Kinetics of Ion Exchange Accompanied by Neutralization Reaction

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In a variety of applications involving ion-exchange resins, the process of ion exchange is accompanied by an instantaneous chemical reaction such as neutralization, association, or complex formation. Helfferich (1965) has classified these reactions into four categories viz. Type I to Type IV. In the present work we have modeled the Type I ion-exchange process represented by neutralization of metal hydroxide (MOH) on a strong acid cation exchange resin in H-form ($\mathcal{R}$H).

$$\mathcal{R}H + MOH \rightarrow \mathcal{R}M + H_2O \tag{1}$$

The model presented here is an extension of our model on an ordinary ion-exchange process (Hasnat and Juvekar, 1996).

Theory

Consider a batch dynamic experiment in which strong acid cation-exchange resin particles of identical radius R_o are introduced in an agitated MOH solution of initial concentration $[OH]_i$. The concentration of OH^- ions in the bulk is being monitored against time.

A resin particle is viewed as a sphere consisting of straight cylindrical pores whose axes coincide with the radial axes (r) of the sphere. The ion-exchange sites ($\mathcal{R}$) are assumed to be uniformly distributed on the surface of the pores. It is assumed that H^+ ions in the pore are partially bound to these sites and are partially mobile. The mobile H^+ ions diffuse towards the particle-fluid interface ($r = R_o$) and react with OH^- ions arriving through a stagnant film of thickness δ surrounding the particle. The diffusion of H^+ ions in the pores is aided by the counterdiffusion of M^+ ions which enter the resin phase from the solution. Exchange between M^+ ions in the pore fluid and H^+ ions on the fixed sites ($M^+ + \mathcal{R}H \rightarrow \mathcal{R}M + H^+$) also aids the diffusion process. At the particle-fluid boundary, the flux of H^+ ions is assumed to be equal and opposite to that of OH^- ions. OH^- ions are assumed to be completely excluded from the resin phase.

The fixed sites of the resin exist in three forms, viz. H-form ($\mathcal{R}$H), M-form ($\mathcal{R}$M) and the dissociated form (based on pore volume, mol·m^{-3}) ($\mathcal{R}_\sigma$). The concentrations of these three forms add up to the resin capacity Q.

$$Q = [\mathcal{R}M] + [\mathcal{R}H] + [\mathcal{R}_\sigma] \tag{2}$$

The negative charge on the surface of the pore is balanced by the cations in the electric double layer. Moreover, since the coions are totally absent, the double layer extends right up to the pore axis. The concentration of cation i ($i = H^+$ or M^+) in the pore can be expressed as

$$[i]_\zeta = [i]_a \exp\left(-\mathcal{F}\frac{\phi_\zeta - \phi_a}{RT}\right) \tag{3}$$

where $[i]_a$ is the concentration of species i at point a on the pore axis while $[i]_\zeta$ is its concentration at point ζ (m) located on the plane passing through a and perpendicular to the pore axis. The respective electrical potentials are denoted by ϕ_a and ϕ_ζ.

The ion-exchange equilibrium is expressed in the form of selectivity factor α

$$\alpha = \frac{q_M/q_H}{[M]_a/[H]_a} \tag{4}$$

The quantity q_i ($i = M$ or H) represents the total amount of ion i in the pore. It comprises of two parts, i.e., a part absorbed on the fixed sites (as $\mathcal{R}$M or $\mathcal{R}$H) and the rest associated with the double layer. Thus, we can write

$$q_i = [\mathcal{R}i] + \frac{2}{R_p^2}\int_0^{R_p}[i]_\zeta \zeta d\zeta \tag{5}$$

where R_p is the pore radius. The charge balance in the pore requires

$$[\mathcal{R}_\sigma] = \frac{2}{R_p^2}\int_0^{R_p}([H]_\zeta + [M]_\zeta)\zeta d\zeta \tag{6}$$

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Substituting $[\mathrm{H}]_\zeta$ and $[\mathrm{M}]_\zeta$ from Eq. 3 into Eq. 6 we get

$$\frac{2}{R_p^2}\int_0^{R_p}\exp\left[-\mathfrak{F}\frac{\phi_\zeta-\phi_a}{RT}\right]\zeta d\zeta=\frac{[\Re_\sigma]}{[\mathrm{M}]_a+[\mathrm{H}]_a}\tag{7}$$

Using Eqs. 3 and 7, we can rewrite Eq. 5 as

$$q_i=[\Re i]+(x_i)_a[\Re_\sigma]\tag{8}$$

where x_i represents equivalent fraction of component i defined as

$$x_i=\frac{[i]}{[\mathrm{M}]+[\mathrm{H}]}\tag{9}$$

Substituting the expressions for q_H and q_M from Eq. 8 into Eq. 4, and subsequently eliminating $[\Re\mathrm{M}]$ using Eq. 2, the following expression for α is obtained

$$\alpha=\left\{\frac{Q-[\Re\mathrm{H}]+(x_\mathrm{M})_a[\Re_\sigma]}{[\Re\mathrm{H}]+(x_\mathrm{H})_a[\Re_\sigma]}\right\}\left\{\frac{(x_\mathrm{H})_a}{1-(x_\mathrm{H})_a}\right\}\tag{10}$$

Area averaged continuity equation for cation i in the pore may be written as

$$\frac{\partial\langle[i]\rangle}{\partial t}=-\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\langle J_i\rangle)-\frac{\partial[\Re i]}{\partial t}\tag{11}$$

Here the terms indicated by $\langle\,\rangle$ represent the quantities which are averaged over the area of the cross section of the pore. The terms $\partial[\Re i]/\partial t$ represents the rates at which $[\Re i]$ is generated through the process of ion exchange.

The area average concentration of ion i can be expressed with the help of Eqs. 3 and 7 as

$$\langle[i]\rangle=\frac{2}{R_p^2}\int_0^{R_p}[i]_\zeta\zeta d\zeta=(x_i)_a[\Re_\sigma]\tag{12}$$

Fluxes of counterion i at any location ζ in the pore can be expressed by Nernst-Planck equations

$$J_i(\zeta)=-\frac{D_i}{\tau}\left[\frac{\partial[i]_\zeta}{\partial r}+[i]_\zeta\frac{\mathfrak{F}}{RT}\frac{\partial\phi_\zeta}{\partial r}\right]\tag{13}$$

Eliminating $\partial\phi_\zeta/\partial r$ using no current condition ($J_\mathrm{M}(\zeta)+J_\mathrm{H}(\zeta)=0$) and expressing $[i]_\zeta$ in terms of $[i]_a$ using Eq. 3, we derive the following expression for the area average flux $\langle J_\mathrm{H}\rangle$

$$\langle J_\mathrm{H}\rangle=\frac{D_\mathrm{H}D_\mathrm{M}[\Re_\sigma]\left[(x_\mathrm{H})_a\frac{\partial(x_\mathrm{M})_a}{\partial r}-(x_\mathrm{M})_a\frac{\partial(x_\mathrm{H})_a}{\partial r}\right]}{\tau(D_\mathrm{H}(x_\mathrm{H})_a+D_\mathrm{M}(x_\mathrm{M})_a)}\tag{14}$$

Using Eqs. 10 and 14, the continuity Eq. 11 can be simplified to

$$\frac{\partial(x_\mathrm{H})_a}{\partial t}=\frac{D_\mathrm{H}D_\mathrm{M}f_\sigma}{\tau\alpha}[\alpha-(\alpha-1)(x_\mathrm{H})_a]^2\frac{1}{r^2}\frac{\partial}{\partial r}\times\left[r^2\frac{\partial(x_\mathrm{H})_a/\partial r}{D_\mathrm{M}+(D_\mathrm{H}-D_\mathrm{M})(x_\mathrm{H})_a}\right]\tag{15}$$

where $f_\sigma(=[\Re_\sigma]/Q)$ represents the fraction of the fixed sites in dissociated form. The initial and the boundary conditions required for the solution of Eq. 15 are

$$(x_\mathrm{H})_a|_{t=0}=1\qquad\left.\frac{\partial(x_\mathrm{H})_a}{\partial r}\right|_{r=0}=0\tag{16}$$

$$\left.\begin{aligned}&(x_\mathrm{H})_a|_{r=R_o}=0\qquad\text{(Particle Diffusion Control)}\\&\left.\frac{\epsilon_pD_\mathrm{H}}{\tau}\frac{\partial(x_\mathrm{H})_a}{\partial r}\right|_{r=R_o}=-\frac{2D_\mathrm{M}D_\mathrm{OH}}{(D_\mathrm{M}+D_\mathrm{OH})}\frac{[\mathrm{OH}]_o}{\delta}\\&\qquad\text{(Film Diffusion Control)}\end{aligned}\right\}\tag{17}$$

Variation of $[\mathrm{OH}]_o$ with time can be obtained by solving the following continuity equation for $[\mathrm{OH}]_o$ in the bulk solution.

$$-\frac{d[\mathrm{OH}]_o}{dt}=\frac{3W[\mathrm{OH}]_i}{QR_o}\epsilon_p\langle J_H\rangle|_{r=R_o}\tag{18}$$

where W is the dimensionless resin loading.

Experimental

The experiments were conducted in the ORION Autochemistry Set (E940). The experimental setup and the impeller speed (600 rpm) were the same as used in our previous work (Hasnat and Juvekar, 1996). Resin in H-form was contacted with alkali hydroxide (NaOH/KOH). Nitrogen blanket was provided over alkali hydroxide solutions during experiments to prevent CO_2 absorption. Two experiments involving ordinary ion exchange between NaCl in the solution and H-form of Amberlite 200 resin were also conducted in order to estimate the magnitude of f_σ.

Results and Discussions

The model parameters δ and f_σ were regressed using unweighted least-square fit of the experimental data with the model equations developed in the previous section. The Neale and Nader (1973) model is used to estimate the tortuosity factor (τ).

Table 1 lists the regression estimates of δ from the linear plots along with standard deviation (σ_d). It also lists the regression estimates of f_σ and δ for various experiments conducted in this study including those of ordinary ion exchange for Amberlite 200 resin. In addition, the average values of f_σ and δ for Dowex 50W X8 obtained from our previous work are also reported for the purpose of comparison. The following observations can be made from these data:

(1) The values of film thickness δ (for both Dowex 50W X8 and Amberlite 200 resin particles) estimated from the neutralization experiments are in good agreement with those obtained from the ordinary ion-exchange experiments.

Table 1. Estimated Values of the Model Parameters (f_σ and δ) (Resins: H-Form)

Resin	Species in the Solution	Initial Solution Conc. $mol \cdot m^{-3}$	Resin Loading W	δ $m \times 10^6$	f_σ $\times 10^2$	σ_d $\times 10^3$
Dowex 50W X8	NaOH	1.00	12.0	3.67		5.22
$R_o = 420\ \mu m$	NaOH	5.00	2.10	3.49		4.47
$Q = 1{,}144.86\ mol \cdot m^{-3}$	NaOH	10.0	2.86	3.18		1.43
$\epsilon_p = 0.428$	NaOH	10.0	1.23	3.27		2.55
	NaOH	10.0	0.820	3.13		1.59
	NaOH	50.0	0.687	3.45	4.22	1.88
	NaCl*	100	0.735	3.60	4.28	2.11
Amberlite	NaOH	10.0	0.878	3.13		5.79
200	NaOH	50.0	1.25	3.61	2.95	7.01
$R_o = 280\ \mu m$	NaOH	50.0	0.576	3.55	2.82	3.55
$Q = 1{,}785.0\ mol \cdot m^{-3}$	KOH	50.0	1.17	3.87	2.93	1.82
$\epsilon_p = 0.200$	KOH	50.0	0.859	3.96	2.85	3.00
	NaCl	10.0	1.45	3.97	2.95	8.01
	NaCl	10.0	0.816	3.83	2.83	1.66

$D_H = 9.31 \times 10^{-9}\ m^2 \cdot s^{-1}$, $D_{Na} = 1.33 \times 10^{-9}\ m^2 \cdot s^{-1}$, $D_K = 1.95 \times 10^{-9}\ m^2 \cdot s^{-1}$, $D_{OH} = 5.21 \times 10^{-9}\ m^2 \cdot s^{-1}$ (Robinson and Stokes, 1959). $\alpha_{Na^+/H^+} = 1.53$ and $\alpha_{K^+/H^+} = 2.20$ (Anderson, 1988).

*Data from our previous work (Hasnat and Juvekar, 1995) on ordinary ion exchange.

(2) Values of f_σ estimated from the neutralization experiments are also in good agreement with those from ordinary ion-exchange experiments.

(3) It is also seen that f_σ is independent of resin loading, solution concentration and the type of ions exchanging. This finding is also in agreement with that made in respect of the ordinary ion exchange.

The above observations are indicative of the internal consistency between our models for the ordinary and the reactive ion exchange.

Notation

$[i]$ = concentration of ion i (i = M, H or OH), $mol \cdot m^{-3}$
D = free diffusion coefficient of ion, $m^2 \cdot s^{-1}$
J = diffusional flux of ion, $mol \cdot m^{-2} \cdot s^{-1}$
R = universal gas constant, $J \cdot K^{-1} \cdot mol^{-1}$
t = time, s
T = temperature, K
$\mathfrak{F}$ = Faraday constant, $C \cdot mol^{-1}$
ϵ_p = fractional pore volume

Subscripts

i = initial state and cationic species ($i = H^+$ or M^+)
0 = bulk solution

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