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Kinetics of Anion Exchange Accompanied by Fast Irreversible Reaction

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The kinetics of binary anion exchange accompanied by a fast irreversible reaction at the exchanger surface was studied. Dowex 1, X-8, in the hydroxyl form was contacted with a strong acid in a well-stirred batch reactor and concentration-time data were obtained by electrical conductivity measurements. The process was analyzed assuming rate control by film diffusion, intraparticle diffusion, and a combination of both mechanisms. The results indicated that models based on the individual mechanisms gave quite satisfactory representations of the data under appropriate conditions, but the combined model appears superior in the nominally intraparticle diffusion controlled range. It was also found that severe particle cracking occurs, particularly with larger resin particles, at high solution concentrations. This results in degradation of the particles as well as apparent intraparticle diffusion coefficients that vary during the exchange process. Care must be taken to avoid or to account for this phenomenon.

Recently Helfferich (*1*) has developed a detailed analysis of ion exchange coupled with chemical reaction based on the generally accepted model of the exchange process but modified to include the effects of reaction. This model considers the exchange process to be controlled by transport of ions to the exchange surface and/or diffusion of counter (exchanging) ions within the exchanger. The first step (film diffusion) is approximated as diffusion through an idealized thin stagnant film of thickness δ. The second step (intraparticle diffusion) is considered to be diffusion of ions in a spherical, quasi-homogeneous exchanger matrix in which there is no co-ion uptake and no solvent flux.

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Helfferich (*1*) derived several rate laws assuming that the chemical reaction is very rapid and that one or the other of these diffusional processes is rate controlling. The Nernst-Planck equations were used to describe the individual ionic fluxes around and within the exchanger particle. These equations account for transport of an ionic species due to a gradient in its own concentration and a gradient in electrical potential, but neglect cross-diffusional effects and variations in activity coefficients. For an individual ion the flux equation takes the following form:

$$J_i = D_i \left(\nabla C_i + \frac{C_i Z_i F}{RT} \nabla \varphi \right) \tag{1}$$

where J_i is the flux of species i relative to the solvent in moles/(cm^2-s). The solvent velocity is assumed to be zero, however, so that $J_i = N_i$ the flux of species i relative to stationary coordinates.

Rate laws of ion exchange based on this model have been tested with good success for both ordinary ion exchange (*2* to *4*) and for cation exchange accompanied by a neutralization reaction (*5* to *7*). However, little experimental work has been published verifying the rate laws for anion exchange, and no test has been made of anion exchange accompanied by a chemical reaction. Therefore, the present study was undertaken to test the validity of the Helfferich model for the neutralization of a strongly basic anion exchanger.

THEORY

Since the basic equations have been derived previously (*1*), they will only be summarized here. In this work strongly basic anion exchange resin (Dowex 1-X8) completely in the hydroxyl form is contacted with an acid solution (HCl or HNO_3). The chloride (or nitrate) ions exchange with the hydroxyl ions, which in turn react with the hydrogen ions at the exchanger surface to form water. Schematically

$$\overline{OH} + Cl^- + H^+ \rightarrow \overline{Cl}^- + H_2O \tag{2}$$

where overbars indicate the species in the resin phase. The base form resin and neutralizing acid are assumed to be completely dissociated. The resin particles are taken to be uniform spheres, and isothermal operation is assumed.

Film Diffusion Control

For this idealized case, the problem is analyzed assuming pseudo steady state diffusion in a planar stagnant film. The fractional approach to equilibrium (complete neutralization of the resin) $F(t)$ is given as follows:

When $CV < \overline{CV}$

$$F(t) = 1 - \exp\left(\frac{-3 D_{HCl} \overline{V}}{r_0 V \delta} t \right) \tag{3}$$

When $CV > \overline{CV}$

$$F(t) = \frac{CV}{\overline{CV}} \left[1 - \exp\left(\frac{-3 D_{HCl} \overline{V}}{r_0 V \delta} t \right) \right], \quad \text{for} \quad 0 \leq t < t_c \tag{4}$$

and

$$F(t) = 1, \quad \text{for} \quad t_c \leq t \tag{5}$$

where

$$t_c = \frac{r_0 V \delta}{3 D_{HCl} \overline{V}} \ln\left(\frac{CV}{CV - \overline{CV}} \right) \tag{6}$$

Finally, when $CV >> \overline{CV}$

$$F(t) = \frac{3 D_{HCl} C}{r_0 \delta \overline{C}} t, \quad \text{for} \quad 0 \leq t \leq t_c \tag{7}$$

and

$$F(t) = 1, \quad \text{for} \quad t_c \leq t \tag{8}$$

where

$$t_c = \frac{r_0 \delta \overline{C}}{3 D_{HCl} C} \tag{9}$$

These equations involve the generally unknown parameter ($D_{HCl/\delta}$) which can be determined by fitting the equations to experimental data.

Intraparticle-Diffusion Control

When intraparticle diffusion controls, the rate equations for neutralization are identical to those for ordinary ion exchange with the "infinite solution volume" boundary condition. In this limiting case the solution composition remains essentially constant during exchange. This problem has been discussed in detail elsewhere (*8*), and tabulated numerical solutions are readily available (*9, 10*).

Thus, when $\overline{CV} < CV$

$$F(t) = G(t) \tag{10}$$

And, when $\overline{CV} > CV$

$$F(t) = \frac{\overline{CV}}{CV} G(t), \quad 0 \leq t \leq t_c \tag{11}$$

$$F(t) = 1.0 \quad t_c < t \tag{12}$$

where $G(t)$ is the tabulated fractional approach to equilibrium for ion exchange in the infinite solution volume case. These solutions involve as unknown parameters the ratio of Nernst-Planck ionic diffusivities of the two diffusing species as well as the absolute value of one of them.

In the absence of other information, the ratio of diffusivities within the ion exchanger can be assumed to be the same as in free solution. Assuming further that the aqueous solution diffusivities may be estimated by the Nernst-Einstein relation

$$D_i = \frac{RT}{F} u_i, \tag{13}$$

the ratio of intraparticle diffusivities can be related to ionic mobilities at infinite dilution.

$$\frac{\overline{D}_{OH^-}}{\overline{D}_{Cl^-}} = \frac{u_{OH^-}}{u_{Cl^-}} \tag{14}$$

Values of the latter are available in the literature (*11*).

The remaining parameter $\overline{D}_{OH^-}$ can be determined by best fit of the experimental data to the theoretical model.

EXPERIMENT

The experimental program was aimed at testing the validity of the two limiting rate models. The experimental equipment and procedure were essentially the same as used by Blickenstaff, Wagner, and Dranoff (*5* to *7*). A well-stirred, isothermal batch reactor was employed. The resin, initially completely in the hydroxyl form, was injected into a known concentration of acid solution in the reactor to initiate the exchange process. The progress of the exchange was followed by continuous monitoring of the electrical conductivity of the solution. Unlike the previous work, it was necessary to shield the two platinum electrodes of the conductivity probe with a nylon mesh screen to exclude resin particles from the space between them. Without the screen the particles significantly influenced the conductivity at high solution concentrations. It was shown experimentally, however, that the nylon mesh screen did not affect the time response of the system under the conditions used.

In order to test the rate equations, the resin particle diameter was varied from 0.0612 cm to 0.0938 cm (OH^- form), the solution concentration from 0.005 N HCl to 0.70 N HCl, and the resin volume from 0.07 ml. to 40 ml. A solution volume of 600 ml. was used throughout. For the experiments designed to test the film diffusion model, very low solution concentrations (0.005 N) and low stirring rates (600 rev./min.) were used, while for the experiments designed to be in the intraparticle diffusion controlled range high concentrations (0.38 to 0.70 N) and stirring rates (1750 rev./min.) were utilized. Table 1 summarizes all the experimental conditions studied.

The Dowex 1-X8 resin particles were sized by wet screening and the average diameter determined by sampling and measurement with a calibrated microscope. The resin diameter was found to be approximately 6.5% smaller in the Cl^- form and 9.8% smaller in the NO_5 form than in the OH^- form. The particles were observed to be essentially all spherical and undamaged. Experimentally determined exchange capacities are listed in Table 2. More detailed descriptions of both the experimental equipment and the procedure may be found elsewhere (*12*).

RESULTS AND DISCUSSION

The results of experiments conducted under nominally film diffusion controlled and intraparticle diffusion conditions will be discussed separately.

Film Diffusion Control

Table 3 presents a summary of the principal experimental results obtained in the test of the film diffusion controlled model. Figures 1, 2, and 3 show how well typical experimental data conform to the various theoretical equations. In each case a straight line was drawn through the points to determine the corresponding values of $D_{HCl/\delta}$ listed in Table 3. These values show a maximum deviation of about 5% from the overall average value reported in the table. This is an indication of the reproducibility and internal consistency of these experiments.

The data show in general that the film diffusion model provides an excellent description of the exchange-reaction process at very low solution concentrations and low stirring rates. There are some deviations from the predicted linear graphs on Figures 2 and 3. However, these occur close to the end of the exchange, where the theory predicts sharp discontinuities. The deviations may well result from a switch in mechanism in these cases as the resin approaches exhaustion.

Table 1. Experimental Conditions

Rate controlling mechanism	Case	Reactant	C, meq/ml	$\overline{V}$, ml	r_0, cm
Film Diffusion					
$\overline{CV} << CV$	1	HCl	0.005	0.07	0.0306
	2	HCl	0.005	0.10	0.0469
	3	HCl	0.005	0.07	0.0469
	4	HCl	0.005	0.07	0.0469
	5	HNO_3	0.005	0.08	0.0469
	6	HNO_3	0.005	0.08	0.0469
$\overline{CV} < CV$	7	HCl	0.005	0.38	0.0306
	8	HCl	0.005	0.97	0.0306
	9	HCl	0.005	0.97	0.0352
	10	HCl	0.005	0.97	0.0469
	11	HCl	0.005	0.51	0.0469
$\overline{CV} > CV$	12	HCl	0.005	5.00	0.0306
	13	HCl	0.005	10.00	0.0306
	14	HCl	0.005	10.00	0.0469
Particle Diffusion					
$\overline{CV} < CV$	15	HCl	0.38	20.00	0.0306
	16	HCl	0.58	20.00	0.0306
	17	HCl	0.38	20.00	0.0469
	18	HCl	0.58	20.00	0.0469
	19	HCl	0.58	40.00	0.0469
	20	HNO_3	0.65	20.00	0.0306
	21	HNO_3	0.75	20.00	0.0469
	22	HNO_3	0.65	20.00	0.0469
	23	HNO_3	0.70	20.00	0.0469

Table 2. Resin Size and Capacity

Mesh size range, Cl^- form	Particle diameter range*, mm, OH^- form	Average particle, radius mm, OH^- form	Exchange capacity, meq/ml OH^- form
18-20	0.89-1.03	0.469	1.097
25-30	0.614-0.772	0.352	1.104
30-35	0.547-0.686	0.306	1.113

* 90% of the particles had diameters within the indicated range.

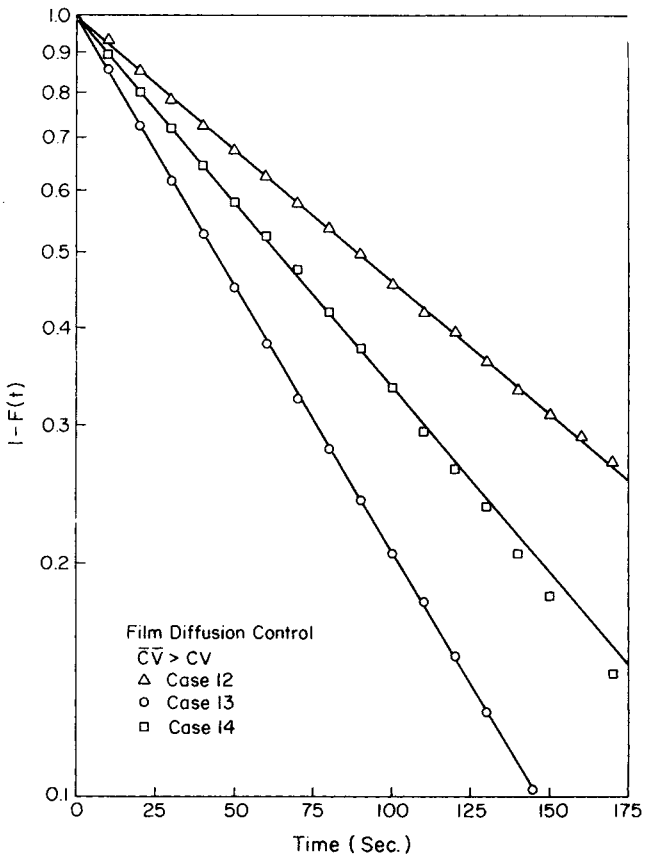

Fig. 1. Experimental test of Equation (3).

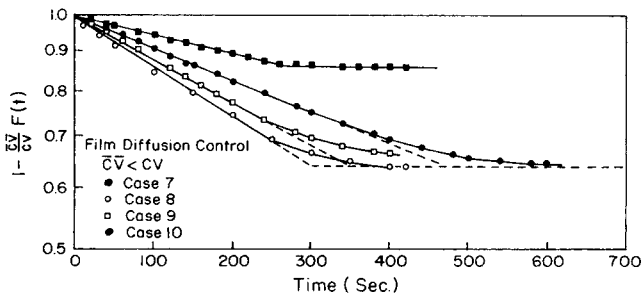

Fig. 2. Experimental test of Equations (4) and (5).

TABLE 3. VALUES OF D_{HCl}/δ FROM FILM DIFFUSION DATA

Condition*	Case	CV, meq	D_{HCl}/δ cm/sec
$\overline{CV} > CV$	12	5.565	1.59×10^{-2}
	13	11.13	1.61×10^{-2}
	14	10.97	1.67×10^{-2}
	Average value		1.62×10^{-2}
$\overline{CV} < CV$	7	0.423	1.64×10^{-2}
	8	1.080	1.52×10^{-2}
	9	1.071	1.52×10^{-2}
	10	1.064	1.52×10^{-2}
	11	0.560	1.51×10^{-2}
	Average value		1.54×10^{-2}
$\overline{CV} << CV$	1	0.0867	1.59×10^{-2}
	2	0.1097	1.60×10^{-2}
	Average value		1.59×10^{-2}
	Overall average		1.58×10^{-2}

* For all these cases, CV = 3.00 meq, stirring rate = 600 rev./min.

Experiments were also made with HNO_3 solution and at two different stirring rates. The results shown in Table 4 indicate that while there is no significant effect due to acid type, the stirring rate appears to be a major variable. The first effect is not unexpected since the diffusion coefficients for the two neutral acid species are almost equal. In fact, one may show (*12*) the calculated ratio of D_{HNO_3} to D_{HCl} for these dilute solutions to be 0.959, while the ratio of (D_{HNO_3}/δ) to (D_{HCl}/δ) is 0.952 and 0.972 at 524 rev./min. and 750 rev./min., respectively.

It was anticipated that stirring rate might be of great importance in the film diffusion range and these few experiments were designed to illustrate this fact. The observed effect of stirring rate is consistent with the postulate that at the higher rate there is greater turbulence and thus the effective value of δ is smaller. However, no attempt was made to develop a quantitative model for the observed variation because of the limited data presently available. In view of the significance of this variable, one should be cautioned about applying the present values of (D/δ) to other experimental situations. Nonetheless, this work does show clearly the utility of the film model in the appropriate range of conditions.

TABLE 4. EFFECT OF ACID AND STIRRING RATE ON D_{HA}/δ

Condition*	Case	$\overline{CV}$, meq	Stirring rate	D_{HA}/δ cm/s
$\overline{CV} << CV$, HCl	3	0.0768	524 RPM	1.47×10^{-2}
	4	0.0768	750 RPM	1.75×10^{-2}
$CV << CV$, HNO_3	5	0.0878	524 RPM	1.40×10^{-2}
	6	0.0878	750 RPM	1.70×10^{-2}

* CV = 3.00 meq for these cases.

Intraparticle Diffusion Control

As shown in Table 1, Cases 15 to 23 were designed to test the theory in the intraparticle diffusion controlled regime for a range of solution concentrations and resin particle sizes. Tests were limited to cases in which $\overline{CV} < CV$ since previous study (*5*) has shown that the case where $CV < \overline{CV}$ will deviate from intraparticle diffusion control as the solution approaches exhaustion. The experimental data for hydrogen chloride are shown in Figures 4 and 5 along with the best fitting theoretical curves. The latter

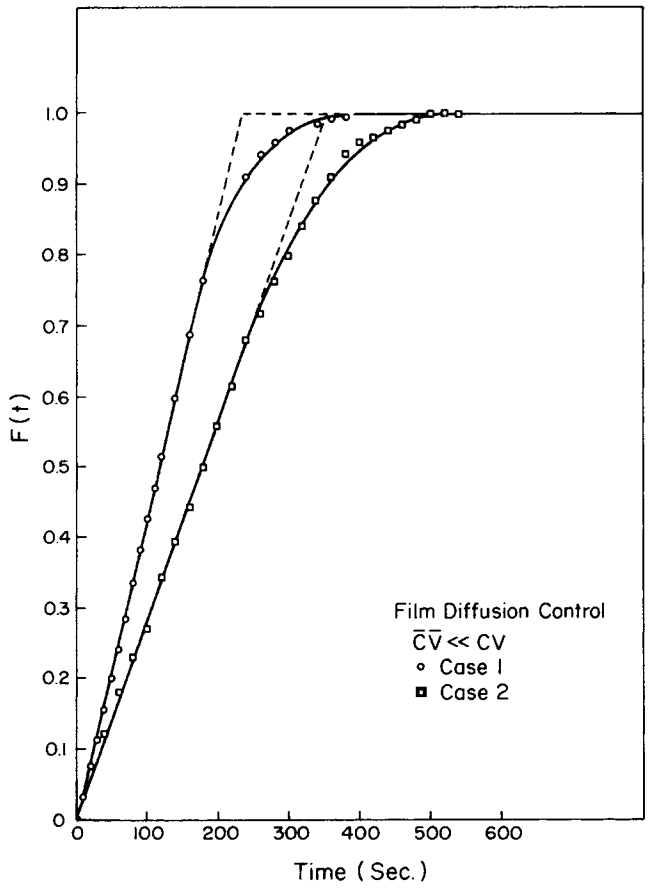

Fig. 3. Experimental test of Equations (7) and (8).

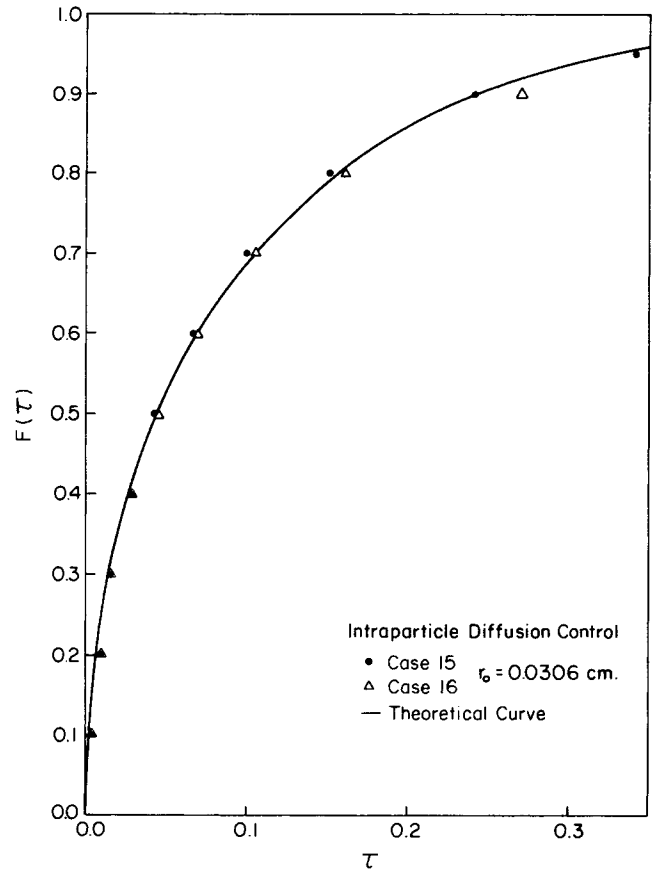

Fig. 4. Experimental test of Equation (10), small particles.

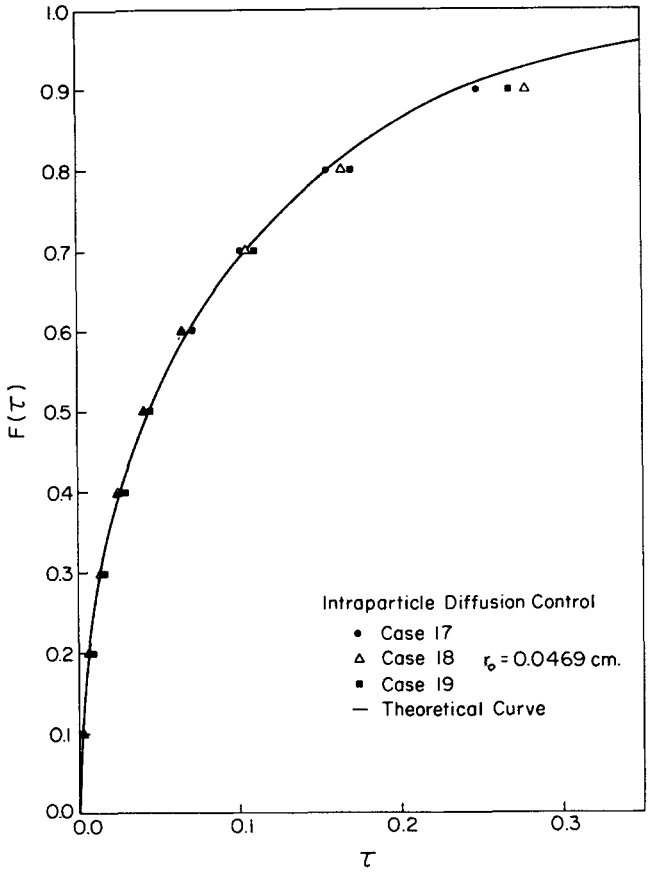

Fig. 5. Experimental test of Equation (10), large particles.

were determined from the spherical particle curves of Helfferich (*10*) using the ionic diffusivity ratio calculated from Equation (14).

$$\frac{\overline{D}_{OH}}{\overline{D}_{Cl}} = 2.6$$

The appropriate value of $\overline{D}_{OH}$ for the experimental data was determined from the time required to achieve an $F(t)$ value of 0.7 and the corresponding theoretical value of the dimensionless time τ defined by

$$\tau = \frac{\overline{D}_{OH}}{r_0^2} t \qquad (15)$$

The 0.7 value was selected since it was found to yield generally excellent fits of theory and experimental data.

The agreement between theory and experiment was apparently independent of bulk solution concentration, resin volume, and the specific acid used. These results were expected on the basis of the previously discussed theory.

However, it was observed that the value of $\overline{D}_{OH}$ was a function of resin particle size, being larger for larger particles, as shown in Table 5. Furthermore, the fit of theory to data was not as good for the larger particles toward the end of the exchange.

The larger resin particles were then examined after exchange and found to contain many apparent cracks or cleavage planes. It was felt that these might somehow be responsible for the observed variation of $\overline{D}_{OH}$ with particle size. To investigate this possibility further, the exchange process was observed microscopically. Within a second after the OH^- form resin on a microscope slide was contacted with acid, many of the particles split open. Large fissures often extending as much as 1/3 of the way into the particle appeared. After about 10 to 15 seconds the fissures began to close, and by the end of the exchange the particles were again completely spherical but with many small cracks or cleavage planes throughout. This "cracking" was apparently due to strong stresses and strains put on the polymer matrix of the ion exchanger as various layers of the particles rapidly shrank when solvent content changed during the exchange.

The destructive cracking phenomenon was observed to be much less severe for the smaller particles which apparently were able to absorb the strain without fissuring or cracking. Similarly, very little cracking was observed for solution concentrations less than 0.1 meq./ml and for the reverse (no reaction) exchange. In these cases the exchange process was slower and hence the large strains necessary to crack the beads were not present.

The cracking of the resin beads obviously opens an easier path for diffusion within the particles and explains the larger diffusion coefficient determined for the larger particle. It also explains the apparent change in diffusion coefficient observed as the exchange progressed. This is illustrated in Figure 6 where the effective intraparticle diffusion coefficient is plotted against $F(t)$. The $\overline{D}_{OH}$ values were calculated for various values of $F(t)$ from 0.1 to 0.95 and for both sizes of particles. After 5 seconds ($F(t) \sim 0.6$) the diffusion coefficient for the smaller particles remains essentially constant at about 1.35×10^{-5} cm²/s for the rest of the exchange. On the other hand the diffusion coefficient for the larger particles initially increases sharply to a maximum (about 1.95×10^{-5} cm²/s in 5 seconds) and then begins to decrease, slowly approaching the diffusion coefficient of the smaller particles. The peak in diffusion coefficient observed for the larger particles apparently reflects the opening and closing of the resin particle structure.

Figure 6 also points up another failure of the simple intraparticle-diffusion control theory. Initially (for at least the first 2 seconds of exchange) the experimental rate was invariably lower than the theoretical rate based on the average intraparticle diffusion coefficient for the particle in question. This is because any exchange must be film-diffusion controlled in the initial stages since for the first fraction of a second the rate of intraparticle diffusion will

Table 5. Effect of Resin Particle Size on $\overline{D}_{OH}$

Particle radius, cm	$\overline{D}_{OH}$, cm²/s
0.0306	1.35×10^{-5}
0.0469	1.80×10^{-5}

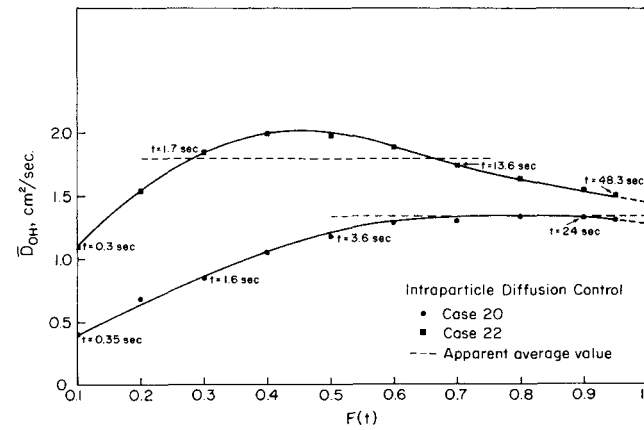

Fig. 6. Effect of fractional exchange on apparent intraparticle diffusities.

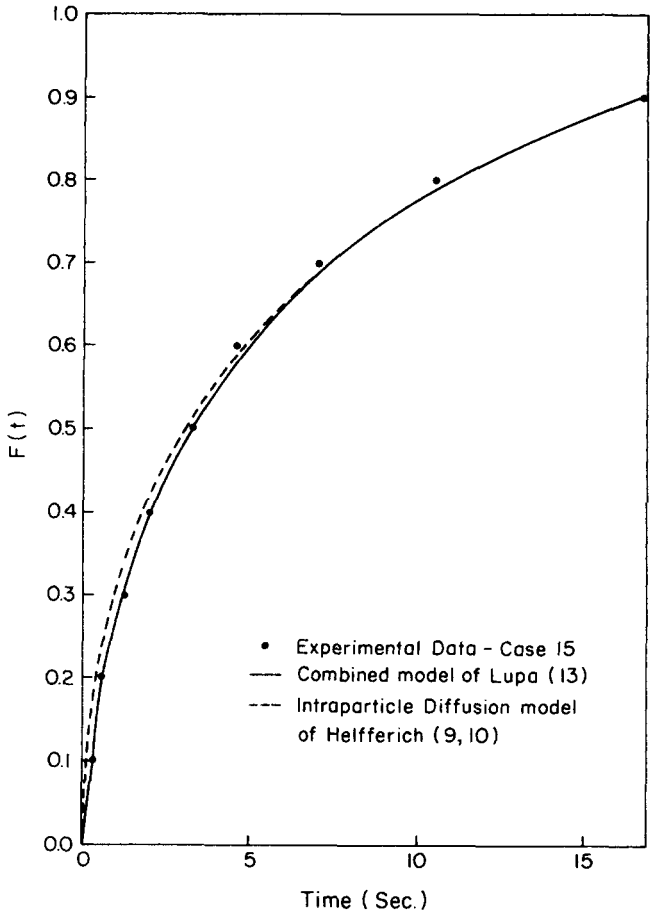

Fig. 7. Comparison of models, apparent intraparticle diffusion control.

approach infinity until the outer layers of the exchanger are exhausted.

A computer solution for this system with a neutralization reaction has recently been developed by Lupa (*13*). This solution takes into account both film-diffusion and intraparticle diffusion effects simultaneously. Figure 7 is a plot of $F(t)$ versus t for both the intraparticle diffusion control model with $\overline{D}_{OH} = 1.35 \times 10^{-5}$ cm²/s and this combined model with $\overline{D}_{OH} = 1.35 \times 10^{-5}$ cm²/s and a film-diffusion mass transfer coefficient (D_{HCl}/δ) of 1.8×10^{-2} cm/s. The latter value was selected based on the film diffusion control results at 750 rev./min. to account for the higher stirring rate used in the intraparticle range. As the figure shows, the experimental results for the smaller particles are in excellent agreement with the theoretical model of Lupa. After $F(t) = 0.7$ the two theoretical models give essentially the same results. The detailed computer output indicates that intraparticle diffusion becomes the rate determining process after 0.33 seconds ($F(t) = 0.13$); however, the effect of the initial film-diffusion control is observable for a large part of the exchange (until $F(t) = 0.7$). This illustrates the initial poor fit of a purely intraparticle diffusion model and the apparent increase in diffusion coefficient observed in Figure 6 for the smaller, noncracking particles.

Based on these studies, a value of 1.3×10^{-5} cm²/s appears to be the best estimate in the intraparticle diffusion coefficient of the OH^- ion for undamaged particles. It is 1/4 the value of the diffusion coefficient of OH^- ions in water calculated from infinite dilution ionic mobility data. Like all the intraparticle diffusion coefficients calculated in this work, this value is based on a constant particle radius, that of the OH^- form. To obtain more exact estimates of $\overline{D}_{OH}$, the change in radius would have to be taken into account.

The results of this study have shown that anion exchange coupled with an irreversible fast reaction can be well described by the limiting models of Helfferich for film diffusion or intraparticle diffusion control. However, a combined model appears to be more successful in the intraparticle diffusion regime. Particle fracture appears to be a serious problem in the latter situation and care must be taken to avoid it.

ACKNOWLEDGMENT

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NOTATION

C = initial solution concentration, meq./ml
$\overline{C}$ = concentration of fixed ionic groups in the solid exchanger, meq./ml
D = solution phase diffusion coefficient, cm²/s
$\overline{D}$ = intraparticle diffusion coefficient, cm²/s
F = Faraday's constant, coulombs/mole
$F(t)$ = fractional attainment of equilibrium dimensionless
$G(t)$ = fractional exhaustion of resin during ordinary exchange with infinite solution boundary condition, dimensionless
J = ionic flux, moles/(cm²-s)
r_0 = radius of exchanger particle, cm
R = gas constant, ergs/(mole-°K)
t = time, seconds
t_c = time for complete exchange, seconds
T = temperature, °K
u = ionic mobility, cm²/(second-volt)
V = solution volume, ml
$\overline{V}$ = resin volume, ml
Z = ionic valence
δ = effective film thickness, cm
τ = dimensionless time of exchange
φ = electrostatic potential, volts
i = refers to species i

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