A generalized model for the measurement of effective diffusion coefficients of heterovalent ions in ion exchangers by the zero-length column method

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Abstract

A generalized theoretical model for the measurement of effective diffusion coefficients of heterovalent ions in ion exchange resins by the zero-length column method was developed. The model included the resistance to mass transfer both in the particle and in the film and described ion fluxes with Nernst–Planck equations. Equilibria were described using a model based on the mass action law. The values of intraparticle diffusivity of Cu²⁺, Cd²⁺, Zn²⁺, and H⁺ on commercial Amberlite IR-120 were obtained by non-linear regression, these values agree fairly well with data reported previously in literature. The following trend was observed: \( D_{\text{Cu}} > D_{\text{Zn}} > D_{\text{Cd}} \).

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1. Introduction

Batch, shallow bed or single-particle methods have been applied for the measurements of intraparticle diffusivities in ion exchangers. In a previous paper (Rodriguez et al., 1998), the authors developed a model for measuring monovalent cations intraparticle diffusivities in ion exchange resins by the zero-length column (ZLC), a very easy and fast experimental technique. Aqueous binary systems with monovalent ions were used to test the validity of the model and the accuracy and reliability of the method. Even though, this model should be changed to use the same method for the determination of heterovalent cations diffusion coefficients, whose values are required for the correct design of industrial processes. This theoretical model considered the ZLC cell as a continuous stirred tank reactor. The model described ion fluxes with Nernst–Planck equations, equilibrium using ideal mass action law, and included the resistance to mass transfer both in the particle and in the film.

Since its development by Eic and Ruthven (1988), the ZLC elution technique has become widely used. Originally introduced for low concentration (linear adsorption isotherm) gaseous hydrocarbon systems, the method has since been both theoretically and experimentally developed to include the study of many other systems, including gaseous (Loos et al., 2000; Eic et al., 1988; Silva and Rodrigues, 1997) and liquid (Brandani et al., 1996; Ruthven and Stapleton, 1993; Brandani and Ruthven, 1995) systems.

The ZLC is a differential bed of resin particles which is primarily saturated with a solution of ions. At zero time a solution containing a different counterion is fed at sufficiently high flow rate and the desorption curve is analysed in terms of the concentration of the ion initially present in the resin phase as a function of time. Once the resin is completely saturated with the entering counterion, the reverse elution operation can be carried out, returning the resin sample to the primitive state.

Ion fluxes can be described either by the Fick approximation or by the Nernst–Planck one. The Nernst–Planck model requires the knowledge of the resin phase self-diffusivity of each ion involved in the process (Chowdhiah and Foutch, 1995). Reliable correlations linking resin-phase diffusivity to liquid-phase diffusivity are not available, and the different values proposed in the literature are somewhat contradictory (Slater, 1991). Anyway, one has to consider the homogeneous or the macroporous nature of the particle, to obtain a reasonable description of the diffusional process.
The Nernst–Planck model accounts for the influence of the electric field caused by the differences in the mobilities of counterions on the ion exchange rate, while Fick’s law considers only diffusion. Differences between uptake and elution kinetics for a given system and the dependence of the exchange rate with the concentration of each counterion can be predicted by the Nernst–Planck model (Chowdiah and Foutch, 1995). External mass transfer resistance also affects the ion exchange rate. In general, at low solution concentrations, external mass transfer is the controlling step (Kraaijeveld and Wesselingh, 1993), while intraparticle diffusion resistance is normally dominant at higher solution concentrations (Helfferich, 1962).

The main objectives of the present study are as follows:

(i) To develop a generalized mathematical model to describe the response of the ZLC system, with independence of the ion valence. The model includes the resistance to mass transfer in the film and inside the particle, a thermodynamic constant to describe the ion-exchange equilibrium at the particle surface, and the effect of the electric field.

(ii) To test again the validity of the ZLC method to obtain in a simple and accurate manner, the ion diffusion coefficients.

(iii) To obtain the intraparticle diffusivity of Cu$^{2+}$, Cd$^{2+}$, and Zn$^{2+}$ on commercial Amberlite IR-120.

2. Mathematical model

Model equations have been derived including the followings simplifying assumptions:

(i) The whole resin is treated as a quasi-homogeneous phase. Resin beads are assumed to be completely spherical in shape with no appreciable volume changes during the ion exchange process.

(ii) The effects of pressure gradients and activity are neglected.

(iii) Co-ion concentrations in the ion exchanger is negligible.

(iv) Ion intraparticle diffusivities do not depend on particle concentration.

Taking into account the previous assumptions, a homogeneous diffusion equation describes more properly the physical reality inside the resin and for the experimental validation of the model a gel-type resin (homogeneous, non-porous) should be used.

An isothermal ion exchange process between an ion $j^r^+$ presaturating the resin and an ion $n^{x^+}$ entering the resin particle, can be described by the following general equation:

$$z_n(R_e,j) + z_j n^{x^+} \leftrightarrow z_j(R_e,n) + z_n j^{r^+}. \quad (1)$$

Systems with heterovalent ions exhibit a non-ideal equilibrium relationship since the exchanging ions have significantly different mobilities. In order to simplify the calculation of the effective diffusion coefficients, the ion–ion interactions in both liquid and solid phases will be neglected. So, Maxwell Stefan relationships for the ionic flux rates will be reduced to the Nernst–Planck equations. The general equations corresponding to the flux of ion expressed in terms of the concentration gradient assuming Nernst–Planck equations for the ion flux of both counter ions ($j$ and $n$) and the electroneutrality condition, are given by

$$N_j = -D_j \frac{\partial q_j}{\partial r} - D_j z_j q_j \frac{\phi}{RT} \frac{\partial \phi}{\partial r},$$

$$N_n = -D_n \frac{\partial q_n}{\partial r} - D_n z_n q_n \frac{\phi}{RT} \frac{\partial \phi}{\partial r}.$$  \hspace{0.5cm} (2)

where $q_j$ is the concentration in the resin phase of the ion $j$, $D_j$ is the effective diffusivity of the ion $j$, $z_j$ is the electrochemical valence of the ion $j$, $r$ is the space coordinate in the particle assumed with spherical geometry, $\phi$ is the electric potential, $\mathcal{I}$ is the Faraday constant, $\Gamma$ is the perfect gas constant, and $T$ is the temperature. Assuming that no electric current develops and that there are not vacant ionic sites inside the resin, i.e., that the electroneutrality condition is verified, the model includes the following equations:

$$z_nN_n + z_jN_j = 0,$$  \hspace{0.5cm} (3)

$$z_n q_n + z_j q_j = \mathcal{I}.$$  \hspace{0.5cm} (4)

The term corresponding to the electric field in Eq. (2) can be eliminated, so

$$\frac{\partial \phi}{\partial r} = \frac{(D_n - D_j) z_j}{D_n z_n Q + (D_j z_j - D_n z_n) z_j q_j} \frac{\partial q_j}{\partial r}.$$  \hspace{0.5cm} (5)

The general equation corresponding to the flux of ion $j$, expressed in terms of the concentration gradient, is then

$$N_j = -D_j D_n \left( \frac{z_n Q + (z_j - z_n) z_j q_j}{D_n z_n Q + (D_j z_j - D_n z_n) z_j q_j} \right) \frac{\partial q_j}{\partial r} - D_{jn} \frac{\partial q_j}{\partial r},$$  \hspace{0.5cm} (6)

where $\delta = D_j/D_n$ is the ratio between the diffusivities of species $j$ and $n, Q$ is the total solid-phase capacity, and $D_{jn}$ is the interdiffusion coefficient.

The mass balance in the resin particle is

$$\frac{\partial q_j}{\partial t} = - \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q_j}{\partial r} \right)$$  \hspace{0.5cm} (7)

and introducing the flux equation, one gets

$$\frac{\partial q_j}{\partial t} = - \frac{2}{r} N_j - \frac{\partial}{\partial r} N_j$$  \hspace{0.5cm} (8)

with initial and boundary conditions:

$$r = 0, \quad \frac{\partial q_j}{\partial r} = 0,$$  \hspace{0.5cm} (9)

$$t = 0, \quad q_j = \mathcal{I}, \quad C_j = C_{jn} = C_T$$  \hspace{0.5cm} (10)
and taking into account the resistance in the film to mass transfer,
\[ r = R_p, \quad -D_{jn} \frac{\partial q_j}{\partial r} \bigg|_{r=R_p} = K_f(C_j^o - C_j), \] (11)

where the concentration at the solid resin surface \( q_j^o \) is related to the concentration of the liquid \( C_j^o \) by the following equilibrium relation (based on the mass action law):
\[ K_f = \frac{(1 - y_j^{o})^2 \cdot (C_j^{o} \cdot C_T \cdot z_j)^{1/2}}{y_j^{o} \cdot [(1 - x_j^{o}) \cdot C_T \cdot z_j]^{1/2}}, \] (12)
\[ x_j^{o} = \frac{C_j^{o}z_j}{C_T}, \] (13)
\[ y_j^{o} = \frac{q_j^{o}z_j}{Q}, \] (14)

where \( y_j^{o} \) is the normalized concentration of species \( j \) in the external surface of the resin phase. Ion exchange equilibrium data were obtained by extrapolation from the values reported in a previous paper (Valverde et al., 2002).

The mass balance for the ZLC is
\[ V(1 - \epsilon) \frac{d q_j}{d t} + V_e \frac{d c_j}{d t} + F C_j = 0, \] (15)

where
\[ \frac{d q_j}{d r} = \frac{3}{R_p} (-N_j)_{r=R_p}. \] (16)

Introducing the following dimensionless variables:
\[ \tau = \frac{D_j}{R_p}, \quad R = \frac{r}{R_p}, \] (17)
\[ \frac{d q_j}{d t} = \frac{D_j}{z_j} \frac{d y_j}{d \tau}, \quad \frac{d c_j}{d \tau} = \frac{R_p}{D_j} d \tau, \quad d \tau = R_p \, d r. \] (18)

Eq. (8) becomes
\[ \frac{\partial y_j}{\partial \tau} = \frac{2(z_n + (z_j - z_n)y_j)}{R \cdot [z_n + (\partial z_j - z_n)y_j]^2} \left( \frac{\partial y_j}{\partial R} \right) \right. \]
\[ + \frac{z_n z_j (1 - \delta)}{[z_n + (\partial z_j - z_n)y_j]^2} \left( \frac{\partial y_j}{\partial R} \right)^2 \]
\[ + \frac{z_n + (z_j - z_n)y_j}{z_n + (\partial z_j - z_n)y_j} \left( \frac{\partial^2 y_j}{\partial R^2} \right). \] (19)

The initial and boundary conditions in dimensionless form are
\[ R = 0, \quad \frac{\partial y_j}{\partial R} = 0, \] (20)
\[ \tau = 0, \quad y_j = 1, \quad X_j = 1, \] (21)
\[ R = 1, \quad -D_{jn} \frac{\partial q_j}{\partial R} \bigg|_{R=1} = \frac{D_j}{R_p} \left[ \frac{z_n + (z_j - z_n)y_j}{z_n + (\partial z_j - z_n)y_j} \right] \frac{\partial y_j}{\partial R} \bigg|_{R=1} = K_T C_T (x_j^{o} - x_j). \] (22)

Taking into account the capacity factor \( C_j^o \)
\[ C_j^o = \frac{Q(1 - \epsilon)}{C_T e}, \] (23)

and defining
\[ N_u = \frac{K_f R_p}{D_j}. \] (24)

To describe the mass transfer through the external film, the following relation (Kataoka et al., 1973) was employed:
\[ K_L = \frac{u}{\epsilon_b} 1.85 R \cdot e^{-2/3} S_c^{-2/3} \left[ 1 - \frac{\epsilon_b}{\epsilon_b} \right]^{-1/3}, \] (25)

where \( u \) is the superficial velocity, \( S_c \) is the Schmidt number and \( R \) is the Reynolds number both defined as
\[ S_c = \frac{\mu}{\rho \cdot D_j}, \] (27)
and
\[ R = \frac{\rho \cdot 2 R_p u}{\mu(1 - \epsilon_b)}. \] (28)

The ZLC mass balance in dimensionless form becomes
\[ 3C_j^o \left[ \frac{z_n + (z_j - z_n)y_j}{z_n + (\partial z_j - z_n)y_j} \right] \left[ \frac{\partial y_j}{\partial R} \right]_{R=1} + \frac{\partial x_j}{\partial \tau} + L x_j = 0. \] (28)

Model parameters are as follows:

(a) Equilibrium parameters: \( K \) and \( C_j^o = \frac{Q(1 - \epsilon)}{C_T e} \).
(b) Diffusivity ratio: \( \delta = \frac{D_j}{D_p} \).
(c) Nusselt number: \( N_u = \frac{K_f R_p}{D_j} \).
(d) ZLC parameter: \( L = \frac{F \cdot R_p^2}{V_e D_j} \).

The above system of equations was solved by using orthogonal collocation on finite elements with Lagrange polynomials as trial functions (Finlayson, 1980). By applying this mathematical technique one can reduce the partial differential equations (19) and (28) to a set of ordinary differential equations. After doing this, one has the values of the solution at each interior collocation point at the new time. Boundary values and the solution at the points between elements must be evaluated by solving the corresponding algebraic equations. To this purpose, Marquardt’s algorithm (Marquardt, 1963) was used.

The Rosenbrock method (Press et al., 1992) was used to integrate numerically the stiff set of ordinary differential equations due to the few steps of integration required to achieve the solution.

A Fortran 6.0 application was developed for solving this model. It was previously verified that four interior collocation points on each of the two finite elements used were enough to attain suitable mathematical solutions (Rodriguez et al., 2002).
3. Simulation results

Fig. 1 shows the desorption curves for different values of the relation between the diffusion coefficients, $\delta(D_j/D_n)$, at fixed and realistic values of the rest of parameters. When $\delta$ is nearly to unity, the desorption curve does approximate to a straight line at long time. That is due to the same mobility of the ions so the electric field is negligible and the behaviour of the system could be well described by the Fick law. This same performance is observed when a single solute is desorbed from an adsorbent in gaseous or liquid ZLC systems (Brandani, 1996).

The initial part of the response curves corresponds with the washing up of the cell (Rodriguez et al., 1998). It can be observed that the concentration of the eluted ion in the effluent diminishes more slowly during the washing up part when the diffusivity of the entering ion is large. Following with the minority rule, the exchange rate in that initial part of the elution process is limited by the diffusivity of the entering ion. Thus, when the diffusivity of the entering ion is low, the ion initially in the resin is more slowly exchanged. In the long time region when the amount of the entering ion inside the resin grows, the flux of the ion initially in the resin increases. In this case, the process is controlled by the self diffusion coefficient of the minority ion, the one initially in the resin.

Fig. 2 shows the effect of the equilibrium constant on the response curves for a fixed set of parameters. As expected, the elution curves agree with the results that can be obtained from a continuous stirred tank reactor set-up for different $K_{j,n}$ values (Rodrigues and Beira, 1979). In the elution curves, the shape of the washing up zone is strongly influenced by the equilibrium constant, $K_{j,n}$. In the long time region, the curves have different slopes, due to the changes achieved in the washing up zone: lower the concentration of the eluted ion in the washing up zone is (corresponding to the less unfavourable equilibrium), faster its elution in the long time region is.

As seen in Fig. 3, the shape of the washing up zone depends on the concentration of the external solution, $C_T$. Thus, the amount of eluted ion is higher when $C_T$ increases. This fact indicates that the driving force has an important influence on the elution of ions.

4. Experimental section

4.1. Chemical

Zinc, copper and cadmium nitrates PRS grade (99%), and nitric acid 65% w/w PA grade, were supplied by Panreac. Demineralized water with a conductivity value lower than 5 $\mu$S/cm was used. The cationic resin Amberlite IR-120, supplied by Rohm & Haas, was used as the ion exchanger.
The resin was pretreated and regenerated to convert it to the H⁺-form, as described by De Lucas et al. (1992).

The physical properties of the resin are summarized in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix type</td>
<td>Geliform</td>
</tr>
<tr>
<td>Functional structure</td>
<td>Sulphonic</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>47–62</td>
</tr>
<tr>
<td>Particle density (kg of dry resin/m³ of wet resin)</td>
<td>0.560</td>
</tr>
<tr>
<td>Total exchange capacity (mol/kg of dry resin)</td>
<td>5.01</td>
</tr>
<tr>
<td>Average particle diameter (m)</td>
<td>7.04 × 10⁻⁴</td>
</tr>
</tbody>
</table>

4.2. Procedure

The experimental system is shown schematically in Fig. 4. A double head peristaltic pump (Masterflex L/S model 751800; maximum flow 5.6 × 10⁻⁵ m³/s), previously calibrated, was used to provide streams of ion solutions at constant flow rates. The switch valve was standard four-port valve, and the detector was a conductivity cell. The ZLC system consisted of a small filter holder of 2.5 cm i.d., with a shallow bed of resin (2 mm, bed volume = 9.8 × 10⁻⁷ m³). The volume of the cell was, V = 4.0 × 10⁻⁶ m³, and the volume of the tubing between the valve and the conductivity cell was approximately equal to 3.7 × 10⁻⁹ m³. The connection of the ZLC with the four-port valve and the conductivity cell were made as close as possible in order to minimize the extra column hold up. Conductivity data were recorded continuously by a computer.

The volume of the cell and its porosity were calculated from blank experiments as described by Ruthven and Stapleton (1993). The blank response of the system was running with the resin in Na⁺ form. Initially, a 150 mol/m³ solution of NaCl was fed and at a zero time a step input of deionised water was introduced, the elution curve of NaCl being analysed. The results are shown in Fig. 5 as plot of ln(C/C₀) against the effluent volume (F = 1.5 × 10⁻⁷ m³/s).

\[
\frac{C}{C_0} = e^{-U_t/V}\epsilon
\]  

(29)

The porosity of the cell, ε, was equal to 0.8 and the porosity of the resin bed, εᵦ, used in Eqs. (25) and (27), was 0.31.

Initially, a thin layer of resin (2 mm) was placed in the ZLC cell and a solution was continuously fed until resin saturation. At zero time, a solution containing a different counterion and the same total concentration was fed at sufficiently high flow rate, and the desorption curve was analysed in terms of the concentration of the ion initially in the resin phase versus time. Once the resin was completely
Table 2
Ion exchange equilibrium constants, \( K_{j,n} \), for the binary systems \( \text{H}^+ / \text{Cd}^{2+} \), \( \text{H}^+ / \text{Cu}^{2+} \), and \( \text{H}^+ / \text{Zn}^{2+} \) on the resin Amberlite IR-120 at 298 K

<table>
<thead>
<tr>
<th>System ((j=n))</th>
<th>( T (\text{K}) )</th>
<th>( K_{j,n} )</th>
<th>Av. dev. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}^+ / \text{Cu}^{2+} )</td>
<td>298</td>
<td>65.01</td>
<td>0.88</td>
</tr>
<tr>
<td>( \text{H}^+ / \text{Cd}^{2+} )</td>
<td>298</td>
<td>11.08</td>
<td>0.02</td>
</tr>
<tr>
<td>( \text{H}^+ / \text{Zn}^{2+} )</td>
<td>298</td>
<td>135.0</td>
<td>3.92</td>
</tr>
</tbody>
</table>

saturated with the entering counterion, the reversal elution curve was carried out returning the resin sample to the primitive state. All the experiments were carried out at 25°C. The systems under study were 150 mol/m³ solutions of \( \text{Cu(NO}_3\text{)}_3 \), \( \text{Cd(NO}_3\text{)}_2 \), \( \text{Zn(NO}_3\text{)}_2 \), and \( \text{HNO}_3 \). Each run was conducted twice, showing good reliability. Experimental measurements demonstrated that the volume of resin in the ZLC was enough to obtain sufficient sensitivity to follow the tails of desorption curves with accuracy.

5. Results and discussion

Table 2 contains for all the systems under study the values of the equilibrium constant, \( K_{j,n} \), of Eq. (12), at 298 K. Likewise, the load and regeneration elution curves for each of the systems \( \text{H}^+ / \text{Cd}^{2+} \), \( \text{H}^+ / \text{Cu}^{2+} \), and \( \text{H}^+ / \text{Zn}^{2+} \) were obtained at different experimental conditions of flow rate (\( F \)). Values of Schmidt (\( \text{Sc} \)), Reynolds (\( \text{Re} \)) and Nusselt (\( \text{Nu} \)) numbers; film mass transfer coefficient (\( K_L \)), and the ZLC parameter \( L \) of each curve are reported in Table 3.

Table 3
Model parameters for the elution curves (Figs. 6, 9, and 10): flow rate (\( F \)); Schmidt (\( \text{Sc} \)); Reynolds (\( \text{Re} \)) and Nusselt (\( \text{Nu} \)) numbers; film mass transfer coefficient (\( K_L \)), and the ZLC parameter \( L \)

<table>
<thead>
<tr>
<th>Curve ( A/B )</th>
<th>( 10^2 F ) ( (\text{m}^3/\text{s}) )</th>
<th>( 10^{-2} \text{Sc} )</th>
<th>( \text{Re} )</th>
<th>( \text{Nu} )</th>
<th>( 10^4 K_L )</th>
<th>( 10^{-3} L )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu}^{2+} / \text{H}^+ )</td>
<td>5.00</td>
<td>1.07</td>
<td>1.08</td>
<td>3850.0</td>
<td>1.87</td>
<td>1.33</td>
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<tr>
<td>( \text{Cu}^{2+} / \text{H}^+ )</td>
<td>8.30</td>
<td>1.07</td>
<td>1.79</td>
<td>4557.0</td>
<td>2.21</td>
<td>2.20</td>
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<tr>
<td>( \text{Cu}^{2+} / \text{H}^+ )</td>
<td>14.5</td>
<td>1.07</td>
<td>3.14</td>
<td>5487.9</td>
<td>2.67</td>
<td>3.85</td>
</tr>
<tr>
<td>( \text{Cd}^{2+} / \text{H}^+ )</td>
<td>6.30</td>
<td>1.07</td>
<td>1.36</td>
<td>6403.3</td>
<td>2.02</td>
<td>2.58</td>
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<tr>
<td>( \text{Cd}^{2+} / \text{H}^+ )</td>
<td>9.10</td>
<td>1.07</td>
<td>1.97</td>
<td>7238.0</td>
<td>2.28</td>
<td>3.72</td>
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<tr>
<td>( \text{Zn}^{2+} / \text{Cu}^{2+} )</td>
<td>13.9</td>
<td>1.07</td>
<td>3.01</td>
<td>8336.1</td>
<td>2.63</td>
<td>5.68</td>
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<tr>
<td>( \text{Zn}^{2+} / \text{H}^+ )</td>
<td>6.40</td>
<td>1.07</td>
<td>1.39</td>
<td>4795.3</td>
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<td>1.95</td>
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<td>5312.1</td>
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<td>2.65</td>
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<tr>
<td>( \text{Zn}^{2+} / \text{H}^+ )</td>
<td>11.0</td>
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<td>2.40</td>
<td>5761.1</td>
<td>2.43</td>
<td>3.38</td>
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<tr>
<td>( \text{Cu}^{2+} / \text{H}^+ )</td>
<td>4.50</td>
<td>584.83</td>
<td>0.97</td>
<td>1.702</td>
<td>0.027</td>
<td>0.036</td>
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<tr>
<td>( \text{Cu}^{2+} / \text{H}^+ )</td>
<td>6.00</td>
<td>584.83</td>
<td>1.30</td>
<td>1.873</td>
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<td>( \text{H}^+ / \text{Cu}^{2+} )</td>
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<td>( \text{H}^+ / \text{Cd}^{2+} )</td>
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<tr>
<td>( \text{H}^+ / \text{Cd}^{2+} )</td>
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<td>0.18</td>
<td>25.14</td>
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<tr>
<td>( \text{H}^+ / \text{Zn}^{2+} )</td>
<td>14.7</td>
<td>14.00</td>
<td>0.32</td>
<td>30.41</td>
<td>0.483</td>
<td>0.1119</td>
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<tr>
<td>( \text{H}^+ / \text{Zn}^{2+} )</td>
<td>2.78</td>
<td>13.89</td>
<td>0.60</td>
<td>17.53</td>
<td>0.279</td>
<td>0.0225</td>
</tr>
<tr>
<td>( \text{H}^+ / \text{Zn}^{2+} )</td>
<td>5.00</td>
<td>13.89</td>
<td>0.11</td>
<td>21.33</td>
<td>0.339</td>
<td>0.0405</td>
</tr>
<tr>
<td>( \text{H}^+ / \text{Zn}^{2+} )</td>
<td>6.00</td>
<td>13.89</td>
<td>0.13</td>
<td>22.67</td>
<td>0.361</td>
<td>0.0486</td>
</tr>
</tbody>
</table>

In order to obtain reliable and meaningful values of the intraparticle diffusion coefficients for \( \text{Cu}^{2+} \), \( \text{Cd}^{2+} \), \( \text{Zn}^{2+} \) and \( \text{H}^+ \) ions, all the experimental data were fitted together by non-linear regression to the mathematical model described in a previous section. As observed in Table 4, a good fitting was obtained since all of the four parameters are highly meaningful from the statistical point of view: the ratio \( t_c/t \) (t-test) is in all cases far higher than the unity. The obtained result for the \( D_H \) is in good agreement with the value reported for the same resin by the authors in a previous work (Rodriguez et al., 1998). The elution curves for the cupper–hydrogen system at \( C_{j0} = 150 \text{ mol/m}^3 \) are shown in Fig. 6. Fig. 7 shows the comparison between the elution \( \text{H}^+ / \text{Cu}^{2+} \) and the reversal \( \text{Cu}^{2+} / \text{H}^+ \) from experimental and simulated data. The asymmetrical behaviour of desorption curves are predicted by the Nernst–Planck model since the values of \( \delta \) and \( K_{j,n} \) are reciprocal to those in the previous step. In the long time region, it can be seen that the exchange rate is faster when \( \text{H}^+ \) is initially in the resin and it is slower when \( \text{Cu}^{2+} \) is the ion initially in the resin.

Table 4
Free diffusion coefficients (Chapman, 1967), \( D_f \), intraparticle diffusion coefficients, \( D_j \), determined in this work by non-linear regression, and t-test of statistical significance for the parameters fitted (significance level of 0.05)

<table>
<thead>
<tr>
<th>Species</th>
<th>( 10^{10} D_f ) ( (\text{m}^2/\text{s}) )</th>
<th>( 10^{11} D_j ) ( (\text{m}^2/\text{s}) )</th>
<th>( t_c/t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu}^{2+} )</td>
<td>7.150</td>
<td>1.71</td>
<td>18.74</td>
</tr>
<tr>
<td>( \text{Cd}^{2+} )</td>
<td>6.260</td>
<td>1.11</td>
<td>37.21</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} )</td>
<td>7.100</td>
<td>1.49</td>
<td>35.21</td>
</tr>
<tr>
<td>( \text{H}^+ )</td>
<td>0.931</td>
<td>0.56</td>
<td>11.79</td>
</tr>
</tbody>
</table>
Theoretical curves

Time (s)

\( F = 4.5 \times 10^{-7} \text{ m}^3/\text{s} \)
\( F = 6.0 \times 10^{-7} \text{ m}^3/\text{s} \)
\( F = 8.4 \times 10^{-7} \text{ m}^3/\text{s} \)
\( F = 14.5 \times 10^{-7} \text{ m}^3/\text{s} \)

Theoretical curves

\( C_{\text{H}} / C_{\text{H0}} \) vs. time for the system H\(^+\)–Cu\(^{2+}\); and (b) semilog plot of \( C_{\text{Cu}} / C_{\text{Cu0}} \) vs. time for the system Cu\(^{2+}\)–H\(^+\).

\( \tau \rightarrow 0.1 \)
\( \tau \rightarrow 0.9 \)
\( \tau \rightarrow 0.7 \)
\( \tau \rightarrow 0.4 \)

\( \tau \rightarrow 0.04 \)
\( \tau \rightarrow 0.02 \)
\( \tau \rightarrow 0.06 \)
\( \tau \rightarrow 0.14 \)

Fig. 6. (a) Semilog plot of \( C_{\text{H}} / C_{\text{H0}} \) vs. time for the system H\(^+\)–Cu\(^{2+}\); and (b) semilog plot of \( C_{\text{Cu}} / C_{\text{Cu0}} \) vs. time for the system Cu\(^{2+}\)–H\(^+\).

Fig. 7. Desorption curves, \( C_{\text{J}} / C_{\text{J0}} \) vs. time calculated from the ZLC model for the systems Cu\(^{2+}\)–H\(^+\) ( ), H\(^+\)–Cu\(^{2+}\) (a), and theoretical curves (—).

As seen in Fig. 8, the evolution of the dimensionless profiles inside the particle is very different for both desorption curves: when the resin is in the H\(^+\)–form (Fig. 8a), abrupt concentration profiles inside the particle are obtained. This is due to the greater affinity of the resin to the ion in the solution with a greater valence together with the higher diffusion coefficient of the eluted ion that allows a faster ion exchange process. However, when the resin is in the Cu\(^{2+}\)-form (Fig. 8b), concentration profiles inside the particle are flat since the resin presents higher affinity to the sorbed ion with a higher valence and a smaller diffusion coefficient.

The experimental desorption curves together with the model results for the zinc–hydrogen system are shown in Fig. 9. In this case, a value of \( D_{\text{Zn}} = 1.49 \times 10^{-11} \text{ m}^2/\text{s} \), a bit smaller than the cupper diffusion coefficient \( D_{\text{Cu}} = 1.71 \times 10^{-11} \text{ m}^2/\text{s} \), was obtained. This result agrees qualitatively with that reported by Slater (1991) for the sulphonic resin Dowex 50WX8. These curves present the same behaviour with the flow as those for the systems H\(^+\)/Cu\(^{2+}\) and Cu\(^{2+}\)/H\(^+\).

Comparing elution curves (at the same flow, \( F = 6 \times 10^{-7} \text{ m}^3/\text{s} \)) for the systems H\(^+\)/Cu\(^{2+}\) and H\(^+\)/Zn\(^{2+}\), it can be noted that, in the washing up zone, the elution of the hydrogen ion for the system H\(^+\)/Cu\(^{2+}\) is faster than in that for the system H\(^+\)/Zn\(^{2+}\). It agrees with the previous comments about the effect of the equilibrium constant on the elution curves.
Fig. 9. (a) Semilog plot of \( \frac{C_{\text{H}}}{C_{\text{H}0}} \) vs. time for the system \( \text{H}^+–\text{Zn}^{2+} \); and (b) semilog plot of \( \frac{C_{\text{Zn}}}{C_{\text{Zn}0}} \) vs. time for the system \( \text{Zn}^{2+}–\text{H}^+ \).

Fig. 10 shows the experimental desorption curves for the system \( \text{H}^+–\text{Cd}^{2+} \), together with the model results. A value of \( D_{\text{Cd}} = 1.11 \times 10^{-11} \text{ m}^2/\text{s} \), a bit smaller than the zinc diffusion coefficient, was found. Bilba et al. (1999) reported a similar value for the intraparticle diffusion coefficient of the cadmium in the sulphonic resin Purolite C-150 (with 8% crosslinking). A similar behaviour with the flow was observed as mentioned above for the rest of systems studied.

It can be observed that the amount of the eluted ion increases in the washing up zone when higher the flow is, and it does not depend on the ion. This increasing in the load of the entering ion could have the same effect than an increase of the concentration.

The values of intraparticle diffusivity of \( \text{Cu}^{2+}, \text{Cd}^{2+}, \text{Zn}^{2+}, \text{and H}^+ \) on commercial Amberlite IR-120 were obtained by non-linear regression, these values agree fairly well with data reported previously in literature. The following trend was observed: \( D_{\text{Cu}} > D_{\text{Zn}} > D_{\text{Cd}} \). The model reproduces the effect of the flow on the elution curves using the diffusion coefficients obtained.

**Notation**

\( C_j, C_i^e \) concentration of species \( j \) in the solution phase at equilibrium, mol/m\(^3\)

\( C_{j0} \) initial concentration of species \( j \), mol/m\(^3\)

\( C_T \) total ionic concentration in solution, mol/m\(^3\)

\( D_j \) intraparticle diffusion coefficient of species \( j \), m\(^2\)/s

\( D_{jn} \) interdiffusion coefficient, m\(^2\)/s
**References**


