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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_2SO_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 $H_2SO_4–OH^-$ 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 theses 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 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 OH^- form of resin and Cl^- and 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 HCl and H_2SO_4 and a strong anion exchanger in the 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 OH^- ions released by an anion exchanger or reactions between strong bases and H^+ ions released by a cation exchanger. Typical reactions dealing with strong acidic cation resins or strong base anion resins are

$$\mathrm{RH + MOH \leftrightarrow RM + H_2O} \tag{1}$$

$$\mathrm{ROH + HA \leftrightarrow RA + H_2O} \tag{2}$$

where R represents the matrix group, and MOH and 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)

$$\mathrm{RNa + HCl \leftrightarrow RH + NaCl} \tag{3}$$

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:

$$dq/dt = K_f(C - C^*) \tag{4}$$

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 OH^- or 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

$$V(C_0 - C) = V_r(q - q_0) \tag{5}$$

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^*:

$$dq/dt = K_f[C_0 - (V_r/V)(q - q_0)] \tag{6}$$

integrating with initial condition $t = 0$, $q = q_0 = 0$:

$$\frac{V_r q}{VC_0} = 1 - \exp\left(-\frac{K_f V_r t}{V}\right) \tag{7}$$

From the mass balance of Eq. (5),

$$x = \frac{C}{C_0} = \exp\left(-\frac{K_f V_r t}{V}\right) \tag{8}$$

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

$$y(t) = \frac{1}{R}\left[1 - \exp\left(-\frac{K_f V_r t}{V}\right)\right] \tag{9}$$

where R is the stoichiometric ratio defined by

$$R = \frac{V_r Q_c}{(VC_0)} = \frac{WQ'_c}{(VC_0)}$$

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 $R < 1$:

$$\begin{aligned} y(t) &= \frac{1}{R}\left[1 - \exp\left(-\frac{K_f V_r t}{V}\right)\right] \text{ for } 0 < t < t_c \\ y(t) &= 1 \text{ for } t > t_c \end{aligned} \tag{10}$$

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

$$F(t) = \frac{y(t)}{y(\infty)} = 1 - \exp\left(-\frac{V_r K_f t}{V}\right) \tag{11}$$

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 $R < 1$:

$$F(t) = G(t) \tag{12}$$

For the case of $R > 1$:

$$\begin{aligned} F(t) &= RG(t) \text{ for } 0 < t < t_c \\ F(t) &= 1 \text{ for } t > t_c \end{aligned} \tag{13}$$

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_2SO_4 with concentrations of about 0.005 to 0.01 N were prepared for the kinetics study of HCl–OH^- and H_2SO_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_2SO_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.

TABLE 1
Summary of Experimental Conditions

Run	Q_c' (meq/g)	W (g)	V (L)	C_0 (N)	R	Stirring rate, rpm
1	3.984	5.008	2.0	0.00476	2.101	800
2	3.984	5.005	2.7	0.00558	1.344	800
3	3.984	5.003	4.0	0.00546	0.916	800
4	3.984	5.017	4.0	0.01023	0.490	800
5	3.984	5.013	2.0	0.00504	1.984	800
6	3.984	4.821	2.5	0.00493	1.558	800
7	3.984	5.005	4.0	0.01003	0.497	800
8	4.028	5.013	2.0	0.00584	1.729	800
9	4.113	5.013	2.0	0.00564	1.827	800
10	3.988	1.007	0.4	0.00581	1.723	400
11	3.988	1.003	0.4	0.00535	1.866	800
12	3.988	1.027	0.4	0.00549	1.864	1000

Experimental Procedure

A typical run started with a predetermined amount of the OH^- form of resin placed in a cubical glass vessel (20 cm × 20 cm × 15 cm) containing a fixed volume of the prepared HCl or H_2SO_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 $H_2SO_4–OH^-$ 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 $K_f V_r / V$ 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

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

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 $1/R$

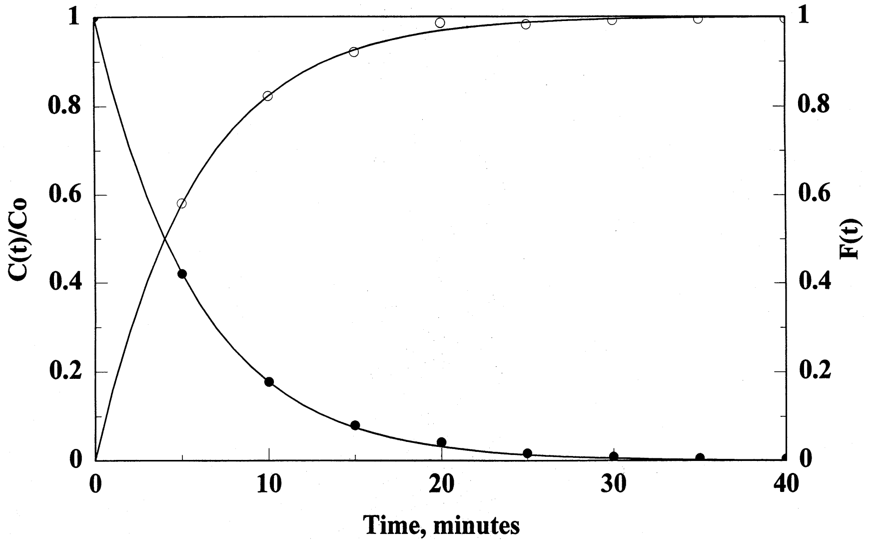

FIG. 1 Experimental and calculated $C(t)/C_0$ and $F(t)$ versus time for HCl–OH^- exchange, $C_0 = 0.00476$ N HCl, $R = 2.101$.

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-

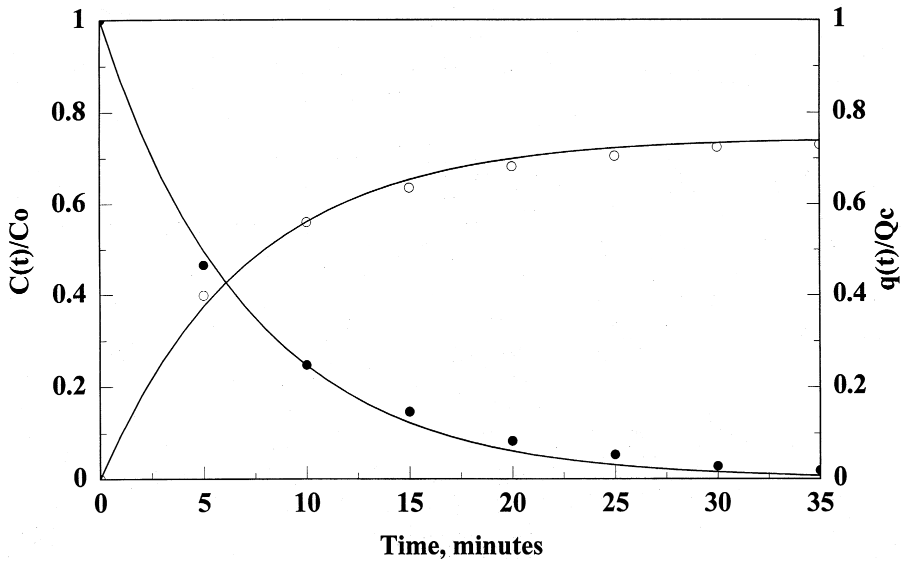

FIG. 2 Experimental and calculated $C(t)/C_0$ and $q(t)/Q_c$ versus time for HCl–OH^- exchange, $C_0 = 0.00558$ N HCl, $R = 1.344$.

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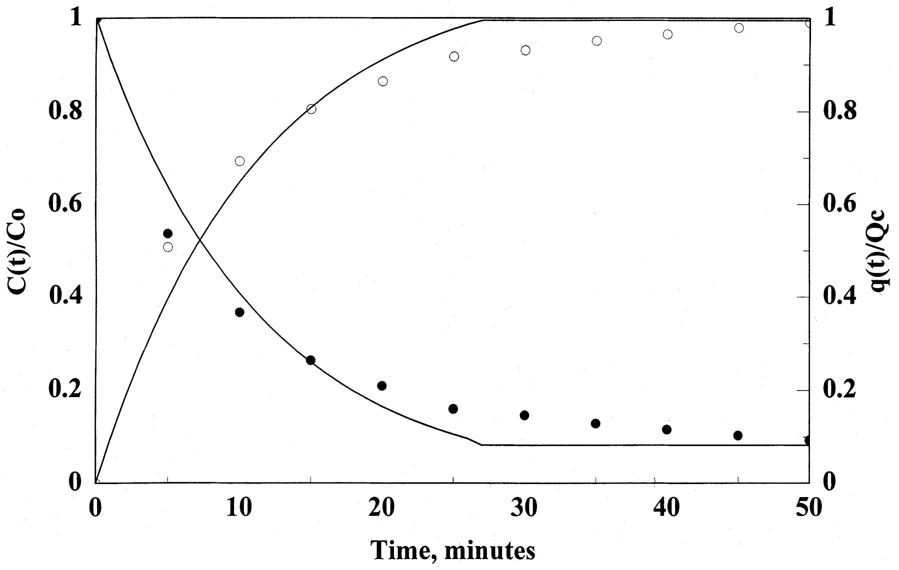

FIG. 3 Experimental and calculated $C(t)/C_0$ and $q(t)/Q_c$ versus time for HCl–OH^- exchange, $C_0 = 0.00546$ N HCl, $R = 0.916$.

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 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_{HCl} can be derived by equating the net flux of H^+

TABLE 2
Summary of Calculations for K_fRC_0/Q_c and $D/r_0\delta$ for Runs 1 to 7

Run	$\frac{K_fRC_0}{Q_c}$ (min^{-1})	R	C_0 (N)	Q_c (meq/mL)	K_f (s^{-1})	$\frac{D}{r_0\delta}$ (s^{-1})
1	0.173	2.101	0.00476	1.507	0.425	0.142
2	0.136	1.344	0.00558	1.507	0.456	0.152
3	0.091	0.916	0.00546	1.507	0.455	0.151
4	0.076	0.490	0.01023	1.507	0.373	0.125
5	0.055	1.984	0.00504	1.507	0.138	0.046
6	0.038	1.558	0.00493	1.507	0.125	0.042
7	0.026	0.497	0.01003	1.507	0.133	0.044

and Cl^- ions and eliminating the electric potential flux term to obtain the following expression (1):

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

Based on the calculated results of Robinson and Stokes (16), the self-diffusion coefficients for hydrogen and chloride ions at 25 °C were $D_{H^+} = 9.31 \times 10^{-5}$ cm^2/s and $D_{Cl^-} = 2.03 \times 10^{-5}$ 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_2SO_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_2SO_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

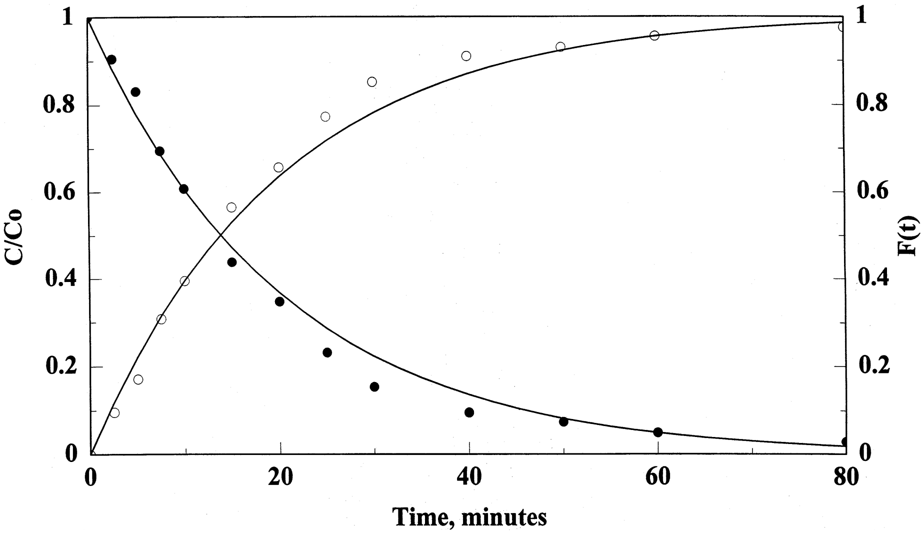

FIG. 4 Experimental and calculated $C(t)/C_0$ and $F(t)$ versus time for H_2SO_4–OH^- exchange, $C_0 = 0.00504$ N H_2SO_4, $R = 1.984$.

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 H_2SO_4–OH^- exchange show that its kinetics of exchange is much slower compared to that of HCl–OH^- exchange.

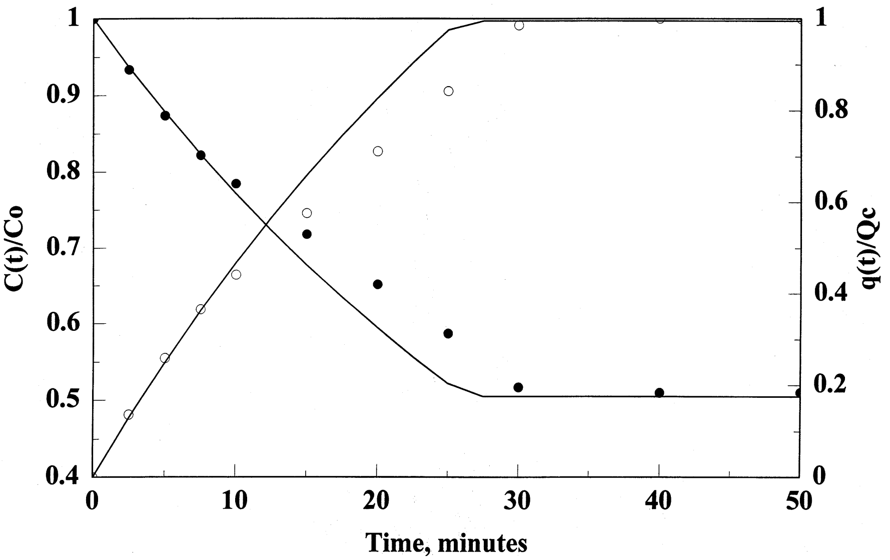

FIG. 5 Experimental and calculated $C(t)/C_0$ and $q(t)/Q_c$ versus time for H_2SO_4–OH^- exchange, $C_0 = 0.01003$ N H_2SO_4, $R = 0.497$.

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^{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 2.59×10^{-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 2×10^{-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.

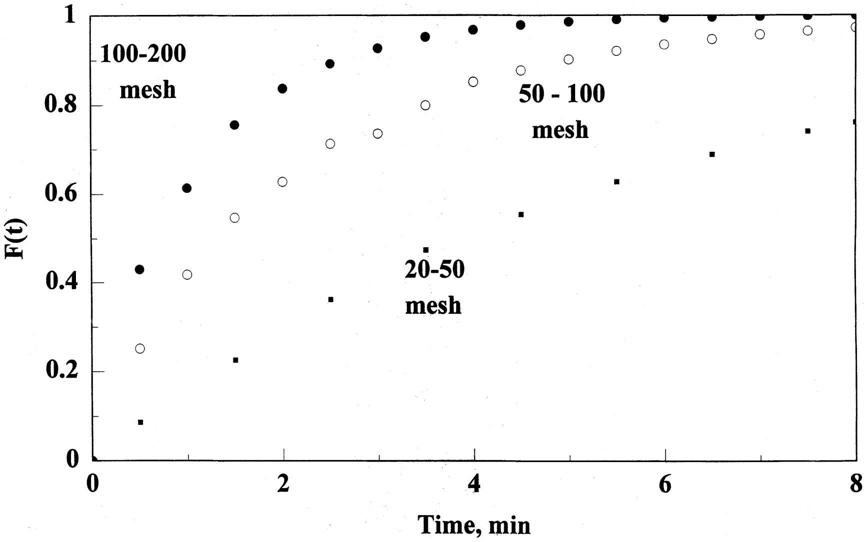

FIG. 6 Effect of resin bead size on the rate of exchange, $C_0 = 0.0054$ N HCl, $V = 2$ L, $W = 5$ g.

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 D/δ and inversely proportional to r_0. When experiments are conducted with the same solution concentration and the same degree of agitation, the value of D/δ 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_fRC_0/Q_c and $D/r_0\delta$ for Resin Size Effect Runs

Run	$\dfrac{K_fRC_0}{Q_c}$ (min^{-1})	R	C_0 (N)	r_0 (mesh no.)	K_f (s^{-1})	$\dfrac{D}{r_0\delta}$ (s^{-1})
1	0.173	2.101	0.00476	20–50	0.425	0.142
8	0.571	1.729	0.00584	50–100	1.434	0.478
9	0.982	1.827	0.00564	100–200	2.471	0.824

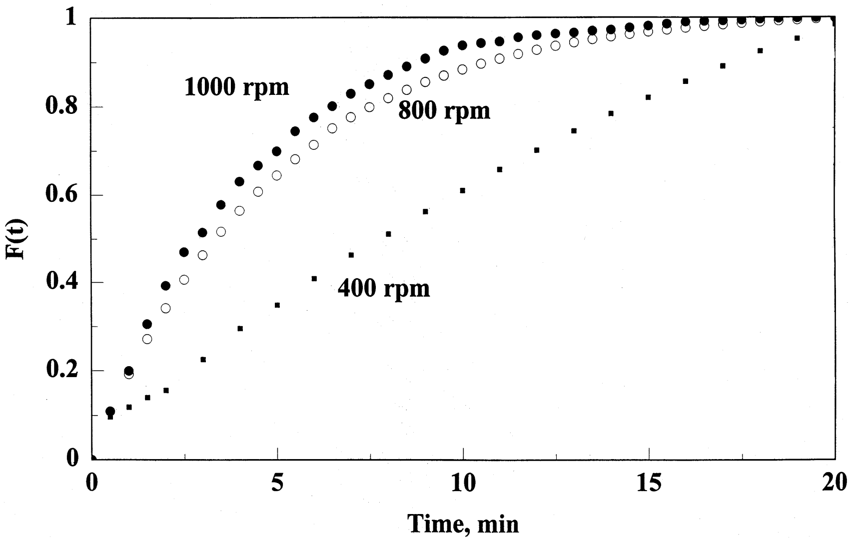

FIG. 7 Effect of stirring speed on the rate of exchange, $C_0 = 0.0055$ N HCl, $V = 0.4$ L, $W = 1$ g.

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.

TABLE 4
Summary of Calculations for $K_f RC_0/Q_c$ and $D/r_0\delta$ for Stirring Effect Runs

Run	$\frac{K_f RC_0}{Q_c}$ (min^{-1})	R	C_0 (N)	rpm	K_f (s^{-1})	$\frac{D}{r_0\delta}$ (s^{-1})
10	0.034	1.723	0.00582	400	0.085	0.028
11	0.198	1.866	0.00536	800	0.498	0.166
12	0.231	1.864	0.00549	1000	0.568	0.189

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CONCLUSIONS

For a solution concentration of less than 0.01 N, the rate of exchange of the $HCl–OH^-$ and $H_2SO_4–OH^-$ systems is film diffusion rate controlled. Because of the negligible interface concentration of Cl^- and SO_4^{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 $K_f R C_0/Q_c$. The quantity K_f, and subsequently the value of D/δ, 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 $HCl–OH^-$ system than for the $H_2SO_4–OH^-$ 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^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)

W	weight of dried resin (g)
x	equivalent fraction of one of the species of counterions in the solution
y	equivalent fraction of one of the species of counterions in the resin

Greek Letter

δ	liquid film thickness (cm)

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