Ion Exchange in Weak Acid Resin: Diffusion in Shrinking Core

Abul Hasnat and Vinay A. Juvekar
Dept. of Chemical Engineering, Indian Institute of Technology, Powai, Mumbai-400 076, India

Ion exchange with chemical reaction forms an important class of ion-exchange processes. As pointed out by Helfferich (1965), the rate laws for such exchanges differ from those for ordinary ion exchange. He categorized these processes into four types (Type I to IV) and presented the theoretical treatment for each of the cases. Since then several works have been published with a view to experimentally verify the Helfferich's hypothesis (Nativ et al., 1975; Kataoka et al., 1977; Zuyi and Jinlong, 1990). Since his hypothesis is based on the quasi-homogeneous resin phase model, there is a need to review it based on our heterogeneous resin phase model (Hasnat and Juvekar, 1996a, 1997). In this work we develop a model for kinetics of ion exchange accompanied by chemical reaction with reference to the following irreversible reaction (Type III)

$$\mathcal{R}-\mathrm{COOH}+\mathrm{Na}^{+}+\mathrm{OH}^{-}\rightarrow \mathcal{R}-\mathrm{COONa}+\mathrm{H_2O} \quad (1)$$

where $\mathcal{R}$ is a fixed site of the weak acid resin.

Our model uses the concept of shell-core mechanism. It assumes that the carboxylic acid and the carbonate groups are partially dissociated into H^+ and $-COO^-$ and Na^+ and $-COO^-$ ions, respectively. The mobile H^+ ions in the unreacted core region are available for counterdiffusion with Na^+ ions. This counterdiffusion is also accompanied by the adsorption and the exchange of ions on the pore surface as in normal ion exchange. We also consider the formation of a double layer in the unreacted core region. In this region of particle, since no OH^- ions could coexist with H^+ ions, the double layer fills the entire pore. In the shell region, since there is no other counterion other than Na^+ ions and because of the presence of an abundant amount of OH^- ions, double layer thickness unlike in the unreacted core would be very small and therefore its effect on the diffusion of Na^+ and OH^- ions could be neglected. The movement of the shell-core boundary is assumed to be governed by the balance of fluxes of H^+ ions from the core region and of OH^- ions from the shell region. The parameters of the model are the degrees of dissociation of counterions from the resin surface (f_σ) and the external film thickness (δ). The value of f_σ for a weak acid resin (Amerlite IRC-50) was found to be much lower than for a strong acid resin. However, even for weak acid resin, f_σ was found to be high enough to yield a significant counterion flux in the unreacted core of the particle so the ideal shrinking core mechanism (one of the regimes of Helfferich's model for Type III process) holds only at very high solution concentration.

Model Development

At time $t > 0$, the resin particle is subdivided into two regions, viz., the reacted shell region and the unreacted core region. The two regions are separated by a moving boundary (R_c). In the shell region, the following expression for flux can be derived

$$J^s_{\mathrm{Na}} = J^s_{\mathrm{OH}} = -\frac{2D_{\mathrm{Na}}D_{\mathrm{OH}}}{\tau(D_{\mathrm{Na}}+D_{\mathrm{OH}})}\frac{d[\mathrm{OH}]_s}{dr} \quad (2)$$

where the tortuosity factor τ is used for correcting the diffusion coefficients of ions inside the pores. In most cases, the movement of the shell-core boundary is slow and therefore the assumption of the quasi-steady state is valid. The continuity equation for OH^- ion in the shell can be written as

$$\frac{d}{dr}(r^2 J^s_{\mathrm{OH}}) = 0 \quad (3)$$

An analytical solution of Eq. 3 can be obtained with the following boundary conditions

$$\text{at} \quad r = R_c \quad [\mathrm{OH}]_s = 0 \quad (4)$$

$$r = R_0 \quad [\mathrm{OH}]_s = [\mathrm{OH}]|_{r=R_0} \quad (5)$$

The particle surface concentration of OH^- ions may be obtained from the flux balance at $r = R_0$

$$\epsilon_p J^s_{\mathrm{OH}}|_{r=R_0} = J_{\mathrm{OH}}|_{r=R_0} \quad (6)$$

Correspondence concerning this article should be addressed to A. Hasnat at his current address: Corporate Technical Services, Reliance Industries Ltd., 4-A, Shanti Nagar Industrial Estate, Vakola, Santacruz (East), Mumbai-400 055, India.

where J_{OH} is the flux of OH^- ions in the external film which can be written as

$$J_{OH} = -\frac{2D_{Na}D_{OH}}{D_{Na}+D_{OH}}\frac{d[OH]}{dr} \tag{7}$$

For the external film, the following continuity and boundary conditions may apply

$$\frac{d}{dr}\left(r^2\frac{d[OH]}{dr}\right)=0 \tag{8}$$

$$\text{at} \quad r=R_0 \quad [OH]=[OH]|_{r=R_0} \tag{9}$$

$$r=R_0+\delta \quad [OH]=[OH]_0 \tag{10}$$

The material balance in the bulk of the extraparticle fluid will yield

$$\frac{d[OH]_0}{dt}=\frac{3W[OH]_i}{\epsilon_p Q R_0}J_{OH}|_{r=R_0} \tag{11}$$

where Q, ϵ_p, and W are the resin capacity (based on pore volume), porosity and dimensionless resin loading, respectively. Equation 11 can be solved for the initial condition of $[OH]_0=[OH]_i$ at $t=0$.

In the unreacted core region, the mutual diffusion of H^+ and Na^+ ions resembles that of diffusion in the Type I exchange (Hasnat and Juvekar, 1996b). Therefore, the following continuity equation for H^+ ion in the unreacted core is reproduced from our previous article (Eq. 15, Hasnat and Juvekar, 1996b)

$$\frac{\partial(x_H)_a}{\partial t}=\frac{D_H D_{Na} f_\sigma}{\tau\alpha}[\alpha-(\alpha-1)(x_H)_a]^2\frac{1}{r^2}\frac{\partial}{\partial r} \times\left[r^2\frac{\partial(x_H)_a/\partial r}{D_{Na}+(D_H-D_{Na})(x_H)_a}\right] \tag{12}$$

where f_σ ($=[\mathcal{R}_\sigma]/Q$) is the fraction of the fixed sites in the dissociated form and $[\mathcal{R}_\sigma]$ is the concentration of the dissociated sites on the pore surface. The appropriate initial and boundary conditions required to solve the above equation are

$$\text{at} \quad t=0 \quad (x_H)_a=1 \tag{13}$$

$$r=0 \quad \frac{\partial(x_H)_a}{\partial r}=0 \tag{14}$$

$$r=R_c \quad (x_H)_a=0 \tag{15}$$

Movement of Shell-Core Boundary

We assume a sharp boundary between the unreacted core and the reacted shell where a reaction between H^+ and OH^- ions takes place. H^+ ions are transported to this boundary by counterdiffusion with Na^+ ions in the unreacted core region. The concentrations of both H^+ and OH^- ions are zero at the shell-core boundary. The location of boundary (R_c) is governed by the fact that at $r=R_c$, the flux of OH^- ions on the shell side must be balanced by the flux of H^+ ions on the core side. The assumption of a sharp boundary between the core and the shell regions is not strictly valid. There exists a diffused region between the core and the shell in which the concentration of OH^- ion is finite and yet influx of H^+ ion occurs in the double layer. It is assumed that this diffused region is sufficiently thin, so that its omission is permissible from the point of view of the accuracy of final results.

Therefore, the position of the moving boundary is determined by the following flux balance equation at $r=R_c$

$$\langle J_H\rangle + J^s_{OH}=0 \tag{16}$$

where $\langle J_H\rangle$ is the area average flux of H^+ ion in the unreacted core which is derived in our previous article (Eq. 14, Hasnat and Juvekar, 1996b)

$$\langle J_H\rangle=\frac{D_H D_{Na}[\mathcal{R}_\sigma]\left[(x_H)_a\frac{\partial(x_{Na})_a}{\partial r}-(x_{Na})_a\frac{\partial(x_H)_a}{\partial r}\right]}{\tau(D_H(x_H)_a+D_{Na}(x_{Na})_a)} \tag{17}$$

The procedure described above for determination of R_c fails at very short times. This is due to the fact that at short times at $r=R_c$, Eq. 2 yields a relatively small magnitude of flux compared to Eq. 17. In fact, at $t=0$, ($R_c=R_0$), it can be shown that

$$J^s_{OH}|_{r=R_0}=-\frac{2D_{Na}D_{OH}}{\epsilon_p(D_{Na}+D_{OH})}\left(\frac{1}{R_0}+\frac{1}{\delta}\right)[OH]_0 \tag{18}$$

which corresponds to the flux due to extraparticle film diffusion and is finite. On the other hand, $\langle J_H\rangle|_{r=R_0}$ becomes infinite due to the mismatch of the initial condition ($(x_H)_a=1$) and the boundary condition at $r=R_c$ where $(x_H)_a=0$. This problem arises due to the failure of quasi-steady-state assumption at initial times where the variations are very fast. We overcome this problem by using the following approximate procedure.

At short times, we assume that $(x_H)_a$ is finite for calculation of flux $\langle J_H\rangle$ using Eq. 17. We fix the reaction surface at $r=R_0$ and obtain $(x_H)_a|_{r=R_0}$ using the flux balance Eq. 16. The value of $(x_H)_a|_{r=R_0}$ decreases with time so that the reaction surface is not allowed to shift from $r=R_0$ until $(x_H)_a$ becomes zero. We can thus overcome the problem of the initial mismatch of fluxes. Since the time required for $(x_H)_a$ to approach zero is very small, the error introduced by this procedure is expected to be negligible.

Results and Discussion

Table 1 presents the regression estimates of f_σ and δ. The small values of the standard deviation (σ_d) between the experimental rate data and the model predictions indicate the ability of the model to represent the experimental rate data in an excellent manner. A preliminary analysis of the data was made by applying the model to the data obtained at very low initial solution concentration (0.1 mol·m^{-3}) on the suspicion that the rate might be controlled by the film resistance

Table 1. Regression Estimates of Model Parameters (Amberlite IRC-50/NaOH)

Init. Solution Conc. mol·m^3	Resin Loading W	δ μm	f_σ $\times 10^4$	σ_d $\times 10^3$	$\bar{D}_{OH}/D^*_{OH}$ Helfferich Model
0.1	30.80	3.42			
	20.21	3.79			
	10.00	3.53			
	3.66	4.00			
1.00	3.56	4.33	2.51	1.52	1.598
	1.70	4.27	2.50	6.73	1.827
10.0	3.33	3.89	2.26	5.85	0.299
	1.18	4.10	2.25	2.33	0.345
50.0	0.680	4.20	2.58	5.26	0.0888
	0.389	3.91	2.66	3.21	0.0288

$D_H = 9.31 \times 10^{-9}$ m^2·s^{-1}, $D_{Na} = 1.33 \times 10^{-9}$ m^2·s^{-1}, $D_{OH} = 5.21 \times 10^{-9}$ m^2·s^{-1} (Robinson and Stokes, 1959); $\alpha_{Na^+/H^+} = 1.53$ (Anderson, 1988); $^*\bar{D}_{OH}$ = the effective diffusion coefficient of OH$^-$ ion in resin phase from Helfferich model.

alone. The simulation of the model showed that f_σ is insensitive to the rate of exchange implying the entire rate is being controlled by film diffusion. In such a case we have, $R_c = R_0$ at all time and Eq. 11 can be integrated using Eq. 18 to yield

$$\ln \frac{[\mathrm{OH}]_0}{[\mathrm{OH}]_i} = -6W \frac{D_{Na} D_{OH}}{D_{Na} + D_{OH}} \left(\frac{1}{R_0} + \frac{1}{\delta} \right) t \qquad (19)$$

It is then possible to determine δ from the slope of the straight line plots of ln([OH]$_0$/[OH]$_i$) vs. t. With an increase in the external solution concentration, the rate is seen to be increasingly controlled by the pore diffusion. However, the initial part of the exchange is governed by the film diffusion. As the resin conversion increases, the particle diffusion becomes predominant. These observations do not conform with the Helfferich's predictions, according to which only the particle diffusion will be the rate controlling factor even at low solution concentrations.

The average value of the film thickness (δ) is 3.94 μm. This value of δ is close to the average value of 3.55 μm for strong acid resins reported in our previous works. The average value of f_σ is 2.46×10^{-4}, which is two order of magnitude lower than that for strong acid resins.

The movement of the shell-core boundary needs comment. Our model predicts that as long as $\langle J_H \rangle \gg J_{OH}$, the position of the shell-core boundary will remain close to the particle surface. Since, for a particular resin f_σ is a characteristic constant, the magnitude of $\langle J_H \rangle$ is also constant. Therefore, the movement of the shell-core boundary will be a function of the strength of external solution.

Comparison with the Helfferich Model

The second mechanism of the Helfferich model for Type III exchange was applied to our experimental data. The best fit values of diffusivity of OH$^-$ ion are reported in Table 1. It seems evident after inspecting the regressed diffusivity values that the Helfferich model is inadequate in its predictions and lacks the exact description of physical processes inside the resin phase. At low solution concentration (1 mol·m^{-3}), $\bar{D}_{OH}/D_{OH}$ is greater than unity, that is, the faster movement of OH$^-$ ion inside the resin phase. This indicates that the pore resistance is negligible, and probably the film diffusion offers the major contribution to the resistance. As the solution concentration increases, the order of $\bar{D}_{OH}$ is $\approx 10^{-10}$ m^2·s^{-1} indicating more particle diffusion control. For a good explanation of the rate processes, it is very important to isolate the physical effects largely playing the lead role in controlling the mechanism. By incorporating the adsorption of ions on the pore surface, the formation of the electrical double layer, influx of coions inside the resin phase, the coupling of pore diffusion and the ion exchange, and the effect of the film resistance, the present model has been adequately able to represent the rate data.

Classification of Controlling Regime

Helfferich has classified the Type I ion-exchange process into two categories viz. particle diffusion and film diffusion controls. He has presented criteria to discern the controlling regimes. These criteria make use of quantity $\bar{D}$, the effective interdiffusion coefficient in the particle. This quantity is sensitive to operating conditions and it is difficult to make an a priori estimate of $\bar{D}$. Using our model, we can obtain a more precise criterion for deciding the controlling mechanisms. From Eq. 17, we can obtain the order of magnitude of $\langle J_H \rangle$ as

$$\langle J_H \rangle |_{r=R_0} = -\frac{D_H [\mathcal{R}_\sigma]}{\tau} \frac{1}{R_0} \qquad (20)$$

The order of magnitude of external flux from Eq. 7 is obtained as

$$J_{OH} = -\frac{2 D_{Na} D_{OH}}{D_{Na} + D_{OH}} \frac{[\mathrm{OH}]_0}{\delta} \qquad (21)$$

Equations 20 and 21 allow us to get the following criterion for particle and film diffusion controlled regimes. Thus, for the particle diffusion regime

$$[\mathrm{OH}]_0 \gg \frac{D_H (D_{Na} + D_{OH})}{\tau D_{Na} D_{OH}} \frac{f_\sigma}{Sh} Q \qquad (22)$$

where Sh ($= 2R_0/\delta$) is the particle Sherwood number. For the film diffusion control regime, the reverse of condition 22 is true. The righthand side of the condition may be denoted by $[\mathrm{OH}]_*$, the threshold concentration of NaOH in the extraparticle solution. The values of $[\mathrm{OH}]_*$ in our experiments are listed in Table 2.

Table 2. Criteria for Controlling Regimes

Resin	Q mol·m^{-3}	R_0 μm	Sh	f_σ $\times 10^2$	$[\mathrm{OH}]_*$ mol·m^{-3}
Dowex 50W X8	11,448.6	420	237	4.22	13.0
Amberlite 200	17,850	280	158	2.88	20.0
Amberlite IRC-50	23,703	312.5	158.6	0.0246	0.230

Literature Cited

Anderson, R. E., "Ion-Exchange Separations," in *Handbook of Separation Techniques for Chemical Engineers*, 2nd ed., P. A. Schweitzer, ed., McGraw-Hill, New York (1988).

Hasnat, A., and V. A. Juvekar, "Ion-Exchange Kinetics: Heterogeneous Resin-Phase Model," *AIChE J.*, **42**(1), 161 (1996a).

Hasnat, A., and V. A. Juvekar, "Kinetics of Ion Exchange Accompanied by Neutralization Reaction," *AIChE J.*, **42**(8), 2374 (1996b).

Hasnat, A., and V. A. Juvekar, "Dynamics of Ion-Exchange Involving Multivalent Cations," *Chem. Eng. Sci.*, **52**(14), 2439 (1997).

Helfferich, F., "Ion Exchange Kinetics. V. Ion Exchange Accompanied by Chemical Reactions," *J. Phys. Chem.*, **69**(4), 1178 (1965).

Kataoka, T., H. Yoshida, and Y. Ozasa, "Intraparticle Ion Exchange Mass Transfer Accompanied by Instantaneous Irreversible Reaction," *Chem. Eng. Sci.*, **32**, 1237 (1977).

Nativ, M. S., S. Goldstein, and G. Schmuckler, "Kinetics of Ion Exchange Processes Accompanied by Chemical Reactions," *J. Inorg. Nucl. Chem.*, **37**, 1951 (1975).

Robinson, R. A., and R. M. Stokes, *Electrolyte Solutions*, Butterworths Scientific Publications, London (1959).

Zuyi, T., and N. Jinlong, "Shell Progressive Model with Changing Bulk Concentration and Exchange Volume," *Solvent Extraction and Ion Exchange*, **8**(1), 99 (1990).

Manuscript received Jan. 21, 1997, and revision received May 12, 1997.