The main objective of the present work was to determine the intraparticle interdiffusion coefficients in weak acid resins containing carboxylic acid groups, namely Purolite PPC 104 gel-like and C106 macroporous. The rate of H⁺/Na⁺ ion exchange process was measured on weak acid resins with gel and macroporous matrices using a potentiometric method under conditions favouring a particle diffusion controlled mechanism. The results obtained in experiments performed at different stirring speeds and size fractions support the mechanism. The H⁺/Na⁺ interdiffusion coefficients on the resins were obtained by modelling the data with quasi-homogeneous resin phase and bidisperse pore kinetic models, considering a parallel and two-stage interdiffusion in macro- and micropores, respectively. The macropore interdiffusion coefficients in the macroporous resin obtained with bidisperse pore kinetic model are higher than those calculated with quasi-homogeneous models and higher than the interdiffusion coefficients in the gel resin.

Keywords: ion exchange kinetics, interdiffusion coefficients, weak acid resins, sodium ion

The ion exchange technology is widely used for water and wastewater treatment, in nuclear plants, for ultrapure water in electronics and semiconductor industries, to remove and recover heavy metal ions arising from chemical and hydrometallurgical industries etc [1]. The knowledge of ion exchange kinetics is important for the design of new ion exchange technologies or of new separation methods for particular applications. At the same time, the rate of the ion exchange process is an important parameter in selecting a resin for a special purpose. The macroporous resins are extremely resistant to osmotic shocks showing no breakage on repeated swelling and shrinking and have a greater chemical stability to oxidation than gel type resins. The use of weak acid resins in applications - such as the treatment of wastewater streams - to reduce environmental pollution is increasing, but the kinetics of the ion exchange process on these ion exchangers was less studied than on strong acid resins [2].

The specific objectives of the present work are:
- the experimental determination of H⁺/Na⁺ ion exchange rates on gel and macroporous polyacrylic resins crosslinked with divinylbenzene in conditions favouring a particle diffusion controlled mechanism, using a potentiometric method modelling the results using both quasi-homogeneous resin phase and bidisperse pore kinetic models considering a parallel and two-stage interdiffusion in macro- and micropores for the macroporous resins;
- to discriminate between the considered kinetic models.

**Experimental part**

The selected resins were the commercial Purolite PPC104 weak acid gel-like and C106 weak acid macroporous. Both resins have a polycrylic matrix and are crosslinked with divinylbenzene carrying –COOH functional groups. The resins were fractionated by drying, purified by consecutive treatment with 1 M HCl, demineralised water, 1 M NaOH, for three cycles. Finally, the resins were converted in the hydrogen form with 300% excess of 1 M HCl and washed with demineralised water until the effluent had a specific conductivity less than 1 µS cm⁻¹. Each size fraction was air-dried at room temperature and kept in a desiccator over a saturated solution of sodium chloride, until a constant mass was reached.

The mean radius of the swollen beads in hydrogen form was measured microscopically. The results are given as the mean of 50 determinations and 99.9% confidence limits according to Student distribution: (0.377 ± 0.003) . 10⁻³, (0.346 ± 0.004) . 10⁻³, (0.312 ± 0.003) . 10⁻³ m for PPC104 and (0.383 ± 0.031) . 10⁻³, (0.321 ± 0.021) . 10⁻³, (0.266 ± 0.018) . 10⁻³ m and (0.206 ± 0.014) . 10⁻³ m for C106.

Analytical reagent grade Merck p.a. NaNO₃, was used to prepare the stock solution, using demineralised water (specific conductivity < 1 µS cm⁻¹).

The ion exchange rate was measured in a batch reactor at (298 ± 0.5) K using a procedure previously described [3,4]. The H⁺/Na⁺ ion exchange kinetics were monitored with a combined pH-electrode provided with a temperature probe and an analog interface type Mettler Delta 350 pH meter or WTW InoLab pH/cond 740 multimeter. The batch reactor was equilibrated at constant temperature in a Memmert WB 20C temperature-controlled water bath. The stirring was kept constant by a Variomag type maxi magnetic stirrer immersed in the water bath, controlled by a Telemodule 20C. The pH variation was measured with an accuracy of ± 0.001 units. The ion exchange rate was measured for systems with an external solution of 1.00 M NaNO₃ with pH = 5.95.

**Results and discussions**

The kinetic experiments for H⁺/Na⁺ ion exchange process on gel and macroporous weak acid resins were performed in conditions favouring a particle diffusion controlled mechanism, namely under efficient stirring (500 and 600 min⁻¹ respectively), and a concentrated external solution of 1.00 M. The fractional attainement of equilibrium F at time t was calculated from the pH variation of the external solution as:

\[ F = \frac{10^{pH} - 10^{pH_0}}{10^{pH_0} - 10^{pH_f}} \]  

The proton activity coefficient is constant for mono to monovalent ion exchange because the ionic strength was...
not modified during the process, justifying the equation (1).

The pH at the time zero, $pH_0$, has been considered being the first $pH$ value read after the addition of NaNO₃ solution under stirring, varying in different measurements between 3.2 and 3.3 for PPC104 and 3.3 and 3.5 for C106. This procedure avoided the interference of the ion exchange process with the electrolyte desorption process.

The results obtained for $H^+/Na^+$ ion exchange rate on gel PPC104 and macroporous C106 resins, for different sizes of the particles and constant stirring are given in figures 1 and 2, respectively.

The experiments show that decreasing of the mean radius of the swollen beads produces an increase of the ion exchange rate. Moreover, figure 3 shows the lack of influence of the stirring speed on the ion exchange rate for both investigated systems. The obtained results support an ion exchange mechanism controlled by particle diffusion [5, 6].

In order to find an empirical kinetic equation several kinetic functions were fitted to the experimental $F$ vs. $t$ curves. The best-fit was selected for the highest values of R-square, F-statistic and for the more randomly distributed residuals.

The best fitted equation for both resin was:

$$F = a(1 - \exp(-bt)) + c((1 - 1/(1 + d/t)))$$

(2)

The coefficients (95% confidence limits) were: $a = 0.300 \pm 0.020$, $b = 0.003 \pm 0.020$, $c = 0.711 \pm 0.024$, $d = 0.038 \pm 0.032$, with a R-square of 0.9983 and F-statistic of 81157, for the gel resin PPC104 with mean radius of 0.377 mm and

$$a = 0.242 \pm 0.084, b = 0.01493 \pm 0.00046, c = 0.678 \pm 0.077, d = 0.00788 \pm 0.00084, \text{with a R-square of 0.9990 and F-statistic of 30691, for the macroporous resin C106 with mean radius of 0.383 mm.}$$

$H^+/Na^+$ interdiffusion coefficients in the corresponding gel and macroporous weak acid resins were computed using interpolated points (t, F) on the above functions for $0.01 \leq F \leq 0.99$.

Quasi-homogeneous resin phase (QHRP) approximation and bidisperse pore model (BDM) were considered in modelling $H^+/Na^+$ ion exchange kinetics on weak acid resins.

The analytical solution of Fick's equation of continuity with constant diffusion coefficient for ideal systems, spherical beads at infinite solution volume (ISV) [5] is:

$$F(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 t)$$

(3)

Reichenberg [7] proposed two simplified equations derived from equation (3), for $F > 0.85$:

$$F(t) = 1 - \frac{6}{\pi} \exp(-\pi^2 t)$$

(4)

and for $F < 0.85$:

$$F(t) = \frac{6}{\pi^2 t^{1/2}} (\pi^2 t)^{1/2} - \frac{3}{\pi} (\pi^2 t)$$

(5)

The analytical solution of Fick's second law for finite solution volume (FSV) boundary condition is:
\[ F(t) = 1 - \frac{2}{3\omega} \sum_{n=1}^{\infty} \frac{\exp(-S_n^2 \tau)}{1 + S_n^2 \omega} \]  

(6)

where \( \tau = \frac{Dt}{\alpha^2} \) and the quantities \( S_n \) are the roots of the equation \( S_n \cos S_n = 1 + S_n^2 / 3\omega \).

Equation (6) converges very slowly for \( \tau < 0.1 \) and Paterson [5,6] derived the approximation:

\[ F(t) = \frac{\omega + 1}{\omega} \left[ 1 - \frac{1}{\alpha^2 - \beta^2} \left( \alpha \exp(\alpha^2 \tau) \left( 1 + \tau \right) - \beta \exp(\beta^2 \tau) \left( 1 + \tau \right) \right) \right] \]  

(7)

where \( \alpha \) and \( \beta \) are the roots of the equation \( x^2 + 3\omega x - 3\omega = 0 \).

Ruckenstein and co-workers [9] proposed a bidisperse pore kinetic model for transient diffusion in porous spherical particles at infinite solution volume (ISV), with constant diffusion coefficients in macropore \( \Gamma \), and in micropore \( \Gamma_c \). A limiting case of the bidisperse pore model (BDM-LC) considered a two-stage ion exchange process with macroporous diffusion being much faster than the diffusion within the micropores. The fractional attainment of equilibrium at any time \( t \) is given by [9]:

\[ F = \frac{M_s}{M_{\infty}} = \left[ 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 \theta) \right] \frac{1}{1 + \frac{3\alpha}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 \omega)} \]  

(8)

where \( \theta = \frac{D_s}{D} = \frac{r_o^2}{r} \) and \( \alpha = 3 \cdot M_{\infty} / M_s \).

The parameters \( \alpha \) and \( \omega \beta \) of BDM are unknown, but have physical significance. The parameter \( \alpha \) is the ratio between the times required for ion penetration by diffusion of resin particle and of one microsphere forming the macroporous resin bead and must be equal to or smaller than \( 10^3 \) in the above case [9]. The parameter \( \beta \omega \) is defined as the ratio of micro- and macropore uptake at equilibrium, \( M_s / M_{\infty} \), equal to the ratio of ion exchange capacity of the resin due to the functional groups grafted onto walls of the micro- and macropores, respectively, available for the considered ions. This correspondence is given in Table 1. The effective self-diffusion coefficients in macropores \( D_s \) and in micropores \( D_c \) are constant.

Another case of Ruckenstein et al. model takes into account a competitive diffusion in micro- and macropores (BDM-CD), and is described by the following equation [9]:

\[ F = \frac{M_s}{M_{\infty}} = \frac{\sum_{k=1}^{16} \sum_{q=1}^{16} \xi_k^4 \left( \frac{\alpha}{\beta} + 1 + \cot^2 \xi_q \right) \xi_q}{k^2 \left[ 1 - \exp(-\zeta_{\infty}^2 \theta) \right]} \]  

(9)

where \( \zeta_f \) are the roots of the transcendental equation:

\[ \beta \left( 1 - \zeta_f^2 \cot \zeta_f \right) + \alpha \zeta_f^2 = k^2 \pi^2 ; \quad k = 1,2,3,...,\infty. \]  

(10)

The parameters \( \alpha \) and \( \beta \omega \) have the same physical meanings as in equation (8), and \( D_s \) and \( D_c \) are constant.

Seven computer programs previously reported [8,10,11] were used to numerically solve the equations (3) – (9). For a given \( F \) the dimensionless time \( \tau \) or \( \theta \) were obtained. Knowing the time \( t \) for the appropriate \( F \), and the mean radius of the swollen beads, the diffusion coefficient \( \Gamma \) or \( \Gamma_c \) can be calculated. For the equations (3), (6) and (8), ten terms ensured a good convergence [8] of series for \( \tau = 0.1 \), considering \( \Gamma \) varied with maximum 0.1%.

In equation (9), a good convergence for \( F > 0.1 \) is obtained if \( k = 125 \) and \( q = 125 \). The convergence of the series in (9) increases rapidly with \( F \), and decreases with the decrease of \( \alpha \) and \( \beta \omega \) [11]. The obtained interdiffusion coefficients for a quasi-homogeneous resin phase \( \Gamma_d \), and for the macropore of the macroporous resins, \( \Gamma_{d\infty} \), are constant for each domain, and vary with \( F \). They are called integral interdiffusion coefficients [8].

Figures 4 and 5 give the \( H^+ / \text{Na}^+ \) integral interdiffusion coefficients on PPC 104 and C106 resins, respectively, versus the fractional attainment of equilibrium, calculated with the equations (3 – 7). It is noteworthy that for low \( \omega \) values the obtained results with eq. (3, ISV) are in good agreement with those for (6) and (7, FSV). The Paterson approximation (7) avoids the convergence problem and can be used to compute values of \( \Gamma \) for \( F < 0.1 \), whereas eq. (6) was not convergent for \( n = 10 \). Furthermore, the results obtained with Reichenberg approximation for \( F < 0.85 \) (eq. 5, ISV) are in very good agreement with those obtained with (6), FSV for both systems because the batch experiments were done for low \( \omega \) values and ISV assumption is realistic. Thus, the interdiffusion coefficients can be calculated with QHRP models at ISV even for batch experiments if the ratio \( \omega \) is low enough as was observed for \( H^+ / \text{Na}^+ \) ion exchange on gel and macroporous weak acid resins.

The shape of variation of the obtained integral interdiffusion coefficients is in good agreement with Helfferich’s minority rule [5,6].

The quasi-homogeneous concept is reliable for gel resins and a rough approximation for macroporous resins, due to their heterogeneous structure. A macroporous resin particle is an aggregate of clusters of spherical polymeric microparticles of gel type, containing micropores and the large pores are formed between the clusters. A better understanding of the ion interdiffusion in macroporous resins could be obtained with the Ruckenstein et al. models, BDM-LC and BDM-CD, respectively.

In the computer programs [10,11] used for solving eqs. (8) and (9) the input data were \( t, F, \alpha, \beta \omega, r \), and the output data were the corresponding \( t, F, \theta, \Gamma_d \). For BDM-LC \( \omega = 0.001 \). Equation (9) was solved by considering two cases, namely \( \alpha = 1 \) and \( \alpha = 0.1 \). The parameter \( \beta \omega \) is unknown and we do not have any

<table>
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<td>CORRESPONDENCE BETWEEN THE VALUE OF ( \beta / \alpha ) PARAMETER AND THE MICROPOROUS AND MACROPOROUS UPTAKE AT EQUILIBRIUM, ( M_s / M_{\infty} )</td>
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method to evaluate it. The calculations were done for a given $\alpha$ and for different $\beta/\alpha$ (varied systematically) and the obtained values of integral interdiffusion coefficients were compared with the integral interdiffusion coefficients in similar gel type resin determined in this work and with the self-diffusion coefficient of Na$^+$ and H$^+$ ions in dilute aqueous solution $1.334 \times 10^{-9}$ and $9.311 \times 10^{-9}$ m$^2$ s$^{-1}$ at 298 K, respectively [12]. The values of $D_a$ higher than $10^{-9}$ m$^2$ s$^{-1}$ can be discarded because they do not have physical meaning. The most likely $\beta/\alpha$ values for a given $\alpha$ for the studied systems can be evaluated from the results given in figures 6-8.

Figures 6 shows H$^+$/Na$^+$ macropore integral interdiffusion coefficients on macroporous weak acid resin at different fractional attainment of equilibrium computed with BDM-LC ($\alpha = 0.001$) for different $\beta/\alpha$ values. Figures 7 and 8 show the H$^+$/Na$^+$ macropore integral interdiffusion coefficients computed with BDM-CD for $\alpha = 1$ and $\alpha = 0.1$, respectively, and different $\beta/\alpha$ values. The analysis of the corresponding integral interdiffusion coefficients reveals the most plausible values for parameters $\alpha$ and $\beta/\alpha$ of the model.

By increasing $\beta/\alpha$, an enhanced $D_a$ is obtained for a given $\alpha$. According to Ruckenstein et al., for $\alpha = 0.001$, a step-by-step diffusion in macro- and micropores occurs. A limiting value of $D_a$ was obtained for $\beta/\alpha = 0.1$, namely $M_i/M_s = 1/30$ (fig. 6). For higher $\beta/\alpha$ values, $D_a$ becomes higher than the proton self-diffusion coefficient in dilute aqueous solution at 298 K and looses the physical significance. The H$^+$/Na$^+$ integral interdiffusion coefficients in the macroporous C106 resin and in PPC104 gel-like resin obtained with QHRP-ISV models are lower than $D_a$ obtained with BDM (figs. 7 and 8). Under the hypothesis of a competitive diffusion in micro- and macropores with an equal time for a macrosphere and microsphere penetration ($\alpha = 1$), the limit value for $\beta/\alpha$ is 300, with $M_i/M_s = 100/1$. If the rate of diffusion in macropores is

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**Figures:**

- **Fig. 4.** The H$^+$/Na$^+$ integral interdiffusion coefficients on the gel resin vs. fractional attainment of equilibrium calculated with QHRP models; 295 K; 0.377 mm; 500 min$^{-1}$; $\omega = 0.0045$

- **Fig. 5.** The H$^+$/Na$^+$ integral interdiffusion coefficients on the macroporous resin vs. fractional attainment of equilibrium calculated with QHRP models; 298 K; 0.383 mm; 500 min$^{-1}$; $\omega = 0.0018$

- **Fig. 6.** The H$^+$/Na$^+$ macropore integral interdiffusion coefficients on C106 vs. $F$ obtained with BDM-LC eq. (8) for different values of the parameter $\beta/\alpha$ and $\alpha = 0.001$, 298 K.
10 times higher than in micropores (α = 0.1), then the limit β/α is 30, corresponding to \( \frac{M_i}{M_a} = 10/1 \). The number of functional groups grafted in micro- and macropores is unknown. The results of this work show that for a weak acid macroporous resin the ratio between the amount of –COOH groups existing inside the micro- and macropores must be higher in case of a competitive diffusion in micro- and macropores than in the case of step-by-step diffusion [11]. Moreover, for competitive diffusion \( \frac{M_i}{M_a} \) must be higher if \( \alpha = 1 \) compared with \( \alpha = 0.1 \).

The \( \text{H}^+/\text{Na}^+ \) integral interdiffusion coefficients in the gel-like weak acid resin obtained with QHRP models are higher but comparable with the same coefficients in a macroporous weak acid resin calculated with QHRP models. The \( \text{H}^+/\text{Na}^+ \) macropore integral interdiffusion coefficients computed with BDM models are higher than those obtained with QHRP models.

Conclusions

The \( \text{H}^+/\text{Na}^+ \) ion exchange kinetics on gel and macroporous weak acid resins were investigated using a potentiometric method, at constant temperature, in conditions favouring a particle diffusion controlled mechanism. The experimental data support this mechanism. The \( \text{H}^+/\text{Na}^+ \) integral interdiffusion coefficients were obtained with quasi-homogeneous kinetic models (QHRP) for gel and macroporous resins (\( D_g \) and \( D_{macroporous} \), respectively). The \( \text{H}^+/\text{Na}^+ \) macropore integral interdiffusion coefficients in the macroporous resin \( D_a \) were computed with the Ruckenstein et al. bidisperse pore kinetic model considering: a) a step-by-step diffusion in macro- and micropores (BDM-LC, \( \alpha = 0.001 \)); b) a competitive diffusion in macro- and micropores with equal times necessary to penetrate the two kinds of pores (BDM-CD, \( \alpha = 1 \)); c) a competitive diffusion in macro- and micropores, with a time required for diffusion in macropores ten times greater than the time necessary to penetrate the micropores (BDM-CD, \( \alpha = 0.1 \)). The following series were observed: \( D_{macroporous} \) (QHRP) ≤ \( D_g \) (QHRP) < \( D_a \) (BDM, \( \alpha = 0.001 \)) < \( D_a \) (BDM, \( \alpha = 1 \)) < \( D_a \) (BDM, \( \alpha = 0.1 \)).

Symbols

- \( D \) = effective diffusion coefficient in the resin phase; self-diffusion coefficient for isotopic exchange; integral interdiffusion coefficient for mutual ion exchange (m² s⁻¹)
- \( D_g \) = effective macropore diffusion coefficient; macropore self-diffusion coefficient for isotopic exchange; macropore integral interdiffusion coefficient for mutual ion exchange (m² s⁻¹)
- \( D_m \) = effective micropore diffusion coefficient; micropore self-diffusion coefficient for isotopic exchange; micropore integral interdiffusion coefficient for mutual ion exchange (m² s⁻¹)
- \( F \) = fractional attainment of equilibrium (dimensionless)
- \( k \) = number of terms in series in Eq. 9
- \( M_i \) = macropore uptake at equilibrium, (eq/kg)
- \( M_m \) = micropore uptake at equilibrium, (eq/kg)
- \( n \) = number of terms in series in Eqs. 3, 6 and 8
- \( pH_0, pH_\infty, pH_t \) of the external solution at initial, equilibrium, and time \( t \)
- \( r_o \) = mean radius of the swollen beads of the resin in a given ionic form (m)
- \( q \) = number of terms in series in (9)
- \( r_i \) = micropore mean radius (m)
- \( S_o \) = roots of Eq.: \( S_o \cot S_o = 1 + S_o^2 / 3\omega \)
- \( t \) = time (s)
Greek Symbols

\[ \alpha = \frac{D_2}{D_1} \] - dimensionless rate parameter

\[ \beta/\alpha = \frac{3M_2}{M_\infty} \] - dimensionless equilibrium parameter

\[ \alpha' \] and \[ \beta' \] are roots of eq: \[ x^2 + 3\omega x - 3\omega = 0 \]

\[ \theta = \frac{D_1 t}{\tau_\infty} \] - dimensionless time

\[ \zeta_{k\ell} = \text{roots of Eq.: } \beta(1-\zeta_{k\ell} \cot \zeta_{k\ell}) + \alpha k \zeta_{k\ell} = k^2 \zeta_{k\ell}^2, \quad k = 1, 2, 3, \ldots \]

\[ \tau = \frac{Dt}{\tau_\infty} \] - dimensionless time

\[ \omega = \text{dimensionless equilibrium parameter, ratio of number of ion equivalents at equilibrium in the resin and solution phases, respectively} \]

References


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