

H⁺/K⁺ ION EXCHANGE KINETICS ON WEAK ACID RESIN

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Cinetica schimbului ionic Proton/Potasiu pe o rășină gel slab acidă a fost studiată folosind o metodă potențimetrică, la 295 K, în condiții care au favorizat un mecanism în care determinanta de viteză este interdifuzia ionilor în particula de schimbător de ioni. Coeficienții integrali de interdifuzie H⁺/K⁺ în rășină au fost obținuți prin modelarea datelor experimentale folosind cinci modele cinetice care consideră particula de rășină ca fiind o fază quasi-omogenă. Coeficienții de interdifuzie obținuți sunt comparați cu coeficienții de interdifuzie pentru H⁺/Na⁺ și H⁺/Sr²⁺ determinați anterior pe aceeași rășină.

Proton/Potassium ion exchange kinetics on weak acid resin gel type were investigated at 295 K using a potentiometric method under conditions favouring a particle diffusion controlled mechanism. The H⁺/K⁺ integral interdiffusion coefficients on the resin were obtained with five quasi-homogeneous resin phase models for particle diffusion control, at different fractional attainment of equilibrium. The obtained interdiffusion coefficients are compared with H⁺/Na⁺ and H⁺/Sr²⁺ interdiffusion coefficients previously determined on the same resin.

Keywords: ion exchange kinetics, weak acid resin, interdiffusion coefficients, potassium ion

1. Introduction

The ion exchange resins are the most used materials in the popular ion exchange technologies as water treatment for ultrapure water in electronics and semiconductor industries, in nuclear plants, removal and recover of metal ions from natural water and industrial wastewaters, etc. The use of weak acid resins in applications, like the treatment of wastewater streams, to reduce the environmental pollution is increasing. The design of a specific separation using ion exchange implies a thorough knowledge of the kinetic proprieties of the system [1]. The rate of the ion exchange process is an important parameter in selecting a resin for a special purpose.

The present study deals with the H⁺/K⁺ ion exchange kinetics on a gel type weak acid resin Purolite PPC104, with –COOH functional group. The goal of the

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research is to investigate the kinetic behaviour of the ion exchange process, to determine the H^+/K^+ integral interdiffusion coefficients in the resin, modelling the data using different kinetic models, based on the assumption that the resin is a quasi-homogeneous phase.

2. Experimental

The commercial Purolite PPC104 is a gel-like weak acid cation exchanger with a polyacrylic matrix crosslinked with divinylbenzene. The resin was fractionated by dry sieving and purified by consecutive treatments with 1 M HCl, 1 M NaOH and washed with demineralised water, for three cycles. The resin was 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 $1\mu S\text{ cm}^{-1}$. 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.

Analytical reagent grade Merck KNO_3 was used to prepare the stock solution, using demineralised water (specific conductivity $< 1\mu S\text{ cm}^{-1}$).

The ion exchange rate was measured in a batch reactor at $(295 \pm 0.5)\text{ K}$ using a procedure previously described [2,3]. The H^+/K^+ ion exchange kinetics were monitored with a combined pH-electrode provided with a temperature probe and a Mettler Delta 350 pH meter. 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 in external solution of 1.00 M KNO_3 with pH = 5.4. Blank experiments showed that the sorbed acid represents a negligible contribution to the pH variation of the external solution in the given conditions.

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: $(0.368 \pm 0.003) \times 10^{-3}$, $(0.339 \pm 0.026) \times 10^{-3}$ and $(0.298 \pm 0.015) \times 10^{-3}\text{ m}$.

3. Results and discussion

The kinetic experiments for H^+/K^+ ion exchange process on gel 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 KNO₃. The fractional attainment of equilibrium F at time t was calculated from the pH variation of the external solution as:

$$F = \frac{10^{-pH_t} - 10^{-pH_0}}{10^{-pH_\infty} - 10^{-pH_0}} \quad (1)$$

The proton activity coefficient is constant and the ratio of the activity differences in equation (1) can be taken equal to the ratio of the concentration differences defining the fractional attainment of equilibrium, because the ionic strength is constant in the ion exchange process implying ions of the same valances.

The pH at time zero, pH_0 , has been considered as the first pH value read after the KNO₃ solution addition under stirring, varying in the range of 3.3 – 2.3.

In Figure 1 are given the experimental results obtained for H⁺/K⁺ ion exchange process on PPC104, for three size-fractions at constant stirring 500 min⁻¹, 1.00 M KNO₃ and constant temperature 295 K. The decrease of the mean radius of the resin bead is associated with the increase of the ion exchange rate in accordance with a particle diffusion controlled mechanism [4,5]. Figure 2 shows the lack of influence of the stirring speed on the ion exchange rate, supporting the same mechanism.

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.

For all the experiments the best fitted equation was:

$$F = a(1 - \exp(-bt)) + c[(1 - 1/(1 + cdt))] \quad (2)$$

In Table 1 the values of a , b , c , d parameters are given, together with the parameters of the goodness-of-fit for H⁺/K⁺ ion exchange process on PPC104. The H⁺/K⁺ interdiffusion coefficients in weak acid resins were computed using interpolated points (t , F) on the above functions for $0.01 \leq F \leq 0.99$.

Table 1

The coefficients of the empirical equation (2) for H^+/K^+ ion exchange process on the weak acid resin PPC 104 for different size fractions, at 500 min^{-1} and 295 K

Mean radius $\times 10^{-3} \text{ (m)}$	a	b	c	d	R^2	$F_{\text{statistic}}$
0.368	0.326 ± 0.025	0.00420 ± 0.00019	0.658 ± 0.029	0.0410 ± 0.0044	0.9992	75884
0.339	0.280 ± 0.037	0.00368 ± 0.00028	0.728 ± 0.043	0.0333 ± 0.0049	0.9984	37816
0.298	0.274 ± 0.045	0.0037 ± 0.0032	0.739 ± 0.052	0.0310 ± 0.0054	0.9978	28840

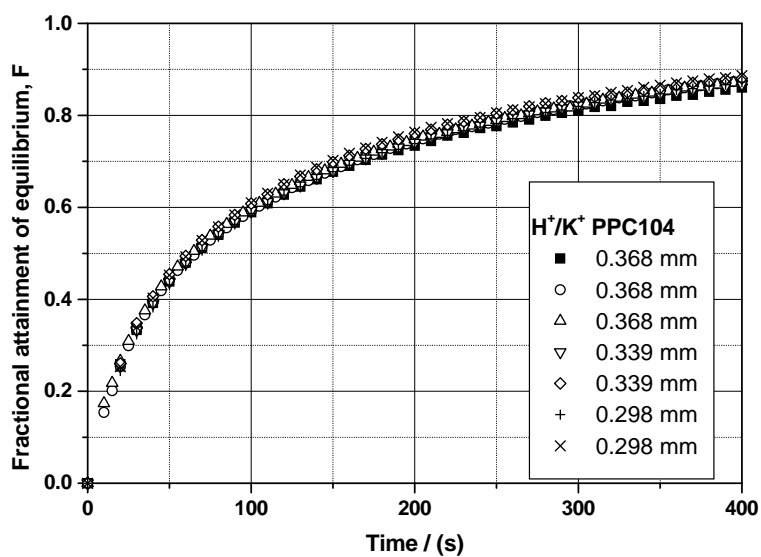


Fig. 1. The fractional attainment of equilibrium vs. time for H^+/K^+ ion exchange process on different size fractions of PPC104 resin; 295 K ; 1.00 M KNO_3 ; 500 min^{-1} .

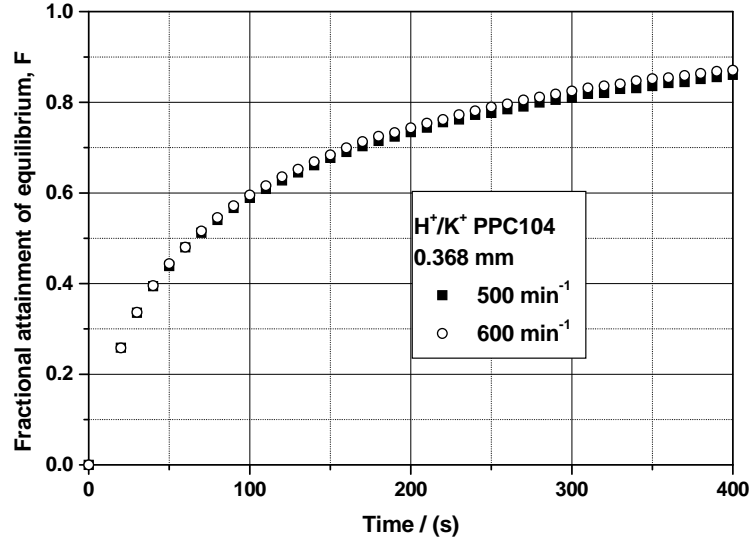


Fig. 2. The influence of the stirring speed on the rate of H⁺/K⁺ ion exchange with PPC 104 resin; 295 K; 1.00 M KNO₃; 500 min⁻¹.

Quasi-homogeneous resin phase (QHRP) approximation and Fick's laws were considered in modelling H⁺/K⁺ ion exchange kinetics on PPC104 weak acid resin.

The analytical solution of the Fick's equation of continuity with constant diffusion coefficient for ideal systems, spherical beads at infinite solution volume (ISV) [4] is:

$$F(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 \tau) \quad (3)$$

Reichenberg [6] proposed two simplified equations derived from equation (3), for $F > 0.85$:

$$F(t) = 1 - \frac{6}{\pi} \exp(-\pi^2 \tau) \quad (4)$$

and for $F < 0.85$:

$$F(t) = \frac{6}{\pi^{3/2}} (\pi^2 \tau)^{1/2} - \frac{3}{\pi^2} (\pi^2 \tau) \quad (5)$$

The analytical solution of Fick second law for finite solution volume (FSV)

boundary condition is:

$$F(t) = 1 - \frac{2}{3\omega} \sum_{n=1}^{\infty} \frac{\exp(-S_n^2 \tau)}{1 + S_n^2 / 9\omega(\omega + 1)} \quad (6)$$

where $\tau \equiv \bar{D}t / r_0^2$ and the quantities S_n are the roots of the equation

$$S_n \cot S_n = 1 + S_n^2 / 3\omega.$$

Equation (6) converges slowly for $\tau < 0.1$ and Paterson proposed for this domain the approximation [4]:

$$F(t) = \frac{\omega + 1}{\omega} \left(1 - \frac{1}{\alpha - \beta} \left[\alpha \exp(\alpha^2 \tau) (1 + \operatorname{erf} \alpha \tau^{1/2}) - \beta \exp(\beta^2 \tau) (1 + \operatorname{erf} \beta \tau^{1/2}) \right] \right) \quad (7)$$

where α and β are the roots of the equation $x^2 + 3\omega x - 3\omega = 0$.

Several computer programs [2] were used to solve these equations. For a given F the dimensionless time τ was obtained. Knowing the time t for the considered F , and the mean radius of the swollen particles, the diffusion coefficient \bar{D} can be calculated. For equations (3) and (6) ten terms ensured a good convergence of series for $F > 0.1$, considering \bar{D} variation with maximum 0.1 %. \bar{D} is constant for each $0 - F$ interval and varies with F . For mutual ion exchange, \bar{D} is called integral interdiffusion coefficient [2].

In Figures 3 and 4 are given the H^+/K^+ integral interdiffusion coefficients on PPC104 *versus* the fractional attainment of equilibrium, calculated with equations (3 - 7). It can be observed that the series (3) and (6) were not convergent for $F < 0.1$, for ten terms. The number of terms necessary to achieve the convergence decreases if F increases. A good agreement was obtained between the results given by eq. (3) and (5) (ISV) and eq. (6) and (7) (FSV), respectively. Figure 5 permits the comparison of the H^+/K^+ integral interdiffusion coefficients on PPC104 resin obtained with equations (5) and (7). The results obtained at ISV and FSV are in very good agreement for low ω value. The Paterson approximation (eq. 7) avoids the convergence problem and can be used to compute values of \bar{D} for $F < 0.1$, whereas eq. (6) was not convergent for $n = 10$.

The shape of variation of the obtained integral interdiffusion coefficients is in good agreement with Helfferich's minority rule [4].

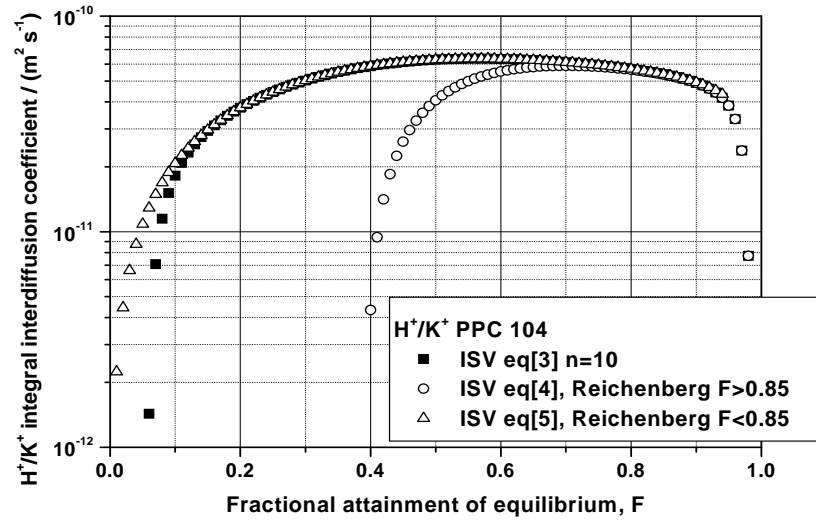


Fig. 3. Proton/Potassium integral interdiffusion coefficient vs. F on PPC104 resin at 295 K obtained using QHRP-ISV models; mean radius 0.368 mm.

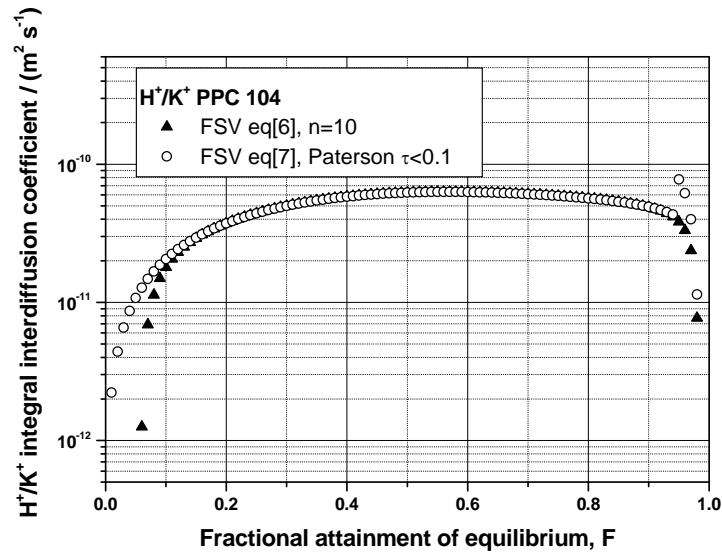


Fig. 4. Proton/Potassium integral interdiffusion coefficient vs. F on PPC104 resin at 295 K obtained using QHRP-FSV models; mean radius 0.368 mm; $\omega = 0.0045$.

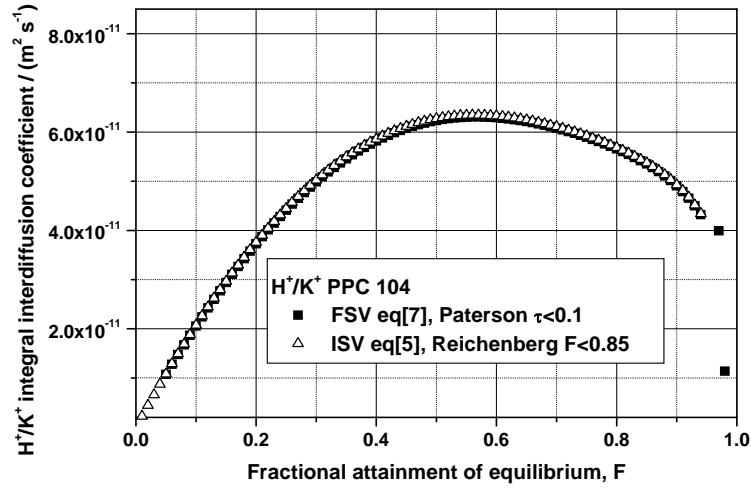


Fig. 5. Comparison of H^+/K^+ integral interdiffusion coefficients on PPC104 resin at 295 K obtained with ISV and FSV QHRP kinetic models; mean radius 0.368 mm; $\omega = 0.0045$.

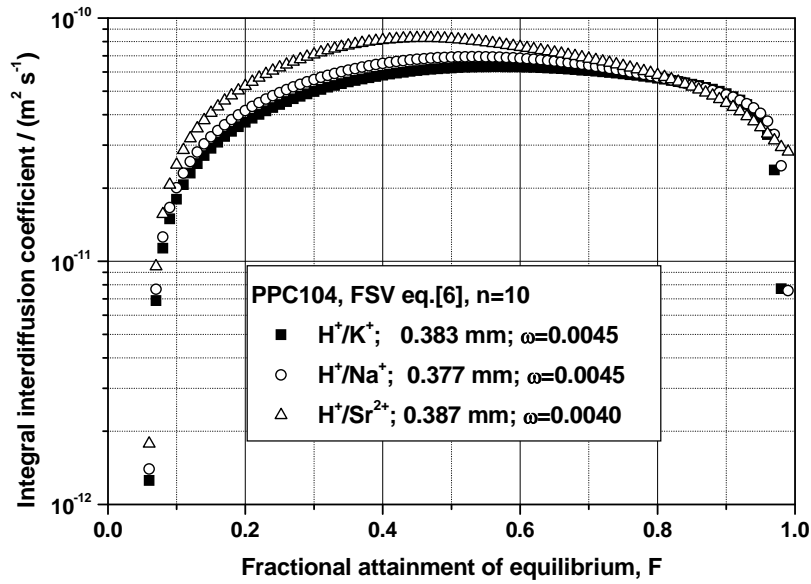


Fig. 6. H^+/M^{m+} integral interdiffusion coefficients on PPC104 resin obtained with QHRP-FSV kinetic model equation (6), $n = 10$; 295 K.

The H⁺/K⁺ ion exchange kinetics on PPC104 resin were compared with those of the H⁺/Na⁺ [7] and H⁺/Sr²⁺ [8] on the same resin reported previously.

In Figure 6 are given the results obtained with the rigorous equation (6). Using the experimental data of the H⁺/Na⁺ and H⁺/Sr²⁺ integral interdiffusion coefficients on PPC104 were also computed with equation (6) and represented in Figure 5. It can be observed that the interdiffusion coefficients on the weak acid resin PPC104 vary in the series H⁺/Sr²⁺ > H⁺/Na⁺ ≥ H⁺/K⁺.

4. Conclusions

The H⁺/K⁺ ion exchange kinetics on PPC104 weak acid resin (polyacrylic divinylbenzene with –COOH functional groups) were investigated using a potentiometric method at constant temperature under conditions favouring a particle diffusion controlled mechanism. The experimental data support this mechanism.

Five kinetic models from literature based on quasi-homogeneous resin phase assumption and Fick's laws were used to obtain the H⁺/K⁺ integral interdiffusion coefficients on PPC 104 resin at different fractional attainment of equilibrium. The models at infinite and finite solution volume boundary conditions gave results in very good agreement for the experiments performed in a batch reactor for a low ratio of the amount of K⁺ ion in the resin and solution phases at equilibrium. The interdiffusion coefficients on the weak acid resin decrease in the series: H⁺/Sr²⁺ > H⁺/Na⁺ ≥ H⁺/K⁺.

List of symbols

\bar{D}	effective diffusion coefficient in the resin phase; self-diffusion coefficient for isotopic exchange; integral interdiffusion coefficient for mutual ion exchange (m ² s ⁻¹)
F	fractional attainment of equilibrium (dimensionless)
F-statistic	parameter of the goodness-of-fit
n	number of terms in series in Eqs. 3, 6 and 7
pH_0, pH_{eq}, pH_t	pH of the external solution at initial, equilibrium, and time t
\bar{r}_0	mean radius of the swollen beads of the resin in a given ionic form (m)
S_n	roots of Eq.: $S_n \cot S_n = 1 + S_n^2/3\omega$
t	time (s)
<i>Greek Symbols</i>	

α and β	roots of Eq: $x^2 + 3\omega x - 3\omega = 0$
$\tau = \overline{Dt}/\bar{r}_0^2$	dimensionless time
ω	dimensionless equilibrium parameter, ratio of number of ion equivalents at equilibrium in the resin and solution phases, respectively

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