

Kinetics of Ion Exchange in Monodisperse Resin

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Received 15 August 1996; accepted 1 January 1997

ABSTRACT: Ion-exchange kinetics within a conventional strong base resin, Dowexl-8X[®], and a resin with uniform particle size, Dowex[®] Monosphere[®] Tough Gel[®] TG550A[®], were investigated using neutron activation analysis and radio-tracer techniques. The kinetics of ion exchange were measured in a batch and in a “shallow-bed” flow system. The experimental data were compared with the results of model computations. The diffusivities of several anions within TG550A and Dowexl-8X were deduced. It was found that at 25°C Br⁻, Cl⁻, OH⁻, and Na⁺ diffuse within TG550A with the diffusion coefficients $D_{\text{Br}^-} = 6.0 \times 10^{-7} \text{ cm}^2/\text{s}$, $D_{\text{Cl}^-} = 1.2 \times 10^{-6} \text{ cm}^2/\text{s}$, $D_{\text{OH}^-} = 7.0 \times 10^{-8} \text{ cm}^2/\text{s}$, and $D_{\text{Na}^+} = 5 \times 10^{-7} \text{ cm}^2/\text{s}$. Diffusion of anions within a conventional resin, Dowexl[®], was slower: $D_{\text{Br}^-} = 3.5 \times 10^{-7} \text{ cm}^2/\text{s}$, $D_{\text{Cl}^-} = 6 \times 10^{-7} \text{ cm}^2/\text{s}$, $D_{\text{OH}^-} = 2.7 \times 10^{-8} \text{ cm}^2/\text{s}$, and $D_{\text{Na}^+} = 5 \times 10^{-7} \text{ cm}^2/\text{s}$. A higher rate of ion diffusion and the bead-size uniformity may make monodisperse Dowex Monosphere Tough Gel TG550A resin attractive for analytical applications. The difference in properties between conventional and monodisperse resins is not sufficient to affect the large volume applications of resins. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1271–1283, 1997

INTRODUCTION

The performance of the ion-exchange column depends on the kinetics of ion exchange and the characteristics of the flow within the column. The column performance improves when the packing has a uniform size, since uniform-size resin beads pack in a regular pattern and the channels between the beads are not filled with the smaller resin particles which restrict the flow of the exchanging solution.^{1–3} Conventional ion-exchange resins have a broad bead-size distribution [Fig. 1(a)].⁴ In a newer product, Dowex[®] Monosphere[®] Tough Gel[®] TG550A[®] anion-exchange resin (from here on abbreviated as TG550A[®]), the resin beads have an almost identical diameter of 0.055 cm [Fig. 1(b)].⁵ The resin bead-size distribution is substantially wider for conventional Dowexl-8X resin (resin bead diameter standard deviation is $\pm 0.011 \text{ cm}$) [Fig. 1(c)] than for the monodisperse

TG550A (resin bead diameter standard deviation is $\pm 0.002 \text{ cm}$) [Fig. 1(d)]. Therefore, the solution flow through the column packed with TG550A should be better than in the columns packed with the conventional resins. The resin performance also depends on the kinetics of ion exchange and resin selectivity. The investigation of ion-exchange kinetics in the monodisperse Dowex Monosphere Tough Gel anion-exchange resin TG550A and conventional Dowexl-8X[®] is presented below.

In previously reported studies of acrylate-based anion-exchange resins, experimentally observed kinetics of exchange deviated from the kinetics calculated using an approximation to the Nernst–Planck equations derived by Helfferich and Plesset.^{1,3} These and other theories of ion exchange include kinetics dependence on the size of the resin bead. The disagreement between calculated and experimental kinetics of ion exchange could arise from the unaccounted bead sizes deviation from the average. The TG550A resin is manufactured with a uniform bead size; therefore, the bead size dispersion would not contribute to ion

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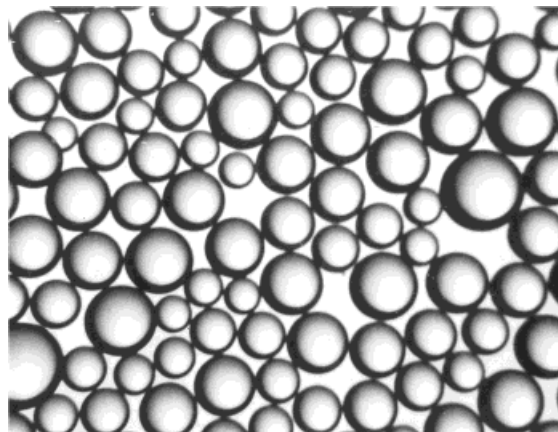
exchange kinetics in TG550A. The exchange kinetics in a conventional ion-exchange resin, Dowexl-8X,⁴ with an average bead diameter (20–50 mesh) equal to the diameter of the beads in the monodisperse resin, was affected by the resin bead-size nonuniformity and was monitored for comparison.

The present studies were conducted to determine whether the monodisperse ion-exchange resin, providing better flow characteristics in continuous exchange applications, has unusual properties in comparison with the conventional polydisperse Dowexl-8X strong-base anion-exchange resin. It was also important for future use to evaluate the kinetics of the ion exchange in the new system and to determine the amount of co-ion uptake by the resin during the exchange process. The self-diffusion coefficients of the ions were deduced using measured exchange kinetics of identical (isotopic) and different ions.

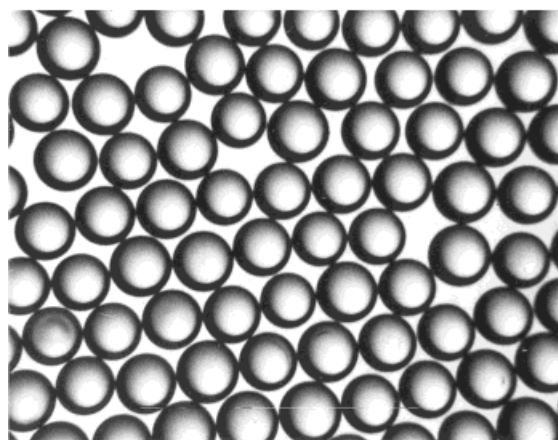
EXPERIMENTAL

Ion-Exchange Resins

Two quaternary ammonium strong base anion-exchange resins were investigated: Dowexl-8X®, in the text and figures abbreviated as Dowexl, and TG550®, full trade name Dowex® Monosphere® Tough® Gel® TG550A®. The average diameter of Dowexl beads is equal to 0.0550 ± 0.0106 cm (20–50 mesh) and comparable to that of TG550A [Fig. 1(a,c)]. The average diameter of TG550A beads is also 0.0550 ± 0.0020 cm; however, the resin bead-size distribution is very narrow [Fig. 1(b,d)]. The resin bead-size distribution was deduced from a microscopic image of the resin using the “Area Morphometry” utility of Optimas 5.2 Image Analysis Package (Optimas Corp.). Bead diameter (width) was used as a measure [Fig. 1(c,d)]. Both resins are 8% crosslinked. Both resins can contain up to 43–45% (by weight) of water. Total water content in the resin depends on the type of co-ion present. Only the relative change in the amount of water due to exchange of Cl^- in the resin with OH^- from solution was measured here. The resins were initially in Cl^- form and were stored in deionized water prior to the experiments. Before use, the resins were placed on a glass filter opened to the atmosphere and excess water in the interstitial volume between the beads was drained using a water vacuum pump at room temperature for approxi-



a)



b)

Figure 1 (a) Micrograph of the conventional Dowexl-8X resin. Average bead diameter is 0.0550 cm. (b) Micrograph of the monodisperse resin Dowex Monosphere TG550A. Average bead diameter is 0.0550 cm. (c) Bead diameter distribution in the conventional Dowexl-8X resin. (d) Bead diameter distribution in the resin Dowex Monosphere TG550A.

mately 1 min. Such a procedure leaves the resin fully saturated with water (i.e., no water is removed from the resin beads), but the weight measurement error arising from varied amount of water trapped between the beads is minimized. After water draining, 2.0 g of the resin was transferred either into a 50.0 mL polyethylene vial for batch mode exchange or into 15.0×0.65 cm Omni® glass columns (Ace Glass, Inc.) for flow mode experiments.

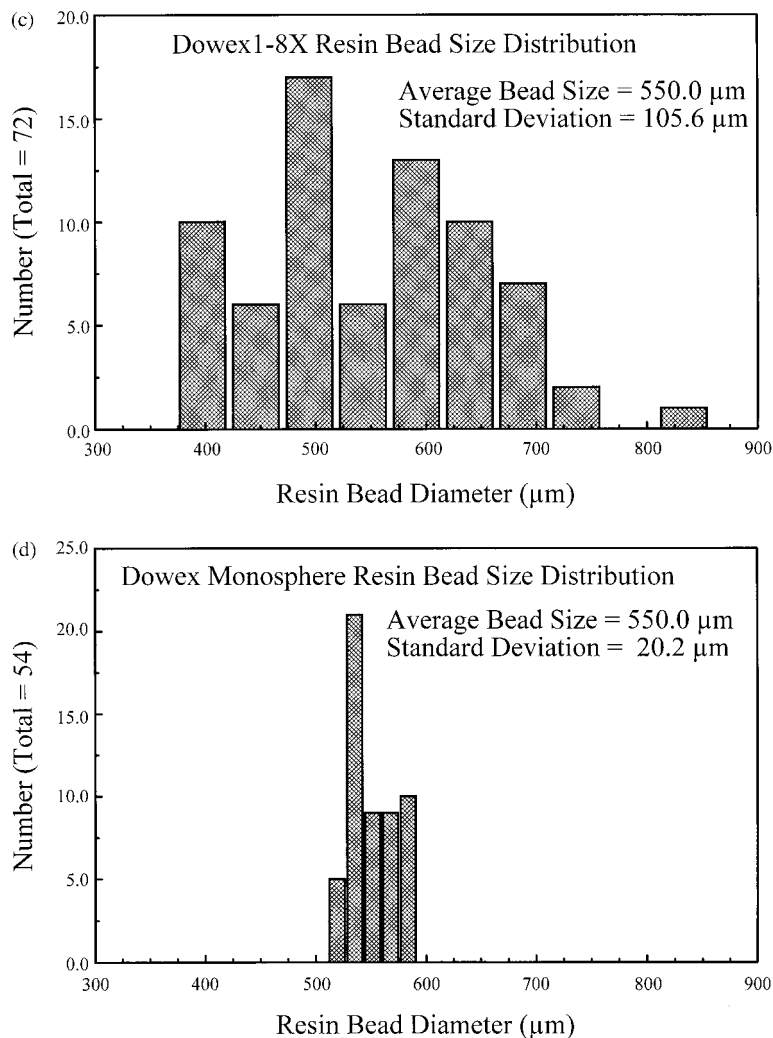


Figure 1 (Continued from the previous page)

Reagents

Research-grade sodium bromide, sodium hydroxide, and sodium chloride (Fisher Scientific Co.) were used. The water used as a solvent and for the resin storage and rinse was filtered and deionized with the Milli-Q water purification system (Millipore Corp.). In all the experiments, a 10% (2.77M) NaOH solution was used. Correspondingly, the concentration of other solutions was selected to be 2.77M.

Production of Radioactive Isotopes

The ion-exchange kinetics was monitored by the γ -radiation emission of isotopes of Cl, Br, and Na. The short-lived isotopes ^{38}Cl , ^{82}Br , and ^{24}Na were produced using a 100 kW Dow TRIGA MARK I nuclear research reactor (General Atomic Tech-

nologies Inc.). From here on, the radioactive isotopes will be labeled with an asterisk: Cl^* , Br^* , and Na^* . To obtain radioactive Cl^* and Br^* , several milliliters of 1.0N HCl or 1.0N NH_4Br solutions were irradiated in the nuclear reactor core. Then, the irradiated solutions were diluted with nonradioactive solutions of the same concentration to yield a radioactivity level desired for the flow mode experiments. To produce the resin containing active Cl^* isotopes for the batch experiments on Cl^- self-exchange kinetics, the ion-exchange resins containing Cl were irradiated in the reactor. The radiation damage to the resin was minor under the radiation conditions employed and did not affect ion transport as was shown by the preliminary measurements of the radiation dose effect on the resin properties (color, cross-linking, density, etc.). Solutions of the radioactive Na^* isotopes were produced by irradiation of the

NaOH solution and dilution with a nonirradiated solution of the same concentration to achieve the desired activity level.

Exchange Kinetics: Flow Experiments

In the flow mode measurements, 2.0 g of the anion-exchange resin (in Cl form) were placed into a 15.0×0.65 cm Omni glass column (Ace Glass, Inc.). Then, the resin inside the column was presaturated by pumping through the column a solution containing a radioactive isotope of interest (e.g., NaBr*). After that, prior to the kinetics monitoring, deionized water was flushed through the column to remove radioactive material from the interstitial volume. To record the exchange kinetics, the γ -radiation emission intensity of the column was continuously monitored, while the solution containing a nonradioactive counterion (e.g., a solution of NaBr) was pumped through the column. The rates of flow of the counterion solution ranged from 10.0 to 30.0 mL/min. The flow rates were sufficiently high to ensure that the resin layer behaved as a "shallow-bed," i.e., the solution residence time in the column was substantially shorter than the time of total ion replacement. The γ -radiation emission intensity was monitored continuously during the exchange using a NaI detector, interfaced with a computer-based multichannel analyzer ND7600 (Nuclear Data System, Inc.). The detector was placed near the column portion filled with the resin containing radioactive ion. To avoid interference from the radiation emitted by the collected effluent, the effluent was collected in a container shielded by lead bricks and located several meters away from the detector. Due to substantial dilution by nonradioactive solution flowing through the column and careful shielding, the radiation emitted by the effluent near the column was below the detection limit and did not interfere with the monitoring of the column radiation. The signal was accumulated and averaged over 1 s intervals. The data were then transferred to a VAX 11/780 system for further processing.

Exchange Kinetics: Batch Experiments

Monitoring of equilibrium attainment kinetics, TG550A resin selectivity, and co-ion (Na^+) invasion kinetics during ion exchange was conducted in a batch mode point by point. In a typical experiment, 2.0 g of the resin, irradiated in the TRIGA reactor to produce resin containing ^{38}Cl isotopes *in situ*, was placed in a 50.0 mL polyethylene vial.

Then, an appropriate counterion solution (NaOH, NaCl, or NaBr) was poured over the resin into the vial. After that, the vial was capped and shaken. Exchange time recording started simultaneously with pouring the solution into the vial. After a predetermined time, the vial contents were dumped on a glass filter and the solution was drained under a vacuum. Three 20.0 mL portions of deionized water were poured over the resin to rinse the remaining counterion solution from the resin surface. Recording of the time of the resin contact with the counterion solution was stopped after the first water rinse. It was established by flow mode measurements that the amount of ions washed out of the resin by deionized water was negligible relative to the total ion contents of the resins. Therefore, in the batch experiments, the decrease in ion concentration caused by the water rinse was neglected. The concentration of the radioactive ions remaining in the resin after the batch exchange and water rinse was determined using NaGe detectors (EG&G Ortec Corp.) interfaced with an ND6700 multichannel analyzer (Nuclear Data System, Inc.).

To determine the amount of Na^+ invading the resin by neutron activation analysis,^{6,7} the resin was irradiated in the reactor core after the batch-mode exchange was completed. The radioactivity of the ^{24}Na (γ 2754 and 1369 keV) generated by the neutron activation was measured. The kinetics of co-ion invasion were deduced using these point-by-point measurements in the batch. The exchange time was recorded as described above. The numerical modeling and computations were conducted on a VAX 11/780 using a FORTRAN compiler.

RESULTS AND COMPUTATIONS

Isotope-Exchange Kinetics

The kinetics of ion exchange in a majority of ion-exchange resin applications is controlled by the diffusion of the exchanging ions. Therefore, along with monitoring the exchange kinetics, the diffusivities of ions within the resin were deduced. The ion-exchange kinetics were monitored in batch and flow modes. Batch experiments yielded absolute concentrations of ions, both in solution and within the resin. The flow experiments provided more precise data on the kinetics of ion exchange. Batch measurements are labor intensive and yield reliable kinetic data only for long exchange times. The flow experiments also reduce the er-

rors associated with the formation of the ion concentration gradient on the ion-exchange bead surface, thus simplifying the data interpretation.

Concentration of the radioactive ion within the resin was recorded as a function of exchange time. The data were used to compute the fractional attainment of equilibrium function, $U(t)$, indicating how far from the completion the exchange process was. In this work, we followed the notations and the names of the variables selected by Helfferich,^{1,3} rather than those used in heat-exchange and molecular-diffusion publications.^{8,9} By definition, $U(t) = [Q_A(t) - Q_A(0)]/[Q_A(\infty) - Q_A(0)]$, where $Q_A(t)$ is the amount of the ion A within the resin at the time t elapsed from the beginning of the exchange and $Q_A(\infty)$ and $Q_A(0)$ are the amounts of the ion A in the resin at the end and at the beginning of the exchange, respectively. The rate of ion-exchange equilibrium attainment depends on the diffusivities of ions in the resin. Thus, $U(t)$ depends on the diffusivities of the exchanging ions. To obtain the coefficients of ion diffusion in the resin, experimentally measured kinetics of equilibrium attainment was compared with the results of numerical simulation of the exchange process. Numerical simulation of ion exchange was based on idealized mathematical models corresponding to the experimental conditions.^{1-3,8,9} It was assumed in the modeling that ions were free to diffuse within the resins. High-concentration solutions (2.77M) were used to ensure that the ion-exchange kinetics was resin particle diffusion-controlled.

The diffusivities of molecules in water are usually several orders of magnitude higher than in the crosslinked polymer.^{8,9} High ion concentration in water, 2.77M, also reduces the possibility of ion-gradient development between the bulk of solution and resin particle surface. Electrostatic hindrances are also minimal during the exchange of the identical ions.¹⁻³ Therefore, it is reasonable to assume that exchange of identical ions from concentrated solution with those in the resin is controlled by ion diffusion within the resin particle. Resin particle diffusion-controlled ion-exchange kinetics may be approximated by eq. (1)^{1-3,9,10}:

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

where $w = C_r V_r / C_s V_s$ (indexes r and s correspond to resin and solution, respectively). In the batch experiments, the resin volume was 2.0 mL, the

solution volume was 20.0 mL, while the ion concentrations were identical in the resin and in the solution. Thus, $w \approx 0.1$. $\tau = Dt/r^2$ and S_n are the roots of the equation $S_n \cotng S_n = 1 + S_n^2/3w$. In ion-exchange resins, the diffusion coefficients are $<10^{-6}$ cm²/s; the radii of the beads in the selected resins are close to 0.0275 cm, and the time of the process <1200 s. Under these conditions, τ does not exceed 0.05. Thus, $\tau < 0.1$ and the approximation of eq. (1) derived by Paterson¹⁰ can be used [eq. (2)]:

$$U(t) = [(w+)/w] \{1 - [1/(\alpha - \beta)] \times [\alpha \exp(\alpha^2 \tau)(1 + \text{erf } \alpha \tau^{1/2}) - \beta \exp(\beta^2 \tau)(1 + \text{erf } \beta \tau^{1/2})]\} \quad (2)$$

where α and β are the roots of the equation $x^2 + 3wx + 3w = 0$. The Cl^{*}-Cl exchange kinetics was computed by eq. (2) using Cl⁻ ion diffusivity in a resin as a parameter [Fig. 2(a)]. The fractional attainment of the equilibrium function was deduced as a function of time using experimental data on Cl^{*}-Cl exchange in the batch mode in TG550A resin. The experimentally derived data on equilibrium attainment kinetics (open squares for the batch mode) were superimposed on the data computed by eq. (2) [solid lines in the Fig. 2(a)]. The agreement between the computed (solid line) and experimental data (batch mode, open squares) was obtained with the Cl⁻ diffusion coefficient equal to $D_{\text{Cl}} = 1.2 \times 10^{-6}$ cm²/s.

When the solution-containing nonradioactive isotopes was pumped through the column packed with the ion-exchange resin containing radioactive ions, the ion-exchange occurred under the conditions corresponding to an infinite solution volume. Apart from relatively small isotope effects, exchange of isotopes is equivalent to the exchange of identical ions. Therefore, the change of the resin volume and electrostatic effects should not have significantly influenced the exchange kinetics. The resin particle diffusion control was assumed. Mathematically, the exchange of identical ions in a flow system is equivalent to the heat flow through a sphere immersed in an infinite heat bath^{1-3,8,9} [eq. (3)]:

$$U(t) = 1 - (6/\pi) \sum_{n=1}^{\infty} \{(1/n^2) \exp(-Dt\pi^2 n^2/r_0^2)\} \quad (3)$$

where $U(t)$ is a fractional attainment of equilibrium function; $Q_A(0)$, $Q_A(t)$, and $Q_A(\infty)$ are the

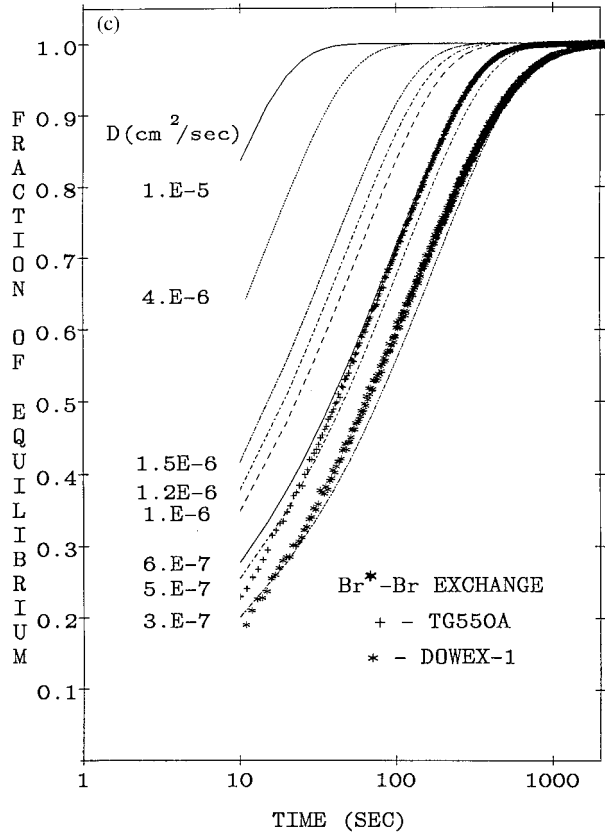
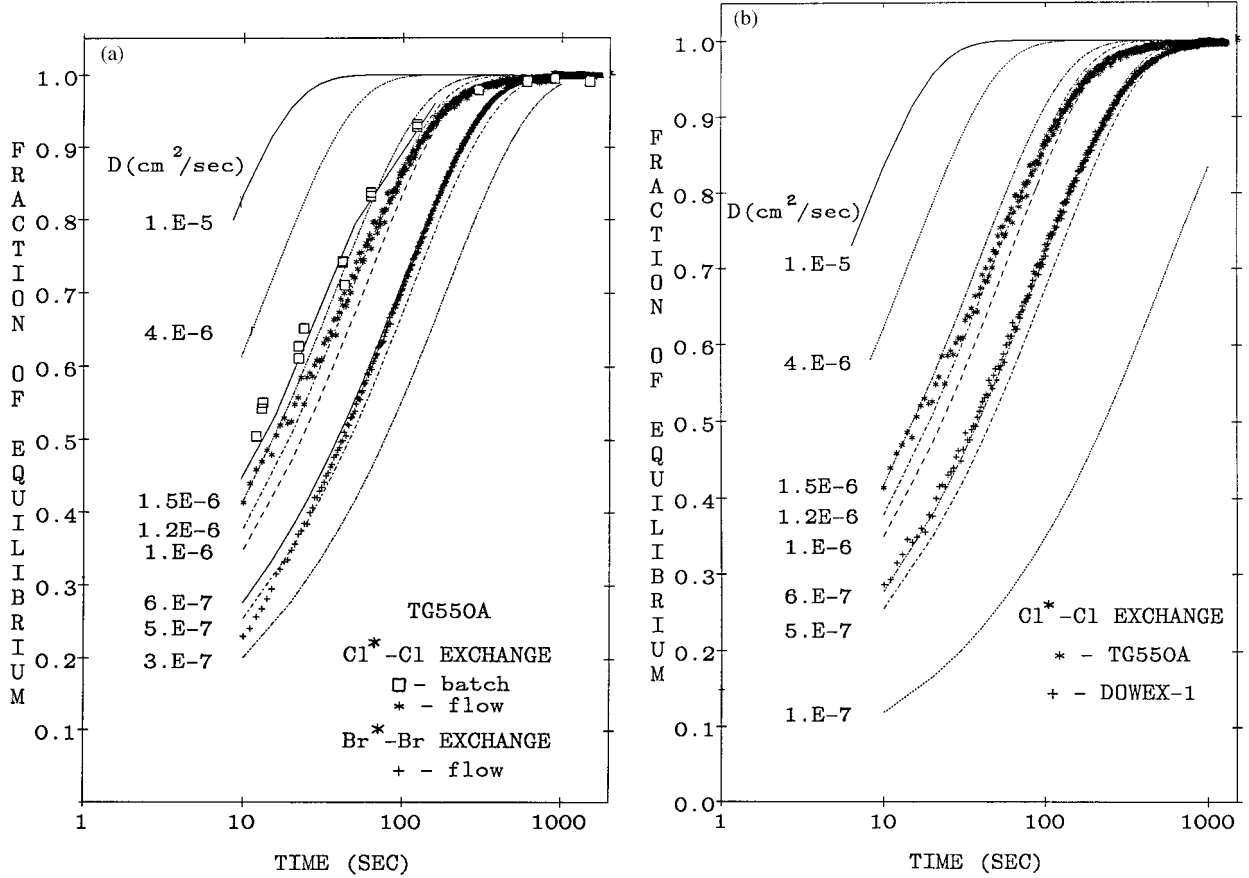


Table I Coefficients of Anions Diffusion Within the Resin

Resin Type	Counterion in Resin	Counterion in Solution	D_{Cl^-} (cm ² /s)	D_{Br^-} (cm ² /s)	D_{OH^-} (cm ² /s)
TG550A®	³⁸ Cl ⁻	Cl ⁻	1.2×10^{-6}		
Dowex1®	³⁸ Cl ⁻	Cl ⁻	6.0×10^{-7}		
TG550A®	³⁸ Cl ⁻	Br ⁻		1.1×10^{-6}	
Dowex1®	³⁸ Cl ⁻	Br ⁻		4.5×10^{-7}	
TG550A®	³⁸ Cl ⁻	OH ⁻			7.0×10^{-8}
Dowex1®	³⁸ Cl ⁻	OH ⁻			2.5×10^{-8}
TG550A®	⁸² Br ⁻	Cl ⁻	5.0×10^{-7}		
Dowex1®	⁸³ Br ⁻	Cl ⁻	4.0×10^{-7}		
TG550A®	⁸² Br ⁻	Br ⁻		6.0×10^{-7}	
Dowex1®	⁸² Br ⁻	Br ⁻		3.5×10^{-7}	
Dowex1®	⁸² Br ⁻	OH ⁻			3.0×10^{-8}

concentrations of isotope *A* in the resin initially, at time *t* (s) from the beginning of exchange and after the equilibrium was attained; *D* (cm²/s) is the diffusion coefficient of ion *A* in the resin; and $r_0 = 0.0275$ cm is an average resin bead radius. The number of series members used in summation (number of iterations in computations), *n*, was determined by the conversion criterion, so that $[U(t, n) - U(t, n - 1)] < 10^{-7}$ for each time value considered. As in the modeling of the batch system kinetics, the diffusion coefficient, *D* (cm²/s), was used as the only adjustable parameter in generation of a series of kinetic curves [Fig. 2(a-c)]. The computed and measured dependencies of *U*(*t*) on time of exchange were superimposed, and the diffusion coefficient corresponding to the best-fit curve was taken as the anion self-diffusion coefficient (Fig. 2). The self-diffusion coefficients for Br⁻ and Cl⁻ were determined using the kinetics of exchange of Br^{*}-Br, and Cl^{*}-Cl in TG550A and Dowex1 resins in a particle diffusion-controlled flow system (Fig. 2 and Table I). The diffusivities of the Cl⁻ ion within the TG550A resin found by batch and by flow methods were the same within the experimental error [Fig. 2(a)].

Exchange of Nonidentical Ions

The exchange kinetics of nonidentical ions within the TG550A and Dowex1 anion-exchange resins was investigated. The exchange of nonidentical particles is usually accompanied by changes in the resin bead shape and charge balance; therefore, the kinetics of nonidentical ions exchange cannot be extrapolated from the data on the exchange of the isotopes. The kinetics of flow-mode exchange of Br^{*}- in the resin to OH⁻ from the solution, of Br^{*}- in the resin to Cl⁻ from the solution, of Cl^{*}- in the resin to Br⁻ from the solution, and exchange of both Br^{*}- and Cl^{*}- in the resin to OH⁻ from the solution were monitored in a flow mode. As described above, the Dowex1 and TG550A resins were presaturated with the solutions containing radioactive Br^{*} or radioactive Cl^{*}. The decrease in intensity of γ -emission of the resins due to exchange with the nonradioactive ions from the solution were recorded.

To deduce ion diffusivities, an approximate solution of the Nernst-Planck equation derived by Helfferich and Plesset was used in conjunction with the experimental data on the exchange kinetics of nonidentical ions [eq. (4)]^{1-3,11,12}:

Figure 2 Measured and computed dependence of fractional attainment of equilibrium function on the time elapsed from the start of isotope exchange. Radioactive isotopes of the counter ion (³⁸Cl or ⁸²Br) are initially in the resin. Solid lines represent the results of computation conducted under the assumption of the resin diffusion-controlled process and infinite solution volume [eq. (3)]¹; ion self-diffusion coefficients used as computational parameters are presented on the left of the corresponding curves. (a) Exchange in TG550A: (■) batch experiments data; solid line passing through corresponds to the solution of eq. (2) for $D_{\text{Cl}^-} = 1.2 \times 10^{-6}$ cm²/s. (b) Cl^{*}-Cl exchange kinetics in resins: (*) in TG550A; (+) in Dowexl. (c) Br^{*}-Br exchange kinetics in resins: (*) in TG550A; (+) in Dowexl.

$$U(t) = \{1 - \exp[\pi^2(f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3)]^{1/2} \quad (4)$$

where $\tau = D_A(t/r_0^2)$; D_A and D_B are the diffusion coefficients within the resin of the A^- (counterion originally in the resin) and B^- (counterion in the solution), and $\alpha = D_A/D_B$. When the ions of equal valence are exchanged (Br^- , Cl^- , and OH^- in the present studies), the coefficients f_i are expressed as

$$f_1(\alpha) = -[0.570 + 0.430\alpha^{0.775}]^{-1}$$

$$f_2(\alpha) = -[0.260 + 0.782\alpha]^{-1}$$

$$f_3(\alpha) = -[0.165 + 0.177\alpha]^{-1}$$

The range of validity of these approximate expressions lies within $0.1 \leq \alpha \leq 10$.^{1,11,12} Isotope ex-

change kinetics measurements presented above demonstrates that Br^- and Cl^- diffusivities differ by less than a factor of 10. The data presented in the literature on ion exchange^{1-3,11,12} indicate that in most systems the OH^- exchange rate is of the same order of magnitude as those of Br^- and Cl^- . Thus, the results of our measurements are within the region where diffusion-controlled ion-exchange kinetics could be described by the above approximation of eq. (4).

Using the diffusion coefficients for Cl^- equal to $1.2 \times 10^{-6} \text{ cm}^2/\text{s}$ in TG550A and 6.0×10^{-7} in Dowexl (measured for Cl^- diffusion as described above), and using the diffusion coefficient of the anion present in solution as an adjustable parameter in computations, a series of kinetic curves were generated to fit the experimental data [Fig. 3(a,b)]. In this way, the self-diffusion coefficients for the hydroxyl anion in TG550A and Dowexl

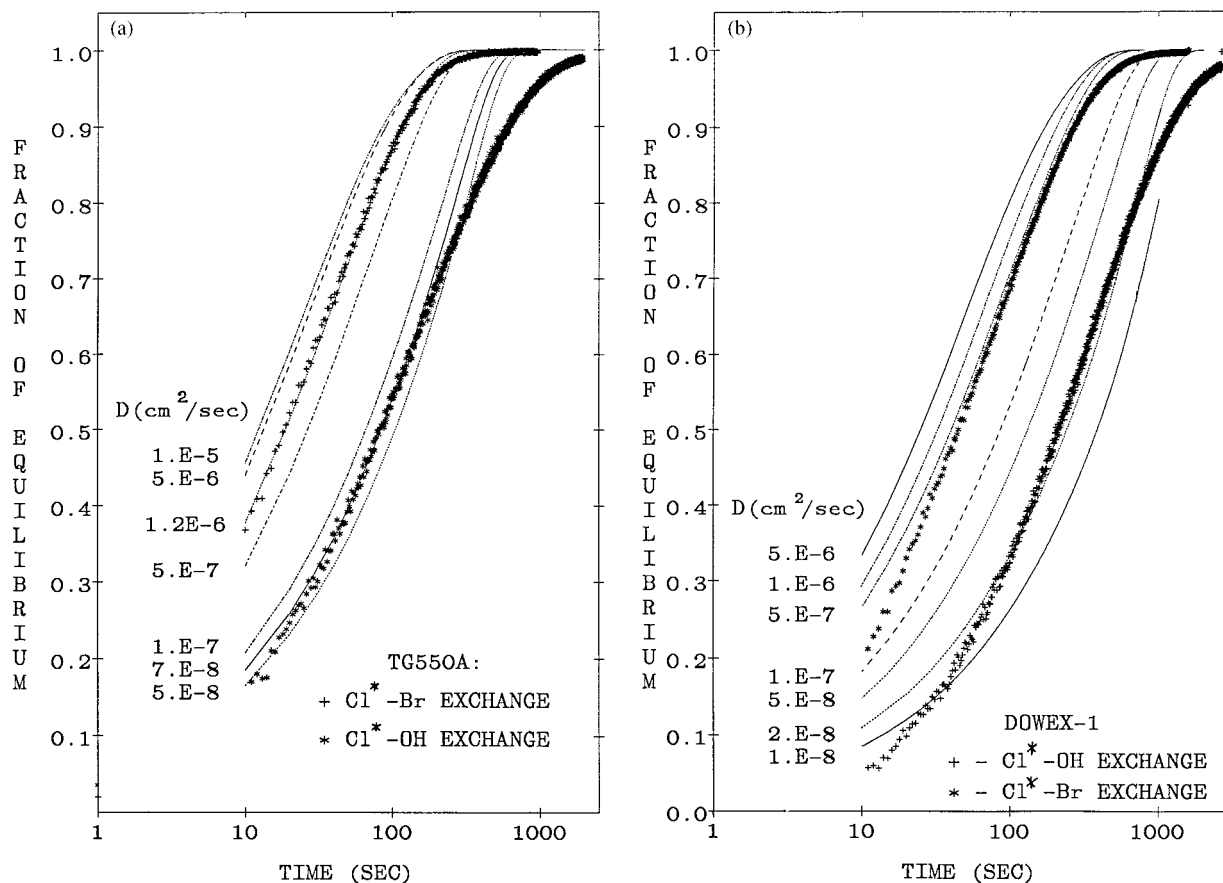


Figure 3 Exchange kinetics of nonidentical ions, $^{38}\text{Cl}^-$ with Br^- and OH^- , in TG550A and Dowexl. The ion of the radioactive ^{38}Cl isotope is initially in the anion-exchange resins. The lines were calculated by eq. (4) using the self-diffusion coefficients of invading counterions presented on the left side of the graphs. (a) Exchange kinetics in monodisperse TG550A; calculations were made using the coefficient for ^{38}Cl diffusion equal to $1.2 \times 10^{-6} \text{ cm}^2/\text{s}$. (b) Exchange kinetics in Dowexl; calculations were conducted using ^{38}Cl self-diffusion coefficient equal to $6 \times 10^{-7} \text{ cm}^2/\text{s}$.

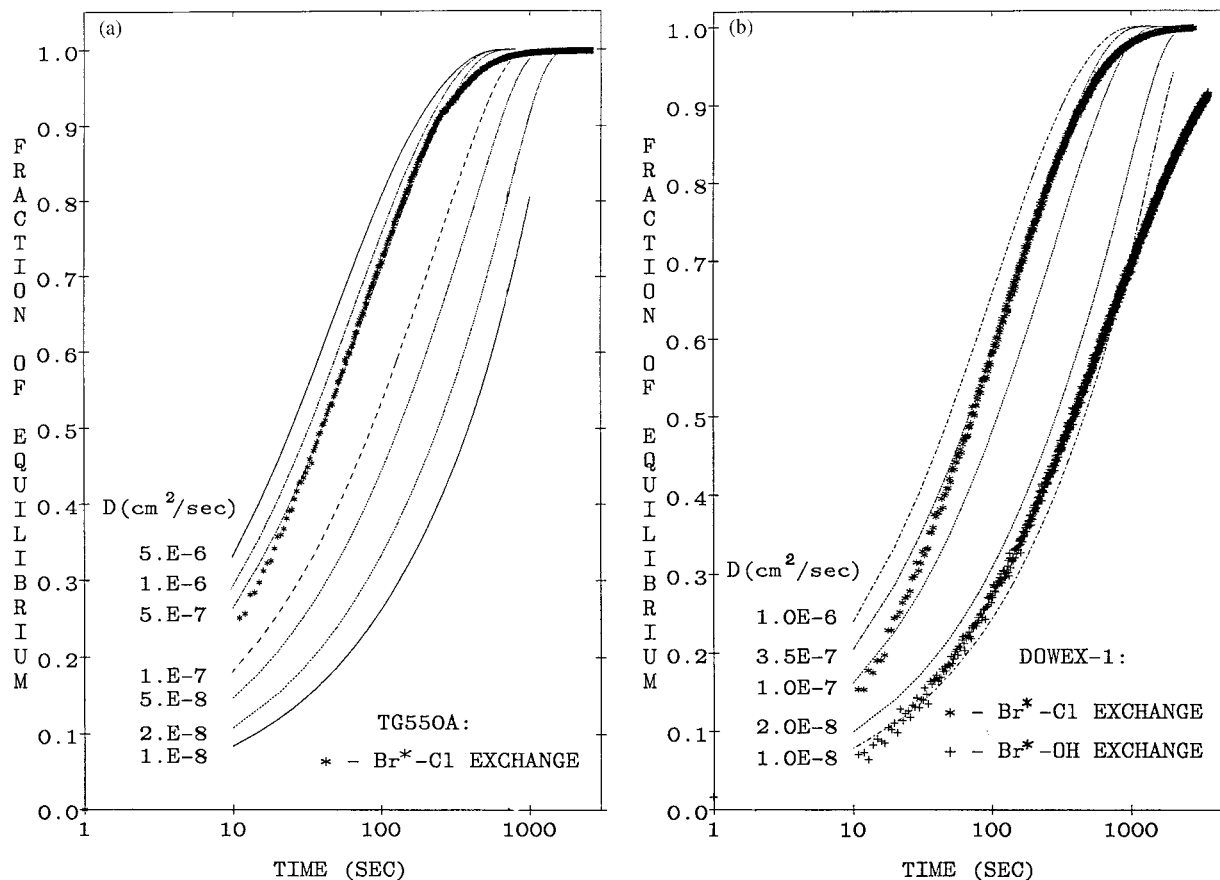


Figure 4 Exchange kinetics of nonidentical ions, $^{82}\text{Br}^-$ with Cl^- and OH^- , in TG550A and Dowexl. Radioactive ^{82}Br isotope is initially in the anion-exchange resins. The data depicted by the solid lines were computed using eq. (4). The self-diffusion coefficients of invading counterions used in computations are presented on the left of the corresponding curves. (a) Exchange kinetics in monodisperse TG550A; computations were conducted using a coefficient for ^{82}Br diffusion equal to $6 \times 10^{-7} \text{ cm}^2/\text{s}$. (b) Exchange kinetics in Dowexl; computations were conducted using the ^{82}Br diffusion coefficient equal to $3.5 \times 10^{-7} \text{ cm}^2/\text{s}$.

were determined (Table I). The Br^- diffusion coefficient controlling the Br^- exchange with the Cl^- anion was also deduced, applying eq. (3) to analyze the Cl^*-Br^- exchange kinetics (Table I).

To evaluate the influence of the counterion in the resin on the invasion kinetics and diffusivity of the invading counterion, the exchange kinetics of radioactive Br^* isotope in TG550A and in Dowexl resins with the stable Cl isotope from the solution were monitored. To deduce the diffusivity of the invading Cl^- ion in the presence of Br^* in the resin, a Br^- self-diffusion coefficient derived from the data on Br^*-Br exchange was used as a constant. The Cl^- diffusivity was used as an adjustable parameter in numerical simulation of the nonidentical ions exchange kinetics by eq. (4).

The Br^- self-diffusion coefficients used in computations were $6.0 \times 10^{-7} \text{ cm}^2/\text{s}$ in TG550A and $3.5 \times 10^{-7} \text{ cm}^2/\text{s}$ in Dowexl [Fig. 4(a,b)]. The Cl^- diffusion coefficients were determined by graphic superposition of the computed and monitored exchange kinetics (Table I). It was observed in other resins¹⁻³ that the diffusivity of Br^- in the presence Cl^- was the same as found in $\text{Br}-\text{Br}$ exchange, while the diffusion coefficient of Cl^- determined in the presence of Br^- in the resin was lower than in $\text{Cl}-\text{Cl}$ exchange. The self-diffusion coefficients determined by us in TG550A during the exchange of nonidentical ions followed the trend reported for other ion-exchange resins.

Almost identical values for the diffusivities of OH^- in the Dowexl were obtained using the exchange kinetics of $^*\text{Cl}^-$ or $^*\text{Br}^-$ in the resin with

Table II Resin Capacity (wt %)

Resin	Cl	Br	Na _{initial}	Na _{Cl}	Na _{Br}	Na _{OH}
TG550A	7.3	14.81	0.008	0.197	0.175	0.05
Dowex1	7.47	—	0.013	—	—	0.092

The weight % of ion uptake was measured relative to the weight of the original resin washed with distilled water and drained on a Büchner funnel under the vacuum. Na_x signifies the amount of Na⁺ invading a resin during exchange of Cl⁻ in the resin with X⁻ in NaX solution, where X is Cl, Br, or OH.

OH⁻ in the solution (Table I). Similar to other ions, the diffusivity of OH⁻ within TG550A was higher than in Dowex1 (Table I).

Sodium Co-ion Invasion

Sodium was the co-ion in all of the experiments. During ion exchange, the co-ion is partitioned between the solution and the resin as a result of concentration gradients and the fluxes of the exchanging counterions. This distribution of the co-ion depends on the type of exchange and the resin properties. No data on co-ion exchange were previously reported for TG550A. Therefore, the total amount of sodium cation invading the resin was measured after the several repeated equilibrations of 2 g of the TG550A with 20 mL of the 10% NaOH solution (fresh solution after each equilibration) (Table II). The kinetics of Na⁺ invasion during isotope and nonidentical anion-exchange in the batch mode were also measured (Fig. 5). The error in measurements of sodium invasion kinetics was larger than that in the other experiments described above. The low amount of Na⁺ entering the resins during anion exchange was partially masked by the Na remaining on the resin bead surface even after a distilled water rinse. Additional errors may have been introduced by low precision in recording the time of termination of the exchange.

The accumulation of the Na⁺ co-ion in the resin was observed in all of the investigated exchange processes (Fig. 5). An increase in co-ion concentration in the resin was detected even when the slower diffusing counterions were initially in solution and the temporary co-ion depletion in the resin was expected based on the data reported in the literature.¹⁻³ Apparently, the high concentration of the solutions used in exchange (2.77M) resulted in a high concentration gradient between the co-ion in solution and within the bead. Therefore, the difference in counterion mobilities was not sufficient to overcome the gradient-driven co-ion flow into the resin. The kinetics of Na⁺ co-ion

uptake varied somewhat for different counterions taking part in the ion exchange. However, the magnitude of the variation was comparable to the experimental error. Therefore, no attempt was made to assign different Na⁺ diffusivities to the different exchange processes (Fig. 5). A small variation in the Na⁺ diffusion rate confirms that electrostatic interactions play a secondary role in Na⁺ co-ion invasion at high solution concentration. According to previously published data of Schlögl, the co-ion self-diffusion coefficient within the resin decreases with the increase of solution concentration.^{13,14} Perhaps at lower concentrations it would be possible to differentiate the electrostatic effects from those induced by concentration gradients. More work on co-ion invasion kinetics is required to fully characterize the resins.

Almost the same amount of co-ion invaded TG550A resin during the Cl*—Cl isotope exchange and during Br*—Br exchange [Fig. 5(a)]. During the exchange of isotopes, electrostatic charges between the resin and solution remain at equilibrium. Therefore, the observed Na⁺ accumulation in the resin at high concentration of exchanging solution (2.77M) is controlled by the Na⁺ concentration gradients. Diffusion from the solution into a spherical resin bead, induced by concentration gradient, was treated as analogous to the heat flow from the infinite heat bath into the cold sphere immersed in it [eq. (3)]. The diffusion coefficient of Na⁺ was found to be 5×10^{-7} cm²/s in both resins studied [Fig. 5(b)].

Resin Capacity

The contents of Cl, Br, and Na in the TG550A and Dowex1 were measured by batch experiments before and after the exchange took place (Table II). As can be seen from the data, the Dowex1 capacity for chlorine is slightly higher than that of TG550A. A correspondingly larger amount of co-ion was absorbed during ion exchange by Dowex1. The lower co-ion uptake may justify selection

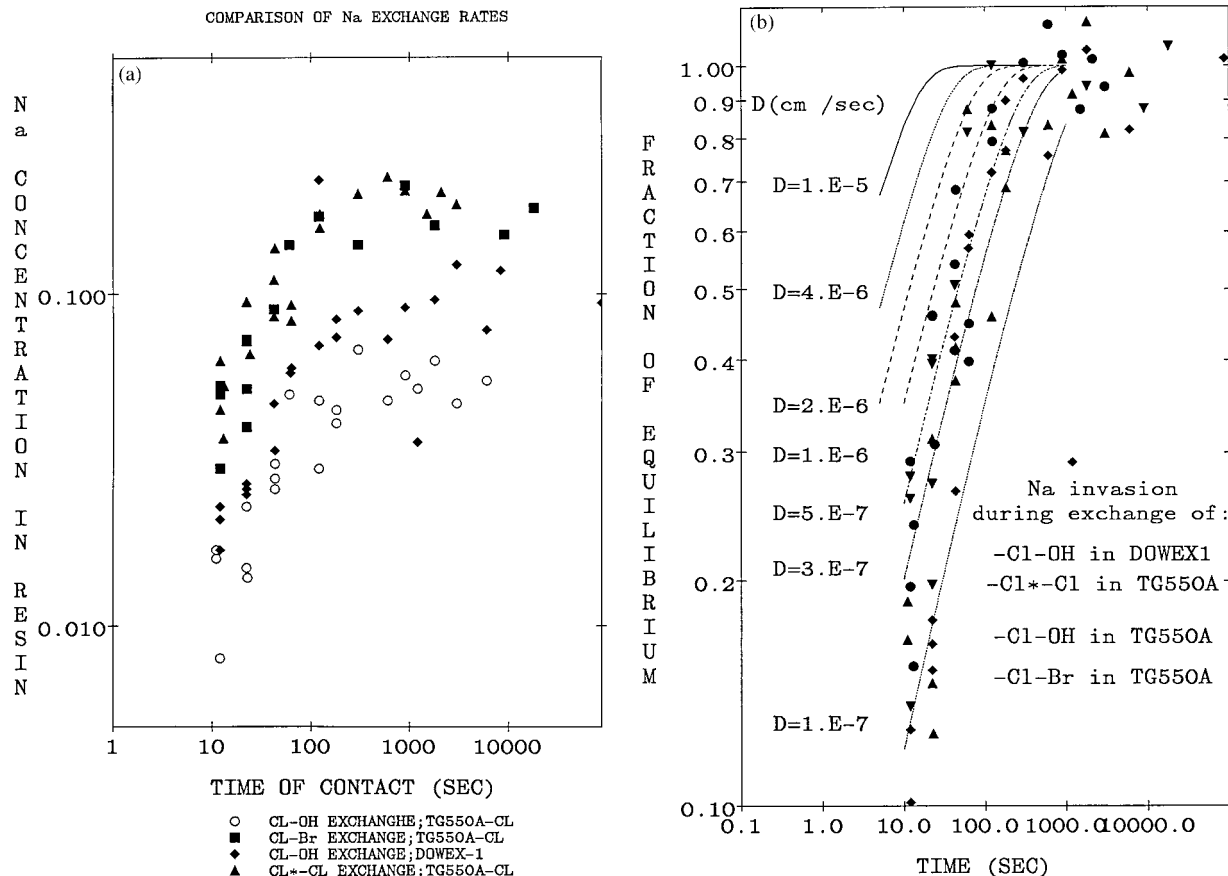


Figure 5 Kinetics of Na^+ invasion into TG550A monodisperse anion-exchange resin during an exchange of $^{38}\text{Cl}^-$ radioactive ion from the resin with nonradioactive ions from solution. The exchange was conducted in a batch. Na^+ concentration within the resin was determined by neutron activation analysis: (a) dependence of the absolute concentrations of the Na^+ within the resin on the time of shaking of 2.0 g of resin in 20.0 mL solution; (b) fractional attainment of equilibrium function dependence on the time of shaking of 2.0 g of resin in 20.0 mL of solution.

of TG550A in applications where buildup of the co-ion in the resin is undesirable. However, in most applications, a small difference in the capacity of Dowex1 and TG550A resins will not affect the results or the choice of the resin.

Ion-Exchange Equilibrium

The batch experiments show that the equilibrium between 2.0 g of TG550A in its chlorine form and 20.0 mL of 2.77M NaOH solution is attained in less than 20 min. The equilibrium selectivity of the TG550A to OH^- versus Cl^- was determined. The total amount of radioactive Cl^* in the resin and in the solution in equilibrium with the resin was deduced by the γ -activity level of Cl^* . The OH^- ion contents were determined using the material balance and solution pH. It was found that

the selectivity coefficient of the monodisperse resin, $K_{\text{Cl}^-}^{\text{OH}^-} = [(M_{\text{OH}}/M_{\text{Cl}})_{\text{resin}}]/[(M_{\text{OH}}/M_{\text{Cl}})_{\text{solution}}]$, increased at 25°C from 0.020 ± 0.005 at $(M_{\text{OH}}/M_{\text{Cl}})_{\text{resin}} = 0.03$ to 0.031 ± 0.005 at $(M_{\text{OH}}/M_{\text{Cl}})_{\text{resin}} = 0.5$. The ion-exchange isotherm for Cl^- ion distribution during Cl^- to OH^- exchange in TG550A- Cl^- also was obtained (Fig. 6). The measurement of Cl^- distributions between the resin and solution equilibrated with the resin demonstrate that the TG550A resin, like the conventional Dowex1 resin, exhibits a higher affinity for Cl^- than for OH^- .

Swelling

The swelling of the TG550 resin beads was measured by the resin weight increase occurring after the Cl^- — OH^- exchange. Following the resin

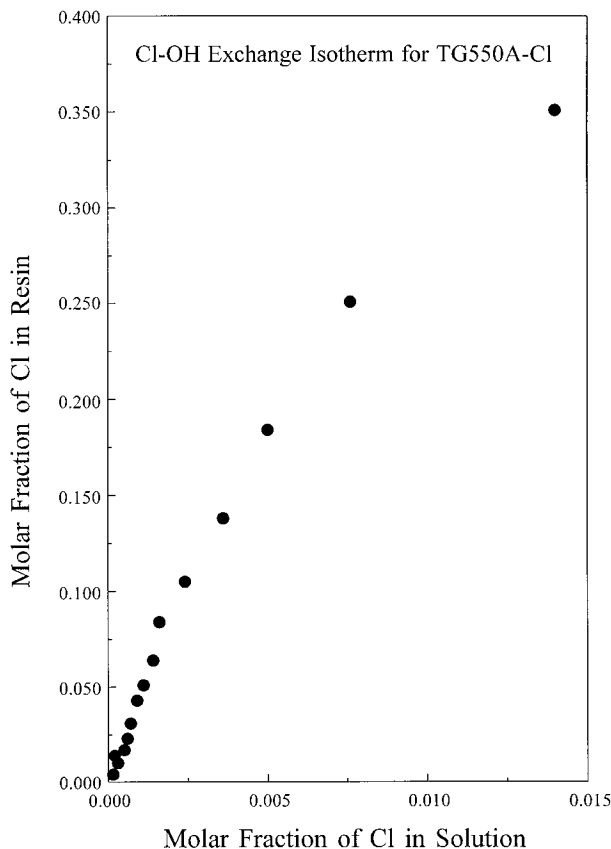


Figure 6 The 25°C isotherm of Cl—OH distribution between TG550A resin and solution in a batch.

equilibration with solution (2.0 g resin, 20.0 mL 10.0% NaOH solution, 20 min of shaking), the batch was dumped on a glass filter, drained under a vacuum, and weighted. After such a batch Cl^- — OH^- exchange with one 20.0 mL portion of solution, the weight increase was 15%. After several repetitions of the exchange procedure with the successive batches of fresh NaOH solution, the asymptotic value of 22% weight increase was reached. The resin volume increase by swelling is proportional to the solution uptake. Therefore, using the TG550A in columns, it is advisable to leave free space between the resin and column inlets to prevent pressure-induced deformation of the resin beads and/or column fracture. A similar volume increase of 20% was observed by other researchers in Dowexl resins during Cl^- to OH^- exchange.⁴

DISCUSSION AND CONCLUSIONS

Diffusion coefficients measured in the presented studies should be called, using the terminology of

Boyd and Soldano,¹⁵ “apparent self-diffusion coefficients” since neither degree of solvation nor the degree of association of the radioactive ions were known. However, the found diffusivities correspond to those determined in other studies and permit meaningful comparison of exchange kinetics in TG550A, Dowexl, and other ion-exchange resins.

No large qualitative difference between the ion-exchange kinetics in TG550A and Dowexl were found. Both resins exhibited Br^* — Br and Cl^* — Cl isotope exchange kinetics well described by the particle-controlled diffusion model (Fig. 4). Exchange of nonidentical ions occurred with a similar deviation from the theoretical model (Figs. 3 and 4). This similarity in behavior indicates similarities in the exchange mechanism and the internal structure of the two resins. However, for good column performance, the uniformity of the packaging size is important; thus, the TG550A resin may be selected over Dowexl resin in some analytical applications. Higher ion diffusivity in the TG550A (Table I) may also present an advantage in ion-exchange chromatography. Indeed, higher diffusion rates are beneficial in the reduction of the eluent dispersion in the column and yield better resolution of the ion-exchange columns. The difference in performance of TG550A and Dowexl is not large enough to affect the choice of the resin in high-volume applications such as solvent purification and desalination.

Since both resins have a similar degree of cross-linking and an even similar capacity for the ions, the cause of the higher ion-exchange rates in TG550A is unclear. Perhaps, the difference in the method of resin bead production leads to some difference in the bead surface structure. This question requires further investigation.

An interesting problem is the deviation of the kinetics of nonidentical ion exchange from the model developed by Helfferich and Plesset^{1-3,11,12} [eq. (4); Figs. 3 and 4]. The rate of the ion exchange decreased at the end of the exchange in each case studied by us. This deviation was previously attributed to the change of the individual diffusion coefficients with the water contents of the resins. Water in the resin occupies part of the free volume and plasticizes the polymer. As a result, molecular diffusion in some polymers is substantially reduced in the presence of moisture.¹⁶⁻¹⁸ Since a 22% weight increase during the Cl^- — OH^- exchange was observed, the water content increase may be the main factor reducing the ion diffusivity at high fractions of equilibrium attainment. Thus, the deviation of observed exchange kinetics from the Helfferich—Plesset

model may be caused by water absorption. The electrostatic effect of co-ion invasion may be also a factor reducing the exchange rate at longer times of exchange.^{13,14} It appears that use of the uniform TG550 resin did not improve agreement between the experimental ion-exchange kinetics and the modeling results. Further investigation of the mechanism of ion exchange is needed. Extensive numerical kinetic modeling, taking into account the bonding sites and hydration sphere variation as well as experimental data obtained at a variety of exchange conditions, is required to further clarify the ion-exchange mechanism. The current data and numerical modeling were designed to assist in selection and practical use of TG550A and Dowexl in analysis and purification.

The values of the diffusion coefficients deduced using kinetic data are always model-dependent.³ Particular attention was paid in this work to the applicability of the models. Other researchers applying the same models to the ion-exchange kinetics measurements in strong base styrene anion-exchange resins obtained Br^- , Cl^- , OH^- , and Na^+ diffusion coefficients close to those reported here, i.e., Br^- diffusivity varied between $8 \times 10^{-8} \text{ cm}^2/\text{s}$, reported by Schlögl,^{13,14} and $9 \times 10^{-7} \text{ cm}^2/\text{s}$, reported by Boyd and Soldano.¹⁵ The self-diffusion coefficients for Cl^- , $3.5 \times 10^{-7} \text{ cm}^2/\text{s}$, reported earlier¹³ were only slightly lower than our measurements. In measurements by Schlögl,¹³ Na^+ diffusivity was found to be $2 \times 10^{-7} \text{ cm}^2/\text{s}$. This value is close to the Na^+ diffusivity determined by us, $5 \times 10^{-7} \text{ cm}^2/\text{s}$.

In general, the presented results are in agreement with the data obtained by other groups, i.e., $D_{\text{Br}^-} > D_{\text{Cl}^-} > D_{\text{OH}^-}$. Availability of the radioactive isotope-producing facility, the 100 kW TRIGA research reactor, greatly simplified the experiments and ensured high precision of the measurements. The neutron activation^{5,6} and radiation-based monitoring of ion-exchange kinetics are proven to be an excellent tools in the evaluation and development of ion-exchange resins and polymeric materials, in general.

The authors would like to thank Dr. L. B. Lindy for providing them with the ion-exchange resin samples and for his helpful discussions. They also would like to express gratitude to Dr. M. Koch and J. Macky for their continued support of the authors' effort. The assistance of W. L. Rigot in processing the radioactive decay counting data is greatly appreciated.

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