(\ln(C_0/C)\) versus time yields a straight line with a slope equal to \(K_fV_r/V\). Figure 5 shows the experimental results for the run in which \(R\) was less than unity. The calculated

### Table 2

Summary of Calculations for \(K_fRC_0/Q_c\) and \(D/r_0\delta\) for Runs 1 to 7

<table>
<thead>
<tr>
<th>Run</th>
<th>(K_fRC_0/Q_c) (min(^{-1}))</th>
<th>(R)</th>
<th>(C_0) (N)</th>
<th>(Q_c) (meq/mL)</th>
<th>(K_f) (s(^{-1}))</th>
<th>(D) (\times 10^{-5}) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.173</td>
<td>2.101</td>
<td>0.00476</td>
<td>1.507</td>
<td>0.425</td>
<td>0.004</td>
</tr>
<tr>
<td>2</td>
<td>0.136</td>
<td>1.344</td>
<td>0.00558</td>
<td>1.507</td>
<td>0.456</td>
<td>0.015</td>
</tr>
<tr>
<td>3</td>
<td>0.091</td>
<td>0.916</td>
<td>0.00546</td>
<td>1.507</td>
<td>0.455</td>
<td>0.015</td>
</tr>
<tr>
<td>4</td>
<td>0.076</td>
<td>0.490</td>
<td>0.01023</td>
<td>1.507</td>
<td>0.373</td>
<td>0.125</td>
</tr>
<tr>
<td>5</td>
<td>0.055</td>
<td>1.984</td>
<td>0.00504</td>
<td>1.507</td>
<td>0.138</td>
<td>0.046</td>
</tr>
<tr>
<td>6</td>
<td>0.038</td>
<td>1.558</td>
<td>0.00493</td>
<td>1.507</td>
<td>0.125</td>
<td>0.042</td>
</tr>
<tr>
<td>7</td>
<td>0.026</td>
<td>0.497</td>
<td>0.01003</td>
<td>1.507</td>
<td>0.133</td>
<td>0.044</td>
</tr>
</tbody>
</table>
$t_c$ is about 26 minutes, which agrees very closely with the experimental data shown in the figure. For this run the fit of the film diffusion rate control model is also very satisfactory. Rate data for $\text{H}_2\text{SO}_4-\text{OH}^-$ exchange show that its kinetics of exchange is much slower compared to that of $\text{HCl}-\text{OH}^-$ exchange.

**FIG. 4** Experimental and calculated $C(t)/C_0$ and $F(t)$ versus time for $\text{H}_2\text{SO}_4-\text{OH}^-$ exchange, $C_0 = 0.00504 \text{ N H}_2\text{SO}_4$, $R = 1.984$.

**FIG. 5** Experimental and calculated $C(t)/C_0$ and $q(t)/Q_c$ versus time for $\text{H}_2\text{SO}_4-\text{OH}^-$ exchange, $C_0 = 0.01003 \text{ N H}_2\text{SO}_4$, $R = 0.497$. 

The values of $K_f$ determined for the three experimental batch runs are listed in Table 2. The calculated values of $D/(r_0 \delta)$ for Runs 5 to 7 are also listed in the same table. As can be seen from the table, the value of $D/(r_0 \delta)$ determined is about one-third of that of the HCl–OH$^-$ system. Since the resin size and the stirring speed were the same in these experiments, the higher rate must be attributed to a higher value of $D$ for the HCl–OH$^-$ system. If one assumes that all sulfate ions are present as $SO_4^{2-}$, the formula for evaluating $D_{H_2SO_4}$ is

$$D = D_{H_2SO_4} = \frac{6D_{H^+}D_{SO_4^{2-}}}{4D_{SO_4^{2-}} + 2D_{H^+}}$$

Substituting $D_{SO_4^{2-}} = 1.06 \times 10^{-5}$ cm$^2$/s and $D_{H^+} = 9.31 \times 10^{-5}$ cm$^2$/s, the calculated value of $D_{H_2SO_4}$ is $2.59 \times 10^{-5}$ cm$^2$/s. If sulfate is assumed to be present entirely in the HSO$^-_4$ form, then

$$D = \frac{2D_{H^+}D_{HSO_4^-}}{D_{HSO_4^-} + D_{H^+}}$$

Assuming $D_{HSO_4^-} = 1.0 \times 10^{-5}$ cm$^2$/s, the calculated $D_{H_2SO_4} = 1.8 \times 10^{-5}$ cm$^2$/s. The first dissociation constant for $H_2SO_4$ is very large. The distributions of $SO_4^{2-}$ and $HSO_4^-$ species are primarily determined from the second dissociation in which $K_2 = [H^+][SO_4^{2-}]/[HSO_4^-] = 0.012$. For a 0.005 N $H_2SO_4$ solution the fraction of $H_2SO_4$ in HSO$^-_4$ form is about 0.26, and for a 0.01 N $H_2SO_4$ solution the fraction in HSO$^-_4$ form is about 0.41. A reasonable estimate for $D_{H_2SO_4}$ can thus be assumed to be about $2 \times 10^{-5}$ cm$^2$/s. It was mentioned previously that the calculated $K_f$ for the $H_2SO_4$–OH$^-$ system is about a third of that of the HCl–OH$^-$ system. Since the estimated value of $D_{H_2SO_4}$ is less than one-half that of $D_{HCl}$, the slower rates for $SO_4^{2-}$–OH$^-$ must be due to its smaller effective diffusivity. Since an ion exchanger tends to prefer ions with a higher valence, the selectivity of sulfate ions is expected to be higher than that of chloride ions. However, because of its smaller size, chloride ions have a faster rate of exchange.

**Factors Affecting the Kinetics of Exchange**

**Solution Concentration**

All the solution concentrations prepared for this study were about 0.005 N with the exception of two runs with a concentration of about 0.01 N. The results shown for Runs 4 and 7 indicate that film diffusion rate control is still valid at a concentration of about 0.01 N. The calculated rate parameter, $D/(r_0 \delta)$, also shows no significant difference compared with the results obtained for a 0.005 N solution. Thus it is reasonable to state that the effective diffusivities do not vary much between 0.005 and a 0.01 N solutions. It is likely that a variation in the rate parameter may arise when concentrated solutions are employed, and that the contribution of particle diffusion to the rate of exchange is significant.
Effect of Resin Size

Figure 6 shows the effect of using three different sizes of resin on the rate of exchange. As expected, the smaller the resin size, the faster the attainment of a final steady-state. With the same experimental conditions except for resin size, the rate of exchange is inversely proportional to the resin radius. This is consistent with the theoretical equation derived for the film diffusion rate control model. The rate parameter is proportional to \( \frac{D}{r_0} \) and inversely proportional to \( r_0 \). When experiments are conducted with the same solution concentration and the same degree of agitation, the value of \( \frac{D}{\delta} \) is expected to be the same. Hence the rate should be linearly inversely proportional to the resin bead radius. For particle diffusion, theoretical derivation (18) indicates that the rate is inversely proportional to the square of the resin radius. The calculations shown in the Table 3 indicate that the rate parameter tends to vary linearly with the reciprocal of the resin radius rather than with the reciprocal of the square of the resin radius. This gives further evidence that the rate is film diffusion rate controlled.

TABLE 3
Summary of Calculations for \( K_f \) and \( D/r_0 \delta \) for Resin Size Effect Runs

<table>
<thead>
<tr>
<th>Run</th>
<th>( \frac{K_f R C_0}{Q_c} ) (min(^{-1}))</th>
<th>( R )</th>
<th>( C_0 ) (N)</th>
<th>( r_0 ) (mesh no.)</th>
<th>( K_f ) (s(^{-1}))</th>
<th>( \frac{D}{r_0 \delta} ) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.173</td>
<td>2.101</td>
<td>0.00476</td>
<td>20–50</td>
<td>0.425</td>
<td>0.142</td>
</tr>
<tr>
<td>8</td>
<td>0.571</td>
<td>1.729</td>
<td>0.00584</td>
<td>50–100</td>
<td>1.434</td>
<td>0.478</td>
</tr>
<tr>
<td>9</td>
<td>0.982</td>
<td>1.827</td>
<td>0.00564</td>
<td>100–200</td>
<td>2.471</td>
<td>0.824</td>
</tr>
</tbody>
</table>
Effect of Agitation Speed

The speed of agitation in the exchange vessel affects the rate of exchange due to its effect on film thickness. A higher rate of agitation tends to reduce the film thickness. However, as pointed out by Helfferich (17), a limiting hydrodynamics efficiency will be approached beyond which any further increase in stirring speed will have no effect on the rate of exchange. Thus it is seen in Fig. 7 that the rate of exchange increases substantially from a stirring rate of 400 rpm to one of 800 rpm, but no significant increase in the rate is observed when a stirring speed of 1000 rpm is employed. The calculated value of $D/(r_0\delta)$ for the three runs of different stirring speed are listed in Table 4. For these three experiments, smaller volumes of solution and resin were used. Assuming the same value of $D/r_0$ for these three runs, it is seen that the calculated film thickness for the run of 1000 rpm is about one-six that of the 400 rpm run.

*FIG. 7  Effect of stirring speed on the rate of exchange, $C_0 = 0.0055$ N HCl, $V = 0.4$ L, $W = 1$ g.*

<table>
<thead>
<tr>
<th>Run</th>
<th>$K_fRC_0/Q_c$ (min$^{-1}$)</th>
<th>$R$</th>
<th>$C_0$ (N)</th>
<th>rpm</th>
<th>$K_f$ (s$^{-1}$)</th>
<th>$D/r_0\delta$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.034</td>
<td>1.723</td>
<td>0.00582</td>
<td>400</td>
<td>0.085</td>
<td>0.028</td>
</tr>
<tr>
<td>11</td>
<td>0.198</td>
<td>1.866</td>
<td>0.00536</td>
<td>800</td>
<td>0.498</td>
<td>0.166</td>
</tr>
<tr>
<td>12</td>
<td>0.231</td>
<td>1.864</td>
<td>0.00549</td>
<td>1000</td>
<td>0.568</td>
<td>0.189</td>
</tr>
</tbody>
</table>
CONCLUSIONS

For a solution concentration of less than 0.01 N, the rate of exchange of the HCl–OH\textsuperscript{2} and H\textsubscript{2}SO\textsubscript{4}–OH\textsuperscript{2} systems is film diffusion rate controlled. Because of the negligible interface concentration of Cl\textsuperscript{−} and SO\textsubscript{4}\textsuperscript{2−}, the rate equation based on film diffusion model can be integrated analytically. A plot of \(\ln(C_0/C)\) versus time yields a straight line with a slope equal to \(K_fRC_0/Q_c\). The quantity \(K_f\), and subsequently the value of \(D/\delta\), can be estimated. The simplified rate equation resulting from neglecting \(C^*\) is identical in form to a rate equation based on a first-order irreversible reaction. The rate for ion exchange accompanied by neutralization is higher compared to that for an ordinary ion-exchange process. The resin size and stirring speed both have a substantial effect on the rate of exchange. The experimental data obtained showed that the rate is inversely proportional to the bead radius of the resin, and that a maximum rate is reached when the stirring speed is near 1000 rpm. The results of this study also indicate that the rate of exchange is faster for the HCl–OH\textsuperscript{−} system than for the H\textsubscript{2}SO\textsubscript{4}–OH\textsuperscript{−} system.

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SYMBOLS

- \(C\) concentration of counter ions in the solution (meq/L)
- \(C_0\) initial solution concentration (meq/L)
- \(C^*\) equilibrium solution concentration at the solid–liquid film interface (meq/L)
- \(D\) effective diffusivity of ions in the liquid film (cm\textsuperscript{2}/s)
- \(K_f\) rate parameter in the film diffusion model (1/s)
- \(F\) fractional attainment of final equilibrium
- \(q\) concentration of one species of counterions in the resin (meq/mL or meq/g)
- \(Q_c\) capacity of resin in wet basis (meq/mL)
- \(Q_c^*\) capacity of resin in dry basis (meq/g)
- \(r_0\) resin bead radius (cm)
- \(R\) stoichiometric ratio of counterions in the resin and in the solution
- \(t\) absolute time (minutes)
- \(t_c\) critical time (minutes)
- \(V\) solution volume (mL)
- \(V_r\) resin volume (mL)
Greek Letter

\( \delta \)  
liquid film thickness (cm)

REFERENCES


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