

The Study of Kinetic Models for Ligand Exchange of Anions as Ligands Using Ligand-Exchange Resin

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ABSTRACT: A comparative study of kinetic models for ligand exchange of $I^- \rightarrow Cl^-$ and $Br^- \rightarrow Cl^-$ as ligands as a function of pH and concentration using diaminoethyl-sporopollenin (DAE-sporopollenin) resin were investigated during the ligand-exchange reaction of the liquid phase. A batch technique was employed for the study of the kinetics of I and Br/Cl exchange as ligands. Five kinetic models were applied to the experimental data. The rate of ligand exchange was increased with decreasing of the hydrated ionic radius and pH. The curve fitting of the mathematical models and the behavior of the kinetic curves are discussed for direct ligand exchange under the conditions employed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1225–1234, 1997

INTRODUCTION

The interaction of organic molecules and ions in an aqueous solution with chelating exchangers has been of increasing importance in recent years because of organic pollutants in ground water and concerns about environmental quality.^{1–10} These studies are important, since they aid in obtaining mechanistic information on the sorption and desorption of organic molecules and on chelating exchangers. The relation between the nature of the ligand and exchangers and the reaction rate is generally complicated by many possible interactions between the ligands and the ligand exchange in exchangers.

A number of chelating exchangers of sporopollenin formed from carboxyl, epoxy, and gloxime functional groups have been investigated as cation, anion, and ligand exchangers.^{11–13} These materials exhibit a high selectivity of metal–ligand complexes toward transition metals and their sorption properties are often connected with a fairly good stability toward pH.^{11–13} On the other

hand, this material may be useful for application at high temperature, since it is appreciably stable under heat temperature and concentrated acids.¹⁴ This aroused the interest of the present authors regarding a study of the anions as ligands on the ligand-exchange rate of sporopollenin. In addition, this study will greatly contribute to an understanding of the ligand-exchange mechanism of sporopollenin by clarifying the relationship between properties of the exchanger matrix and ligand-exchange rates.

Proper design of many practical ion-exchange processes requires an extensive knowledge of the system. The analysis of single ligand exchange is a first step toward establishing the correct model for the process. During a systematic investigation of the anion-exchange reaction on different anion resins, it was found that both the Nernst–Planck theory and developed theoretical models were inadequate to explain the experimental kinetics.^{15–17} Interpretation of the ligand-exchange kinetics by curve fitting of the experimental data to kinetic model equations may be misleading for several reasons: (i) the same model equation may apply to different physical situations¹⁵; (ii) too rough approximations are commonly introduced into the

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physicochemistry of the system investigated¹⁷; and (iii) kinetic theories based just on diffusion, like Fick and Nernst–Planck theories, have so far been applied mainly to ion-exchange kinetics and are the standard against which new theories are measured, while their accuracy in explaining real situations still has to be proved.^{17,18}

In this study, the kinetics of ligand exchange were fitted to different proposed kinetic models and compared with the predicted values. The preliminary efforts for a new approach for an explanation of the experimental kinetics for direct ligand exchange and the effect of pH on the ligand sorption rate of anions between the exchanger and aqueous solutions, based on analysis of the modification occurring during the exchange in the liquid phase, are described.

EXPERIMENTAL

Materials

The resin used was *Lycopodium clavatum* of a 20 μm particle-size mesh from BDH. Salt solutions were prepared by dissolving a weighed quantity of Analar salts in buffered solutions adjusted to a desired concentration and desired pH (4.70–8.65), which was used without further purification. KCl, KBr, KI, CoCl_2 , H_2SO_4 , ethylene diamine, and citric acid monohydrate were obtained from Merck; H_3BO_4 , from Riedel-de Haën ag Seelze; and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, from Panreac Co. The buffer solutions were prepared from anhydrous boric acid, citric acid, and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ at the pH 4.70–8.65 range.

Preparation of Diaminoethyl–Sporopollenin (DAE–Sporopollenin)

The sporopollenin was aminated according to the method described previously.¹¹ Then, DAE–sporopollenin was treated with a Co^{2+} ion which was fixed to the resin matrix.

Kinetic Procedure

The direct ligand exchange of $\text{Cl}^- \rightarrow \text{Br}^-$ and $\text{Cl}^- \rightarrow \text{I}^-$ was determined using an Orion ion analyzer (Orion EA 940) and a Cl-ion-specific electrode (Orion 9417-B). For this, 0.1 g of air-dried resin was weighed into a 30 mL beaker and dispersed in 10 mL of the buffer solutions and allowed to stand at $30 \pm 0.5^\circ\text{C}$. This tem-

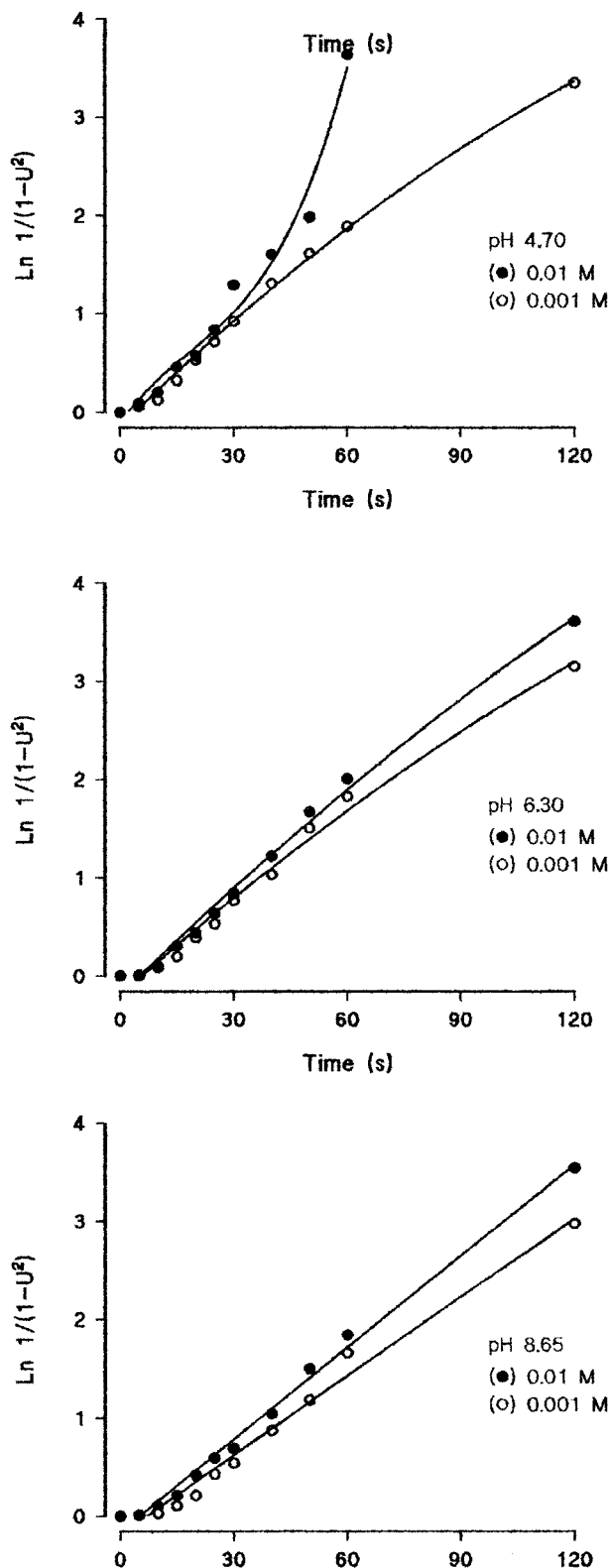


Figure 1 Curve fitting of experimental kinetics for direct exchange of $\text{Cl}^- \rightarrow \text{Br}^-$ to Nernst–Planck, particle diffusion control.

perature was chosen to accommodate the natural existence conditions of the ions. The 5 mL bromide and iodine solutions were poured very rapidly into the homogeneous suspension. The mixture was stirred by a magnetic stirrer and releasing of the chloride concentration was determined by an ion-selective electrode. The bromide or iodine displaced the exchangeable chloride ligands from the exchanger and the activity of chloride in the suspension increased. A continuous record of chloride activity vs. time was recorded every 10 s. The amount of the chloride ion released to the resin was then calculated from the change in its concentration in the solution. The sorption of bromide and the iodine concentration in the resin were also controlled by the difference between the initial bromide or iodine concentration in the solution and in the resin phase using bromide (Orion 94-35) or iodide (Orion 9453) ion-selective electrodes. For the reverse exchange, the resin was washed with 2.0M H₂SO₄. All experiments were performed in duplicate to ensure reproducibility of the process. The results agreed to within $\pm 5\%$.

RESULTS AND DISCUSSION

In direct ligand exchange (Cl to Br or I, resin initially in chloride form), chloride release from the resin is followed by ion-selective electrodes. The obtained data are processed to obtain U ($[Cl]_t/[Cl]_\infty$, conversion degree of the resin) vs. time and to curve-fit experimental results to five different model equations, discussed in detail elsewhere,¹⁵ as a function of pH and are reported in Figures 1–10.

This leads one to infer that existing ion-exchange kinetic theories, such as those based on Fick's and Nernst-Planck's diffusional models, provide only a rough idealization of the real situation, like the one investigated (i.e., a highly selective system and/or high solution concentration), where ideal behavior cannot be assumed.²⁰

Ligand exchange is a heterogeneous chemical reaction. Ligands in solution (liquid phase) are exchanged with ligands in the resin (solid phase). As in other heterogeneous reactions between solid and fluids, there are a number of sequential processes that determine the rate of ligand-exchange reactions as follows:

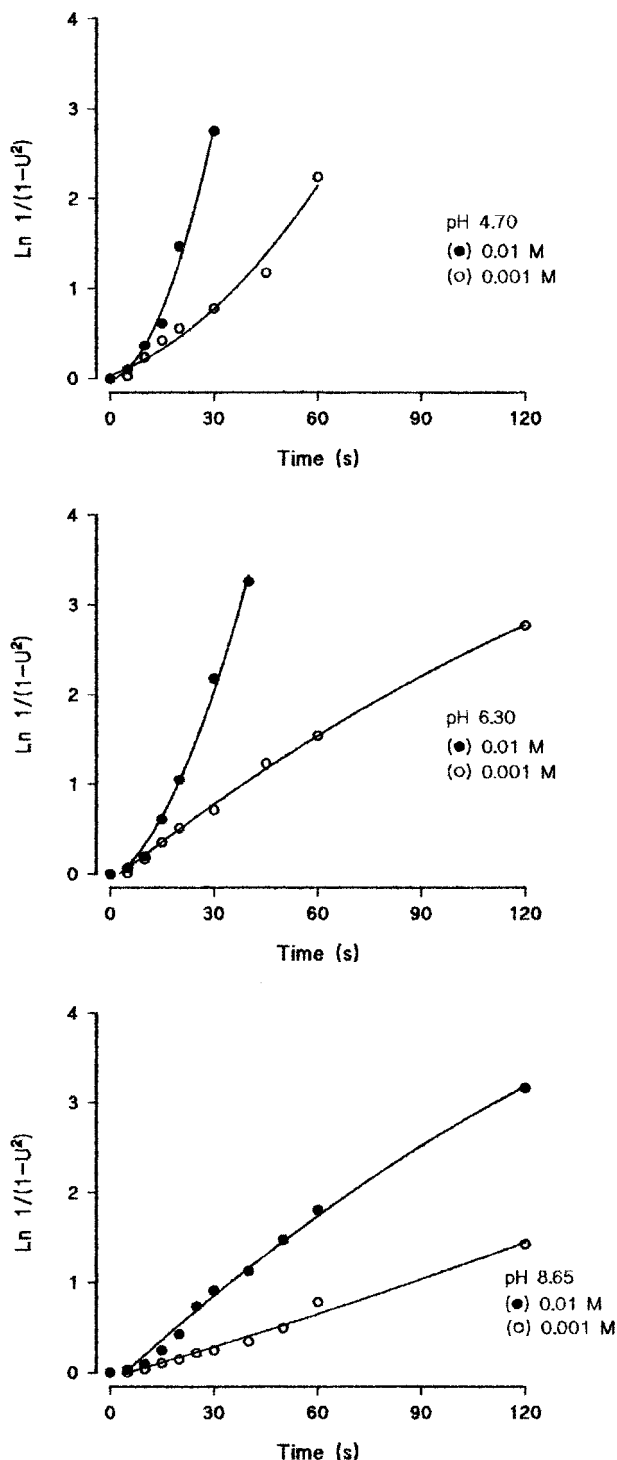


Figure 2 Curve fitting of experimental kinetics for direct exchange of $Cl^- \rightarrow I^-$ to Nernst-Planck, particle diffusion control.

- Diffusion of the ligands through the liquid film surrounding the particle.
- Diffusion of the ligands through the polymeric matrix in the resin.

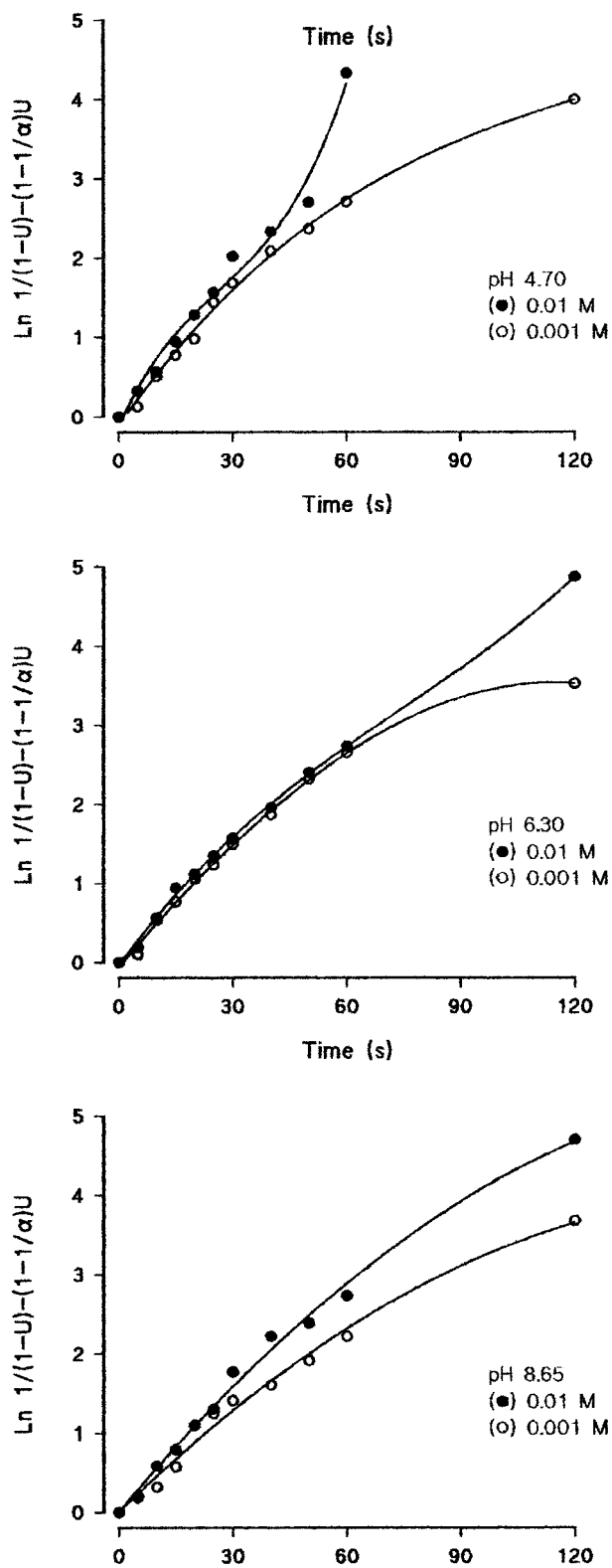


Figure 3 Curve fitting of experimental kinetics for direct exchange of $\text{Cl}^- \rightarrow \text{Br}^-$ to Nernst-Planck, film diffusion control.

- Chemical reaction with the ligands in solution and attached to the matrix.

The above steps appear to qualify for rate control: mass transfer in either the bead or the liquid, whichever is slower. One of the steps usually offers much greater resistance than do the others, so it can be considered as the limiting step of the process. The differences in the conclusions concerning the rate-determining step in the literature show that kinetic studies of the ion-exchange process are difficult. Even the more sophisticated theories on ion exchange are sometimes incapable of clarifying the rate-determining step in the process. In many cases, ion-exchange kinetics is limited by the step of diffusion inside the particle.

Studies of the kinetic model on the ligand-exchange process may have two objectives: (i) to approach, as accurately as possible, from the point of view the complexation and real physical chemistry of the ligand-exchange process and (ii) to get empirical or semiempirical equations for the design of the equipment.

The explaining of the model on the ligand-exchange phenomena that take place in the process fits the real physical chemistry and is suitable for equipment design such as for the development of a model for the sorption of the ligands for waste water treatment. Kinetic curves of ligand exchange can be fitted adequately with only one parameter. They are all very similar and it is not easy to find a model with two parameters that cannot explain all the different experimental data. The basic principles of the ion-exchange kinetic theories are reviewed for the ligand-exchange process. So, in this work, we chose the simplest kinetic models which have only one experimental fitting parameter.

The most characteristic kinetic model for ion exchange is the Nernst-Planck particle diffusion model. It takes into account the peculiarity imposed by the Donnan exclusion of the coupled diffusion of ions inside the particle. Electric neutrality requires that the diffusion of ions of type 1 in one direction have to be compensated by the diffusion of type 2 in the opposite direction. Diffusion is still guided by the Fick law. However, the rate of ligands in the solution depends now on the ionic composition of the particle and especially on the ionic mobility of the slower ion.^{18,20}

The film model has been amply studied due to its wide application in all kinds of heterogeneous reactions. It is assumed that ions find the main resistance to diffusion in a thin film of the solution

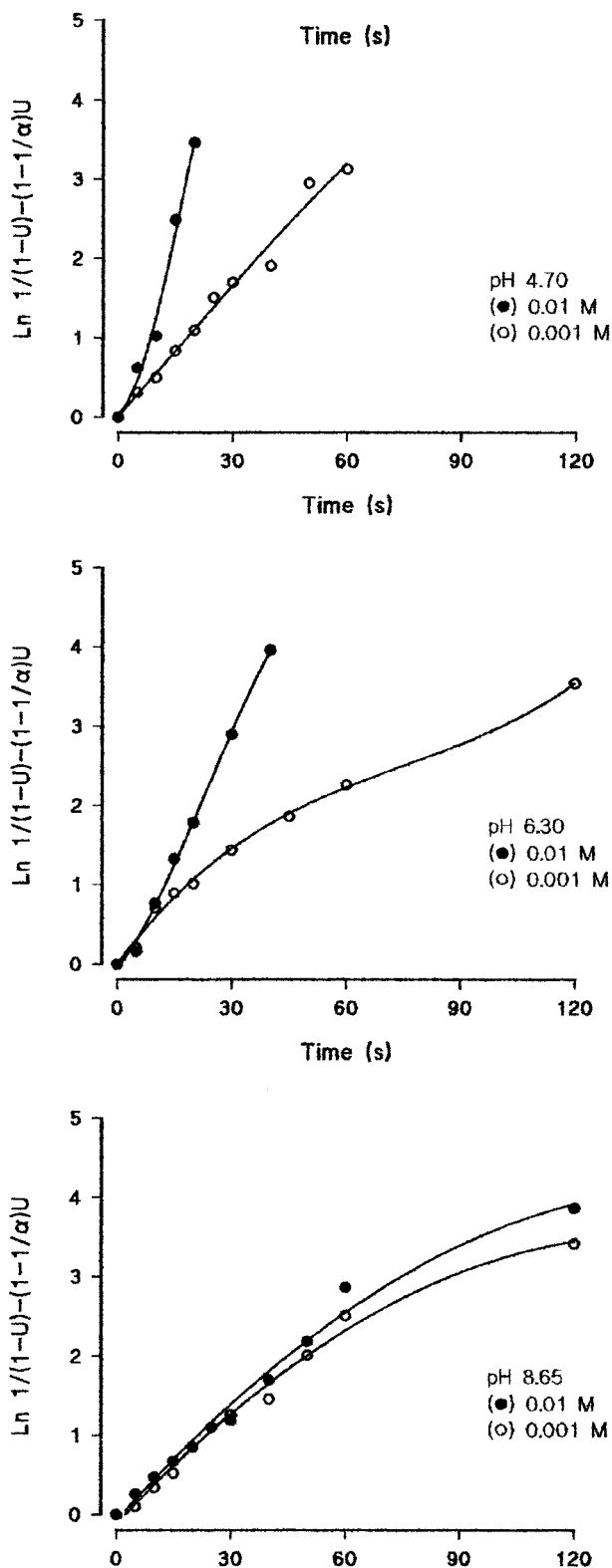


Figure 4 Curve fitting of experimental kinetics for direct exchange of $\text{Cl}^- \rightarrow \text{I}^-$ to Nernst-Planck, film diffusion control.

that surrounds the particle surface. The driving force of the mass transfer is assumed to be linear. It can be assumed that ions or ligands are homogeneously distributed inside the particle. The mass-transfer parameter depends on the diffusivity of the ligand in the solution and the thickness of the film. This model predicts the ionic concentration in the solution, the particle size, the stirring of the solution, the equilibrium isotherms, and the nature of ligand exchanged.

Generally, diffusion in the bead is obstructed by the matrix; on the contrary, in the solution, it is not. Moreover, the distance to be covered from the surface to the center of the bead is much greater than that across the liquid film or the boundary layer between the liquid which is stirred and the bead surface. Indeed, given the same concentration difference as a driving force, intraparticle diffusion would always be slower than the liquid-phase mass transfer. However, the driving force is not the same. In the liquid, there is a concentration difference between the bulk liquid and the bead surface, and the bulk concentration is always larger than the bead surface, whereas the concentration difference between the bead surface and the center can be same as the concentration of fixed ionic groups (ligands). Provided that the rate of exchange can be proved to be governed predominantly by the "particle-diffusion" step, such measurements lead to values of the diffusion coefficient of the exchanging species.

In chemical exchange, it is assumed that ligand exchange takes place between ligands with identical physical-chemical properties. The ligands are assumed to be excluded from the inside of the particle.¹⁸ The kinetic curves predicted by this model are dependent on the particle size and the nature of the ligand exchanged.

The chemical reaction can play a major role in ion-exchange kinetics. If the reaction is very slow compared with the mass transfer and concentration gradients in the liquid and the bead is the same level, the rate-limiting step will be controlled by the reaction. However, the ligand-exchange reaction was observed to be very fast, and the rate-limiting step in this process is not affected so much by the chemical reaction. There are only a few cases in which the rate of ligand exchange is determined by the chemical reaction. When a kinetic study is in its initial stage, it is generally assumed that the chemical reaction is infinitely fast. Helfferich¹⁸ gave 11 examples in which reactions have an influence on the rate of

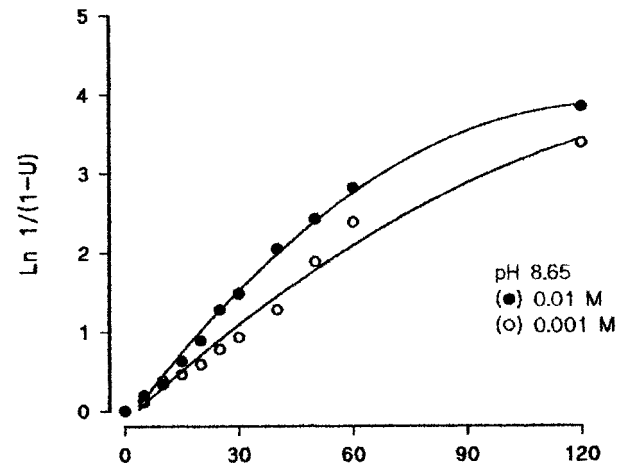
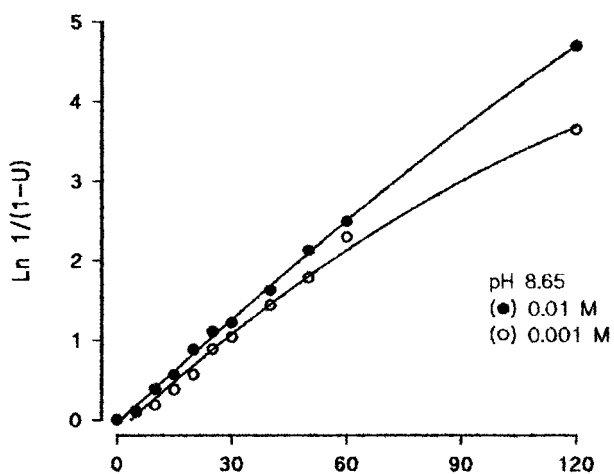
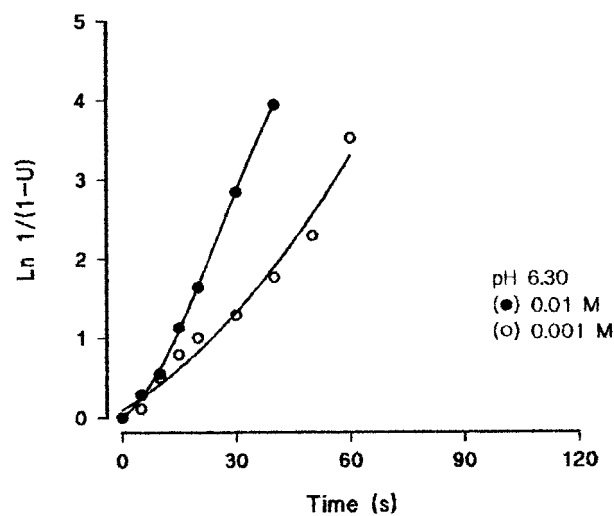
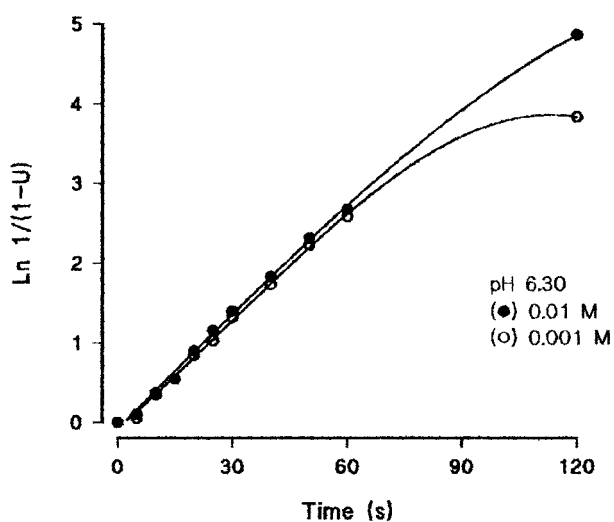
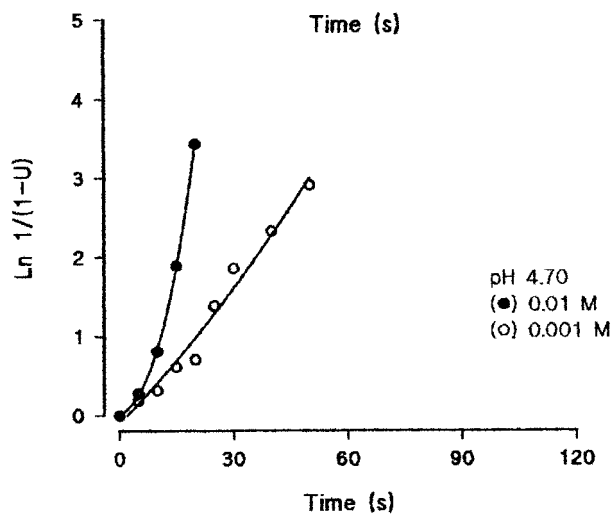
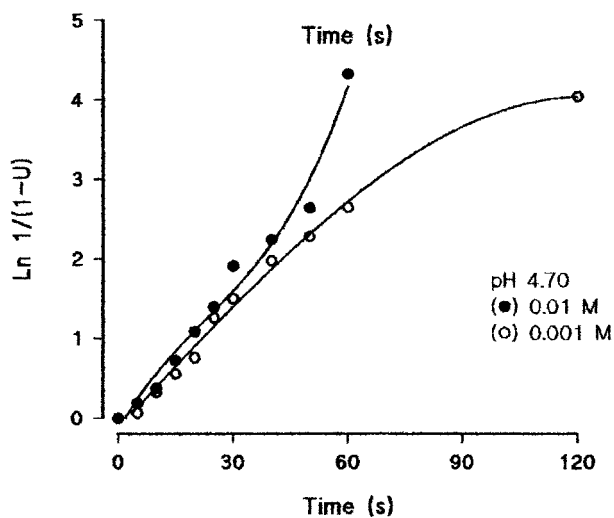


Figure 5 Curve fitting of experimental kinetics for direct exchange of $\text{Cl}^- \rightarrow \text{Br}^-$ to SN_2 chemical diffusion control.

Figure 6 Curve fitting of experimental kinetics for direct exchange of $\text{Cl}^- \rightarrow \text{I}^-$ to SN_2 chemical diffusion control.

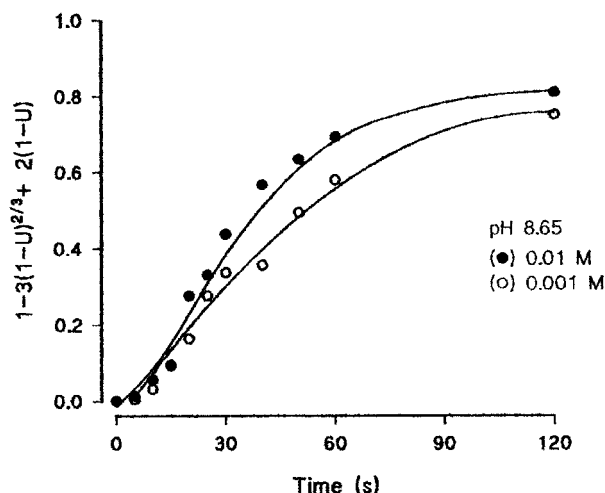
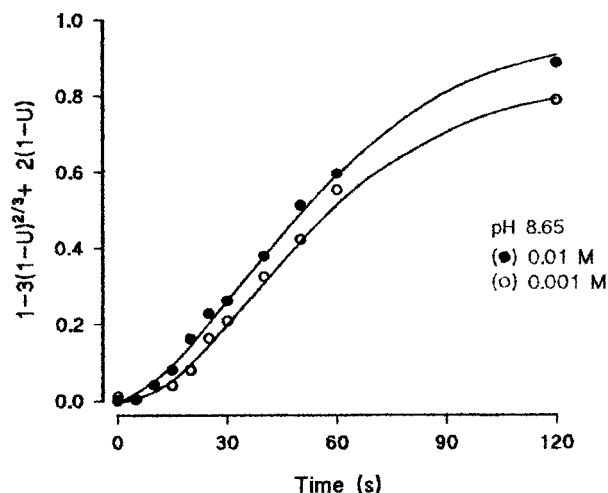
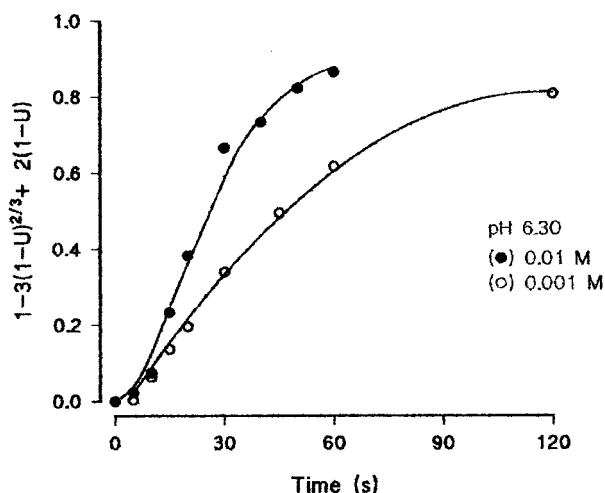
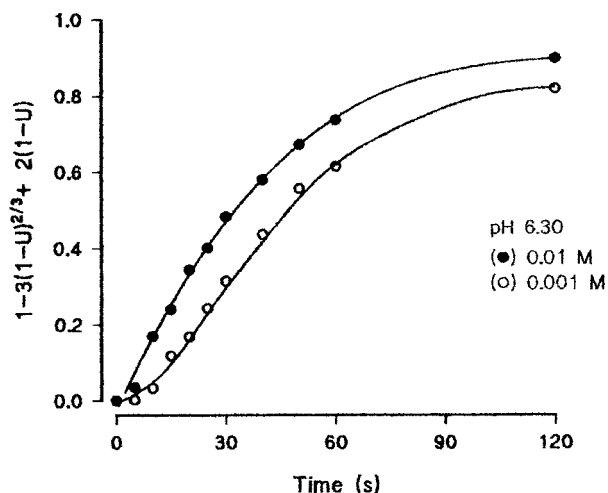
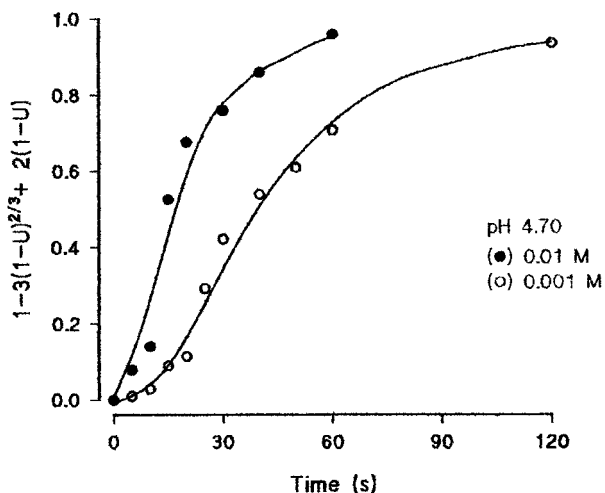
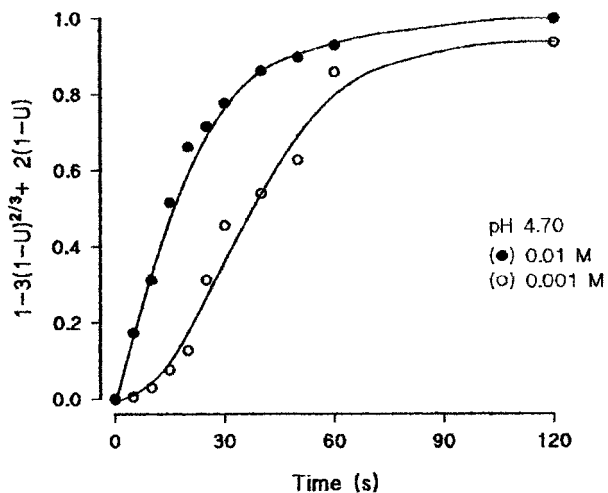


Figure 7 Curve fitting of experimental kinetics for direct exchange of $\text{Cl}^- \rightarrow \text{Br}^-$ to unreacted core particle diffusion control.

Figure 8 Curve fitting of experimental kinetics for direct exchange of $\text{Cl}^- \rightarrow \text{I}^-$ to unreacted core, chemical control.

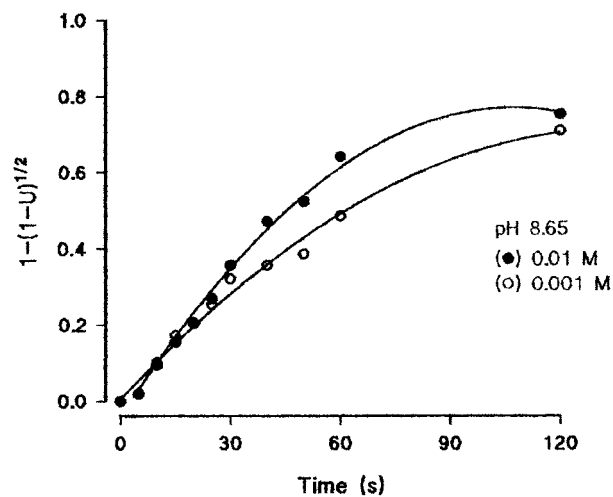
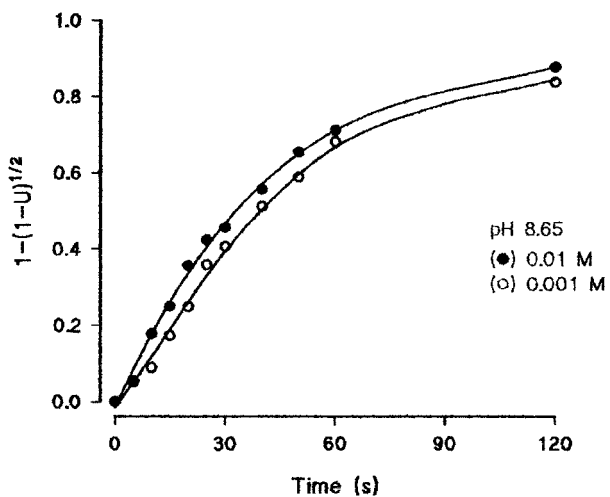
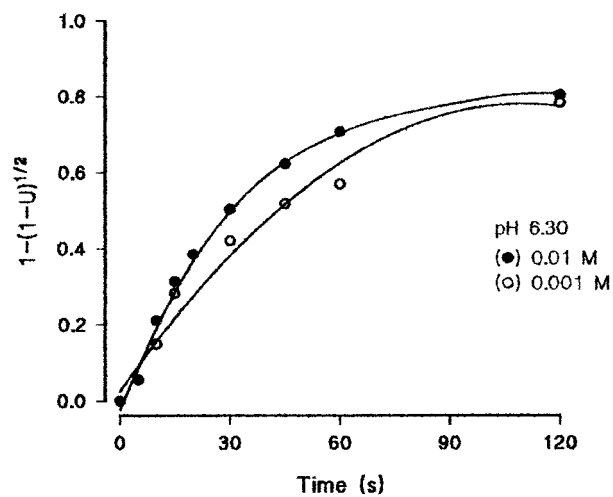
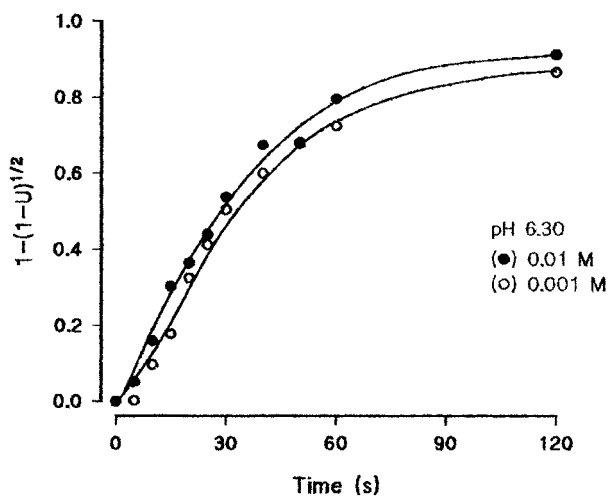
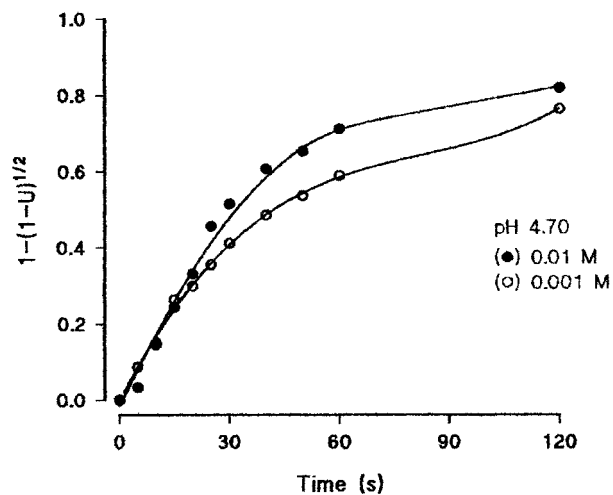
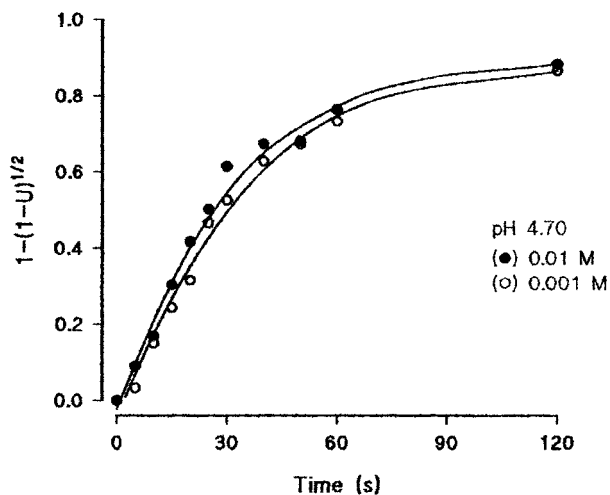


Figure 9 Curve fitting of experimental kinetics for direct exchange of $\text{Cl}^- \rightarrow \text{Br}^-$ to unreacted core, chemical control.

Figure 10 Curve fitting of experimental kinetics for direct exchange of $\text{Cl}^- \rightarrow \text{I}^-$ to unreacted core, chemical control.

exchange; they are all related to some kind of parallel ionic reaction that changes the identity of the ions involved. Kinetic curves are dependent on the particle size, the nature of presaturant ligand, and the nature of the exchanged ligand.

In the unreacted core model, ligands move into the particle of the resin, leaving the outer shells of the particle in the equilibrium with the surrounding solution. A concentration gradient between the external solution and the zero value of the particle core is assumed.²¹ The shape of the kinetic curves depends on the particle size and the nature of the ligand exchanged.

A very fast initial sorption results in an almost instantaneous attainment of the bulk of the equilibrium sorption, followed immediately by a very slow rate of sorption. This suggests that the bulk of the sorption possibly takes place in a shallow outer layer of the resin bead with high diffusivity while inner layers contribute very little to the sorption.

For the determination of the forward exchange I^- , Br^-/Cl^- , the resin is initially of Cl^- form and I^- or Br^- as its only ligand. For the determination of the kinetic curves of the reverse exchange, the resin was washed with $2.0M H_2SO_4$ and the concentration of I^- or Br^- ligands in the resin phase was also controlled for confirming the mass balance.

The rate of $I^- \rightarrow Cl^-$ and $Br^- \rightarrow Cl^-$ ligand exchanges in DAE-sporopollenin were compared in Figures 1 and 2 (also other figures), respectively. It is interesting that the exchange of Br^- into the DAE-sporopollenin is slower than that of I^- ; this is a consequence of the nature of the hydration value (also the hydration energy) of I^- ions compared with the Br^- and slightly higher degree of the I^- . The larger hydration shell of Br^- compared with I^- means that the former ion usually diffuses more slowly in the resin frameworks than does the latter. The concept of a more or less strong bond among molecules of water and ions is only in the case of strongly hydrated ions.

The amount of exchanged ligand increased with decreasing pH at about pH 4.70 and with the concentration of the ligands. The overall effect of the solution pH is to increase the effectivity of the OH^- ions at higher pH levels and the OH^- ion would be act as ligand. At higher pH levels, the hydrated radius of the ions is also increased and so there can be resistance of the ligand to enter the resin matrix.

The high number of variables involved in the ligand-exchange process and the long time spent on each experiment does not permit the prepara-

tion of a complete table of experiments covering every combination of values of variables adequately. However, a minimal table of experiments was designed, allowing obtainment of the most accessible information within a fair aspect of working time.

All the experimental points were fitted to five mathematical models. The quality of the curve fittings can be seen in the figures. A good statistical fitting is not sufficient to choose a mathematical model. The values of the parameters obtained must correspond to the predictions of the theoretical model applied. The particle diffusion control model had the best curve fitting compared with the others.

The purpose of this kinetic study was to find a mathematical model that fits the experimental data and to determine the influence of different variables on mass transfer for ligand-exchange processes. The studied variables were the nature of the ligand exchanged, pH, and concentration.

Credit for evidencing these limits of the theory should be assigned to the comprehensive investigation approach adopted in this study. From the experimental results, it is concluded that refinements are required in existing theories to explain the experimental mechanisms of the system investigated.

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