

# DISCRIMINATION AMONG SEVERAL KINETIC MODELS FOR OH<sup>-</sup>/Cl<sup>-</sup> ION EXCHANGE IN A STRONG-BASE ANION EXCHANGER

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Five quasi-homogeneous resin phase kinetic models at infinite and finite solution volume were analyzed for hydroxide/chloride ion exchange process, in a microreticular strong-base type-1 anion exchanger. The kinetic measurements were performed at 298 K using a potentiometric method, in a batch system. The conditions were selected to favor a particle diffusion control. The obtained rate data support this mechanism. The equilibrium ratio of the chloride ions in the resin and external solution was smaller than 0.1, justifying the use of the infinite solution volume boundary conditions. The comparison of OH<sup>-</sup>/Cl<sup>-</sup> integral interdiffusion coefficients revealed the similitude and the differences between the investigated models. The infinite solution volume models give higher values (up to 35 %) for the interdiffusion coefficients than the finite solution volume models, even in the conditions of low concentration of the leaving counterions in the external solution.

## Introduction

The literature devoted to the kinetics of anions exchange processes in different anion exchangers reported until now is not very rich.

Soldano and Boyd [1] have measured the self-diffusion coefficients for chloride, bromide, iodide, bromate, tungstate and orthophosphate anions in strong-base anion exchangers (Dowex-2) at 298 K and Krongauz and Kocher [2] for chloride, bromide and hydroxide ions in the quaternary ammonium strong-base anion exchange resins (Dowexl-8X and Dowex Monosphere Tough Gel TG550A) at 298 K. Liberti and co-workers [3-8] have done a systematic investigation on Cl<sup>-</sup>/SO<sub>4</sub><sup>2-</sup> ion exchange kinetics on a large number of resins with different functional groups and matrix, considering different kinetic models. Gopala Rao and Gupta [9] studied the kinetics of sorption of acids on a weak-base macroporous anion exchange resin (Dowex MWA-1) and proposed a modified shrinking core model.

The present work aims to: i) measure OH<sup>-</sup>/Cl<sup>-</sup> ion exchange rate on a gel-like strong-base anion exchange resin type-1 (Vionit AT-1) at 298 K, in batch system, with a low concentration of the leaving ion in the external solution, in conditions favoring a mechanism of particle diffusion control; ii) model the experimental data using five kinetic equations derived from Fick's laws for a quasi-homogeneous resin phase hypothesis; iii) reveal how large are the differences in the numerical results of the OH<sup>-</sup>/Cl<sup>-</sup> integral interdiffusion coefficients obtained with these kinetic models at different fractional attainment of equilibrium.

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## Experimental

The selected resin Vionit AT-1 (produced at Victoria, Romania) is a gel-like copolymer of styrene with 4 % divinylbenzene carrying quaternary ammonium type-1 strongly basic ionogenic groups, supplied in  $\text{Cl}^-$  form. Two size fractions with narrow bead-size distribution were separated by dry-sieving, purified by repeated treatments with 2 N HCl, deionized water and 2 N NaOH, converted into  $\text{OH}^-$  form with 100 % excess of 1 N NaOH, and washed with bidistilled water until negative test with phenolphthalein. The beads were filtered and then dried under vacuum at room temperature, and kept in a desiccator in closed weighing bottles to prevent contact with the carbon dioxide from air.

The sodium chloride aqueous solution (2N) was prepared from an analytical reagent grade product (Reactivul), dried until constant weight at 110°C.

A known amount of resin in  $\text{OH}^-$  form was introduced in a known volume of bidistilled water, let to swell in a closed vessel, and the water volume was corrected for swelling. The kinetic measurements were started immediately after a fast addition of the same volume of 2 N NaCl solution, under controlled stirring (850 and 1800 rpm) at  $(298.0 \pm 0.5)$  K, in the same vessel. The interference of the sobbed electrolyte existing in the resin was reduced to a negligible effect by this experimental procedure. The ion exchange kinetics was monitored by a potentiometric method, using a Mettler Delta 350 pH-meter and a combined pH electrode, provided with a temperature probe. The accuracy in the pH variation was  $\pm 0.001$  units, and of the pH absolute value  $\pm 0.01$  units, limited by the standard buffers accuracy. The pH variation during different kinetic runs was around two pH units. The pH at equilibrium was measured after 24 hours, keeping the sample in the closed vessel, to prevent the contact with air.

The radii of the swollen ion exchanger beads of each size fraction were determined microscopically as a mean of at least 40 measurements and reported together with the standard error using the Student distribution:  $(0.160 \pm 0.050) \cdot 10^{-3}$  m and  $(0.280 \pm 0.066) \cdot 10^{-3}$  m.

## Results and Discussion

The kinetics of  $\text{OH}^-/\text{Cl}^-$  ion exchange process on a strong-base anion exchanger belong to the class of kinetics controlled by interdiffusion of ions in the Nernst film or/and inside the resin particle [1, 10].

In this work the experiments were carried out at high concentration of the external solution, with an efficient stirring, with size-fractions having moderate diameters, favoring a particle diffusion control kinetics [10]. The  $\text{OH}^-/\text{Cl}^-$  ion exchange rates were measured for two size fractions of the resin, at two stirring speeds (850 and 1800 rpm) at 298 K, from the pH variation of the external solution with an initial concentration of 1 N NaCl. The fractional attainment of equilibrium  $F$  at time  $t$  was calculated from the pH variation as:

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

where  $pH_t$ ,  $pH_0$  and  $pH_{eq}$  represents the  $pH$  of the external solution at moment  $t$ , initially and at equilibrium, respectively. The equation 1 represents the ratio of the differences in the proton activity and was considered equal to the corresponding concentration ratio. This is true because the ionic strength of the external solution is constant during the ion exchange process of anions of the same charge and the proton activity coefficient remains also constant. Fig. 1 shows the experimental results  $F$  vs.  $t$  obtained for  $OH^-/Cl^-$  ion exchange in Vionit AT-1 resin, for two beads radii, at constant stirring. It can be observed that the process is more rapid for the smaller particles.

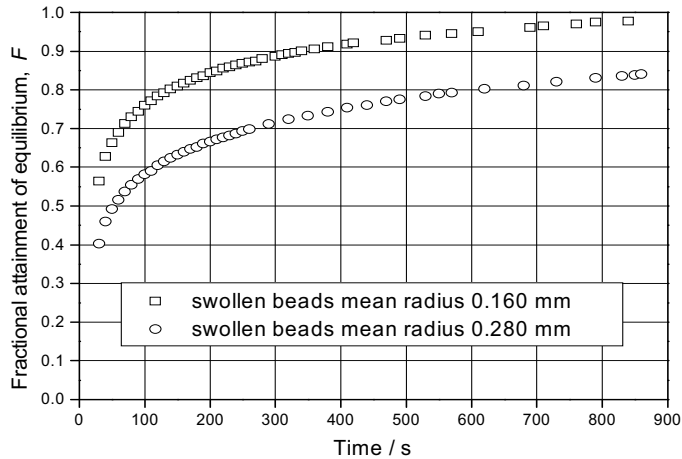


Fig. 1: The fractional attainment of equilibrium variation in time for  $OH^-/Cl^-$  ion exchange process in Vionit AT-1, at 298 K, 850 rpm, for two size fractions.

The experiments done at different stirring speeds (850 and 1800 rpm) show that stirring do not influence the rate of  $OH^-/Cl^-$  ion exchange in this region. The observed behavior supports an ion exchange kinetics with a mechanism controlled by the interdiffusion of ions inside the resin bead [1, 10]. The concentration of the leaving counterions in the external solution ( $OH^-$ ) was at least ten times smaller than the concentration of the invading counterions ( $Cl^-$ ). The rigorous boundary condition for batch kinetic experiments is the finite solution volume, but in our experiments the infinite solution volume is still a reasonable assumption.

The exchange kinetics of nonidentical ions can be treated with the quasi-homogeneous resin phase (QHRP) kinetic models derived from the Fick's laws, if we consider that the interdiffusion coefficient is a constant for a  $0-F$  or  $0-t$  interval [11]. This coefficient is called the *integral interdiffusion coefficient* and represents a mean value of the actual interdiffusion coefficients for  $0-F$  domain [11].

The analytical solution of Fick's second law at infinite solution volume (ISV) boundary condition is [10]:

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

where the kinetic parameter  $B$  is given by [10]:

$$B = \bar{D} \pi^2 / \bar{r}^2 \quad (3)$$

where  $\bar{D}$  is the effective intraparticle diffusion coefficient, in our case  $\text{OH}^-/\text{Cl}^-$  integral interdiffusion coefficient and  $\bar{r}$  is the mean radius of the swollen resin particles.

Reichenberg [12] proposed two simplified equations derived from equation 2, one for  $F < 0.85$ :

$$F(t) = \frac{6}{\pi^{3/2}} \sqrt{Bt} - \frac{3}{\pi^2} (Bt) \quad (4)$$

and the other for  $F > 0.86$ :

$$F(t) = 1 - \frac{6}{\pi^2} \exp(-Bt) \quad (5)$$

The analytical solution of the Fick's second law at finite solution volume (FSV) boundary condition was given by Paterson [10]:

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

where  $\tau$  is a dimensionless time ( $\tau = \bar{D} t / \bar{r}^2$ ),  $S_n$  are the roots of the equation:

$$S_n \cot S_n = 1 + S_n^2 / 3\omega \quad (7)$$

and  $\omega$  is a dimensionless equilibrium parameter, representing the ratio of the amount of ions at equilibrium in the resin phase and in the external solution.

Paterson [10] proposed also an equation for FSV, for  $\tau < 0.1$ , where series 6 is slowly convergent:

$$F(t) = \frac{\omega + 1}{\omega} \left\{ 1 - \frac{1}{\alpha - \beta} \left[ \alpha \exp(\alpha^2 \tau) (1 + \text{erf } \alpha \tau^{1/2}) - \beta \exp(\beta^2 \tau) (1 + \text{erf } \beta \tau^{1/2}) \right] \right\} \quad (8)$$

where  $\alpha, \beta$  are the roots of the equation:

$$x^2 + 3\omega x - 3\omega = 0 \quad (9)$$

In order to investigate the  $\text{OH}^-/\text{Cl}^-$  ion exchange kinetic behaviour at very low fractional attainment of equilibrium, a kinetic curve was fitted to the experimental data  $F$  vs.  $t$ , and some points were extrapolated at  $F \rightarrow 0$ . For the curve  $F$  vs.  $t$  corresponding to a swollen beads mean radius  $0.160 \cdot 10^{-3}$  m presented in Figure 1, the fitted kinetic curve was:

$$F = a(1 - 1/(1 + abt)) + c(1 - 1/(1 + cdt)) \quad (10)$$

where the numerical parameters and their standard deviations were:  $a = (0.7961 \pm 0.0069)$ ,  $b = (0.0932 \pm 0.0031)$ ,  $c = (0.27996 \pm 0.00423)$ ,  $d = (0.00960 \pm 0.00055)$ , for a correlation coefficient 0.99995.

Five computer programs previously reported [11] were used to solve equations 2, 4 - 6, and 8.

In Fig. 2 are given the results obtained for  $\text{OH}^-/\text{Cl}^-$  integral interdiffusion coefficients calculated with equations 2, 4 - 6 and 8 using the experimental data and the extrapolated points.

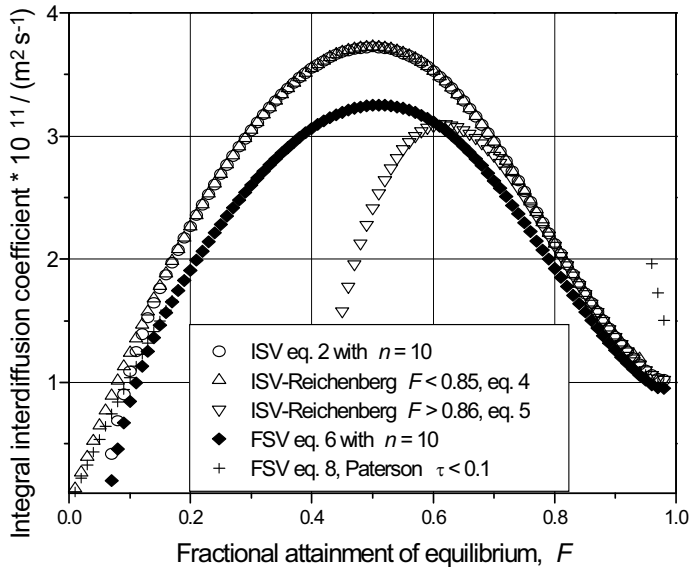


Fig. 2. The  $\text{OH}^-/\text{Cl}^-$  integral interdiffusion coefficients versus the fractional attainment of equilibrium at 298 K, obtained with five QHRP kinetic models; swollen beads mean radius 0.160 mm;  $\omega = 0.09818$ .

The convergence of the series 2 and 6 was investigated computing  $\bar{D}$  for one, two, ..., ten terms in the series. The convergence was estimated by the relative error between  $\bar{D}$  obtained for  $n - 1$  and  $n$  terms in the series:

$$E \% = \frac{(\bar{D})_n - (\bar{D})_{n-1}}{(\bar{D})_n} \cdot 100 \quad (11)$$

Both series 2 and 6 are not convergent for  $F < 0.09$  and  $n = 10$ . The number of terms necessary to ensure a good convergence, namely for  $E \% \leq 0.1$ , decreases as the fractional attainment of equilibrium increases. For  $0.09 \leq F \leq 0.25$  the error  $E$  between  $(\bar{D})_{n=9}$  and  $(\bar{D})_{n=10}$  decreases from 18 % to 0.1 %. For  $F \geq 0.25$  ten terms in the series ensure a very good convergence. If the conversion  $F$  increases the convergence is attained even for a lower number of terms  $n$  in the series, as follows:  $F \geq 0.30$   $n = 7$ ,  $F \geq 0.40$   $n = 6$ ,  $F \geq 0.45$   $n = 5$ ,  $F \geq 0.50$   $n = 4$ ,  $F \geq 0.60$   $n = 3$ ,  $F \geq 0.70$   $n = 2$ ,  $F \geq 0.95$   $n = 1$ .

Some interesting results are obtained by the analysis of the data presented in Fig. 2:

- the  $\text{OH}^-/\text{Cl}^-$  integral interdiffusion coefficients in Vionit AT-1 anion exchanger vary with the fractional attainment of equilibrium from  $1.10 \cdot 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$  at  $F = 0.01$ , to  $3.25 \cdot 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$  at  $F = 0.51$ , and decrease for higher  $F$ . Taking into account the Helfferich minority rule [10],  $\text{Cl}^-$  self-diffusion coefficient is lower than  $\text{OH}^-$  self-diffusion coefficient, in the considered resin. The decrease of  $\bar{D}$  at higher conversions can be assigned to a non-ideal behavior of the system due to ion association;
- the  $\text{OH}^-/\text{Cl}^-$  integral interdiffusion coefficients calculated with the equations derived for ISV are higher than the corresponding values calculated with the equations for FSV. The differences are around 35 % at  $F = 0.09$  and decrease to 8 % at  $F = 0.90$ . The use of ISV boundary condition for experiments in batch systems, even at low concentration of the leaving ions in the external solution, gives higher values for  $\bar{D}$  with about 10 – 35 %, as a function of  $F$ ;
- equation 8 gives results in very good agreement with equation 6 (for an adequate number of terms ensuring the convergence). For  $0.20 \leq F \leq 0.98$  the differences in  $\bar{D}$  are less than 0.01 %. This equation is recommended to treat the kinetic data obtained in batch experiments for  $0.01 \leq F \leq 0.98$ . Equation 8 cannot be used for  $F > 0.98$ , giving results in evident disagreement with equation 6 with  $n = 10$ , but can be used for  $F < 0.25$  when equation 6 is not convergent for  $n = 10$ ;
- the Reichenberg simplified equation 4 recommended for  $F < 0.85$  gives results in very good agreement with equation 2 with  $n = 10$ , for  $F \geq 0.25$ , the differences in  $\bar{D}$  being less than 0.01 %. For  $F < 0.25$  when equation 2 is not convergent for  $n = 10$  with 0.01 % error in  $\bar{D}$ , equation 4 can be used with good results. This equation 4 can be used for an extended domain than was proposed by Reichenberg, namely for  $F < 0.95$ ;
- the Reichenberg simplified equation 5 was proposed for  $F > 0.86$  and derived from equation 2 when  $n = 1$ . For our system at  $F = 0.60$  this equation gives a value for  $\bar{D}$  with 12.5 % error reported to the value obtained with equation 2 with  $n = 10$ . For  $F > 0.86$  the differences in  $\bar{D}$  obtained with this two equations are less than 0.1 %.

## Conclusions

The  $\text{OH}^-/\text{Cl}^-$  ion exchange kinetics on a gel-like strong-base type-1 resin (Vionit AT-1) was investigated at 298 K using a potentiometric method.

Under the specific experimental conditions, a particle diffusion control mechanism was assumed.

The  $\text{OH}^-/\text{Cl}^-$  integral interdiffusion coefficients in the studied resin were calculated with five kinetic equations derived from Fick's second law for a quasi-homogeneous resin phase model. The  $\text{OH}^-/\text{Cl}^-$  integral interdiffusion coefficients vary with the fractional attainment of equilibrium from  $1.10 \cdot 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$  at  $F = 0.01$  to  $3.25 \cdot 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$  at  $F = 0.51$ .

The series in equations 2 and 6 are not convergent for ten terms and 0.1 % error in  $\bar{D}$  for  $F < 0.25$ , but for  $F > 0.25$  they are convergent.

Equation 8 for finite solution volume boundary condition is recommended for batch experiments for  $0.01 < F < 0.98$ , instead of the more rigorous equation 6, which is difficult to handle, because more than ten terms must be used to ensure the convergence at  $F < 0.25$ .

The results obtained with the equations for infinite solution volume boundary condition are greater up to 35 % than those obtained with equations for finite solution volume, even when the leaving ion concentration in the external solution is at least ten times smaller than the invading counterions concentration.

The Reichenberg simplified equation 4, for  $F < 0.85$ , can be used for  $0.01 < F < 0.95$ , instead of equation 2, which is not convergent for  $n = 10$  at  $F < 25$ . This equation is easier to be used from mathematical point of view, but gives higher values for the integral interdiffusion coefficients than the equations for finite solution volume, up to 35 %, for our batch measurements.

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