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Kinetics of Neutralization of Weak Electrolyte Ion-Exchange Resins

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SUMMARY

The adsorption of acids and alkalis by weak electrolyte resins is described by diffusion of the ions through the resin bead, with an accompanying neutralization reaction. A model proposed by Helfferich has been extended to account for the situation where the solution concentration of the reagent is changing during the rate experiment. Two mechanisms are necessary, depending on the concentration of the reagent. The rate expression for systems where the reagent concentration is greater than 0.01 M is given. It predicts that the adsorption rate is dependent on the solution hydrogen ion concentration in the case of weakly basic resins, and that it varies inversely with the square of the particle radius. The rate should also be unchanged by the resin of added salt.

Experimental evidence in the form of rate data for the uptake of

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hydrochloric acid by a commercial weakly basic resin support the derived equation, which can be modified further to account for the diffusional resistance of the liquid film around the resin particle.

INTRODUCTION

Interest in the rate of adsorption of ions by weak electroylte ion-exchange resins has arisen from the proposed "Sirotherm" process, which exploits the thermal dependence of the equilibrium

$$R_3N + R^1CO_2H + Na^+ + Cl^- \rightleftharpoons R_3NH^+Cl^- + R^1CO_2^- \ Na^+$$

for the development of a desalination process based on regeneration of the resins with hot water [1]. The kinetics of mixed beds are complex; a study of the individual resins was therefore selected as a starting point in a program aimed at eventually elucidating the mechanism of adsorption in mixed-bed systems.

A model for the adsorption of alkali by a carboxylic acid resin under conditions where the concentration of alkali remains constant has been put forward by Helfferich [2], with the assertion that the adsorption of acid by weakly basic amine resins is analogous. No experimental data have been available to date to test these models. The present study is concerned with the uptake of hydrochloric acid by the macroporous amine resin Amberlite IRA-93,* which may be represented by the equation

$$R_3N + H^+ + Cl^- \rightarrow R_3NH^+ \ Cl^-$$

However, it is first necessary to obtain a rate expression, based on Helfferich's model, but which applies to the more practical conditions of changing acid concentration which prevail when the reagent is not present in a vast excess.

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* "Amberlite IRA-93" is a product of the Rohm and Haas Company, Philadelphia, U.S.A.

THEORETICAL BACKGROUND

Possible Rate Limiting Steps

The three kinetic limitations to ion exchange which are theoretically possible are:

1) The electrostatically coupled diffusion of at least two ions between the bulk solution and the solid-liquid interface (film controlled diffusion).

2) A similarly coupled diffusion into the ion-exchange particle (particle controlled diffusion).

3) The rate of the neutralization reaction at the exchange site (chemical reaction controlled).

Since the diffusivities of ions are higher in water than in resins [2], and the thickness of the static liquid film around the ion-exchange particle is small compared to the size of the particle [3], diffusion through the surface film will not normally be rate limiting for weak electrolyte resins. In strong electrolyte resins the equilibria which apply at the resin-solution boundary provide a considerably larger driving force for diffusion within the bead than do the corresponding equilibria for weak electrolyte resins. Diffusion within the bead is therefore much more rapid for the strong electrolyte resin. Hence film controlled diffusion will be significant in this case, but is likely to be of only minor importance for weak electrolyte resins.

In the system under study, the rate of the neutralization reaction between hydrochloric acid and the tertiary amine site can be expected to be rapid. It will be shown that the diffusion of the ions within the resin beads is the major rate-limiting step.

Equilibria at the Bead Surface and Within the Resin Bead

The concentration of acid at the bead surface provides the driving force for the diffusion process in the amine resin. It has been observed in this system [4] that the hydrogen ion concentration at the bead surface is approximately equal to the solution concentration, although Attridge and Millar [5] have obtained contrary results in other weak electrolyte resins. Adsorption rates are affected as much by this equilibrium as they are by the diffusion properties of the resin.

The concentration of chloride ions within the exchanger is considerably higher than in the contacting solution. However, no suppression of hydrogen ion concentration in the resin pores has been observed [4], which suggests that the Donnan equilibrium does not apply to electrolyte invasion into the resin and that the ions are free to diffuse through the pores of the beads.

The concentration of hydrogen ions within the resin phase is also governed by the equilibrium at each exchange site. This equilibrium may be estimated with sufficient accuracy for our purposes by the dissociation constant

$$K_a = \frac{[R_3N][H^+]}{[R_3NH^+]}$$

although more complete expressions have been suggested [6].

The Model

Helfferich [2] has proposed the following diffusional model for the adsorption of ions by weak electrolyte resins when the adsorption is accompanied by a neutralization reaction: As adsorption proceeds, an inwardly expanding shell of the converted form of the resin gradually fills the bead as the inner core of unreacted resin is reduced in size. A sharp boundary is maintained between the zones of un-ionized and more greatly swollen ionized forms of the resin. In the case of hydrochloric acid uptake by a weakly basic resin, a shell of amine resin hydrochloride is formed as the entering protons are immobilized by the first available basic sites in their diffusion path. A typical concentration profile for this mechanism is shown in Fig. 1. It is postulated to hold for reagent concentrations greater than about 0.01 M, as used in the present study.

At lower solution concentrations a further model is necessary because of the restriction imposed by the dissociation mechanism. The concentration of protons within the resin will not be sufficient to completely convert the resin to they hydrochloride form, so that no discrete shell will be formed. The concentration profile for this situation is shown in Fig. 2.

Analysis of the Diffusion Process

Diffusion through a liquid film on the surface of the resin bead can be simply analyzed by assuming that the film has negligible curvature [7] when the following expression is obtained:

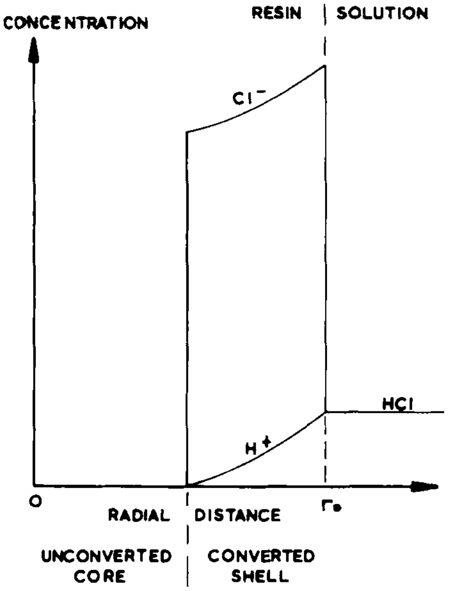

Fig. 1. Concentration profiles for the diffusion of hydrochloric acid of solution concentration greater than 0.01 M into a weakly basic resin.

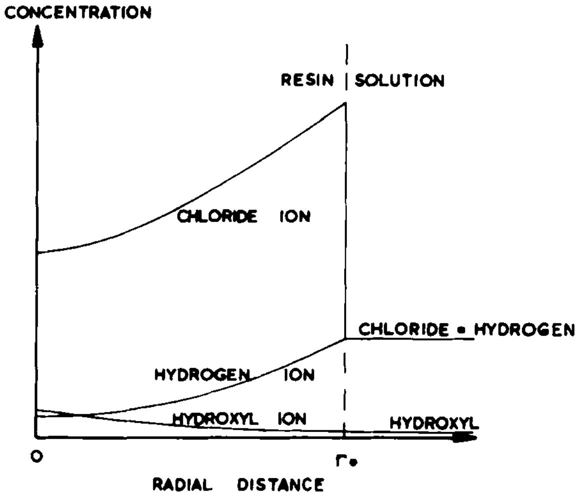

Fig. 2. Concentration profiles for the diffusion of hydrochloric acid of solution concentration less than 0.01 M into a weakly basic resin.

$$\frac{dF}{dt} = \frac{3D_{HCl}(C_H^S - C_H^o)}{Dr_0\delta} \qquad (1)$$

where F is the fractional approach to equilibrium, t is the time (sec), D_{HCl} is the combined diffusion coefficient of hydrochloric acid through the liquid film (cm^2/sec), C_H^S is the hydrogen ion concentration in the bulk of the solution (meq/ml), C_H^o is the hydrogen ion concentration at the inside of the film (meq/ml), C is the capacity of the resin in the dry free base form (meq/ml), r_0 is the radius of the ion-exchange beads (cm), and δ is the thickness of the film (cm).

It is desirable to obtain the rate expression for the diffusion of ions into the exchanger in a similar form. This has been done by Helfferich for the neutralization of carboxylic acid resins [2], but at constant reagent concentration. However, the equation is difficult to apply because of the indirect and inexact analytical method which must be used under these experimental conditions. A more practical rate expression for the neutralization of weakly basic resins under conditions of changing acid concentration (but above about 0.01 M) has been obtained. It has been assumed that the concentration of chloride ions in the resin is much greater than the concentration of hydrogen ions, and that the inside boundary of the shell is quasi-stationary. The full derivation is given elsewhere [4]; the rate expression which results is

$$\frac{dF}{dt} = \frac{3D_H C_H^o}{Cr_0^2[(1-F)^{-1/3} - 1 + k]} \qquad (2)$$

where D_H is the diffusivity of protons in the resin (cm^2/sec), C_H^o is the hydrogen ion concentration at the particle surface, and

$$k = \frac{\partial C_H^o/\partial F}{2C}$$

which can be determined directly from the liquid-to-resin ratio.

For the situation where the solution concentration remains constant, k = 0, the resultant version of Eq. (2) can be deduced from Helfferich's analysis [2].

Equation (2) predicts that the rate will be inversely dependent on the square of the bead radius and directly dependent on the hydrogen ion concentration. As it has been assumed that equilibrium at the solid-liquid interface is independent of chloride ion concentration, it is expected that the rate will not be dependent on the concentration of added salt.

The two diffusional resistances provided by the liquid film and the resin phase may be considered in series if the hydrogen ion concentration is continuous at the solid-liquid interface. Equations (1) and (2) can be combined to yield an expression which describes diffusion through the liquid film and the exchanger bead:

$$\frac{dF}{dt} = \frac{3D_H C_H^S}{Cr_0 \left\{ r_0 \left[(1 - F)^{-1/3} - 1 + k\right] + \frac{D_H}{D_{HCl}} \right\}} \tag{3}$$

Here k must be found by trial and error as C_H^0 is not equal to C_H^S. In general k is small and can often be neglected.

At concentrations below 0.001-0.01 M the flux equations for the individual diffusing ions cannot be manipulated to obtain equations in terms of one ion only, and solutions to the equations must be sought with a computer. Helfferich [2] has reduced the equations to a form suitable for machine computation, using the dissociation constant to obtain the concentration of hydrogen ions at the exchange site.

RESULTS AND DISCUSSION

Measurements of the rate of hydrochloric acid uptake by closely sieved fractions of Amberlite IRA-93 have been made by direct analysis of the changing acid concentration [4, 8]. The results obtained are shown in Fig. 3 in the form of fractional neutralization of the resin time. Also shown are the effects of changing the particle size and adding salt to the solution. By using an integrated form of Eq. (2), the rate expression for particle diffusion control, the graphs shown in Fig. 4 are obtained [8].

The data quantitatively confirm the bead radius and added salt effects demanded by the Helfferich model. The deviation of the plots from linearity in the early stages of the reaction is attributed to the diffusional resistance of the liquid film becoming of significance for that stage of the reaction. When the shell of converted resin is thin compared with the thickness of the external liquid film, the resistance of the film to the

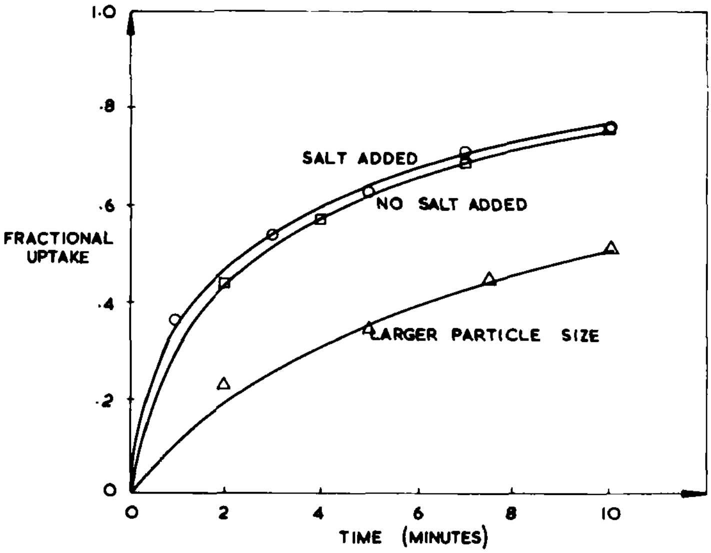

Fig. 3. The uptake of hydrochloric acid by Amberlite IRA-93 using equimolar quantities of resin and reagent. (□) r_0 = 0.0198 cm, no salt present. (○) r_0 = 0.0198 cm, in 0.17 M saline. (Δ) r_0 = 0.0335 cm, in 0.019 M saline.

diffusion of ions can become comparable with the resistance to diffusion provided by the outer shell of the resin. However, as adsorption proceeds the thin liquid film becomes a less important barrier to the diffusion process.

The two diffusional resistances have been considered in series to give the rate expression (3). The calculated product of diffusivity times solution concentration obtained from Eq. (3) has been plotted against the actual solution concentration in Fig. 5. The graph obtained approximates to a straight line for solution hydrogen ion concentrations greater than 0.01 M. This test of the concentration dependence of the rate is much more sensitive than the more common approach of comparing the shapes of predicted and experimental rate curves.

The approach described here has therefore successfully described the adsorption of acid by a weakly basic ion exchange resin for reagent concentrations above 0.01 M. Further work is necessary to completely account for the adsorption phenomena at lower reagent concentrations, although the existing experimental data are qualitatively in agreement with the predictions

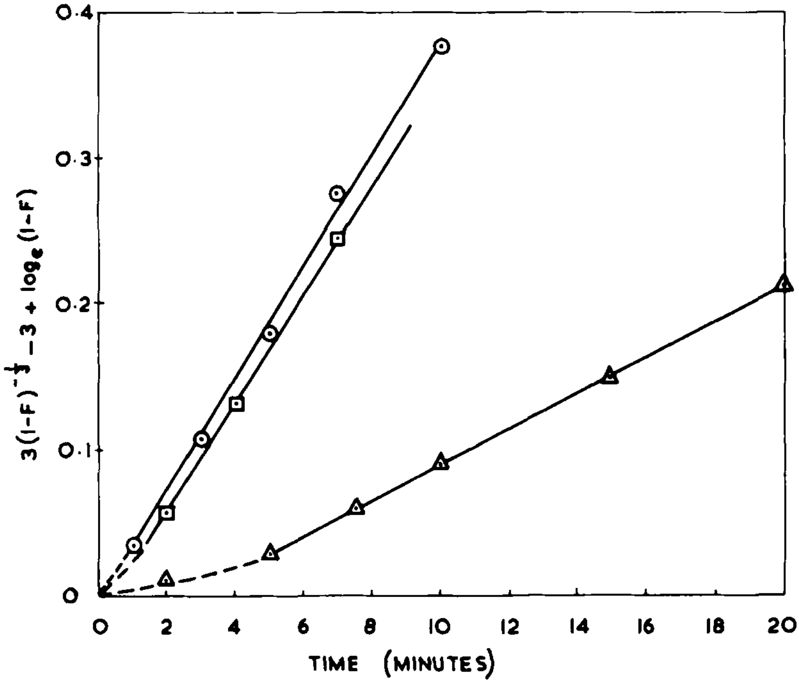

Fig. 4. Test of the validity of the diffusion model when the concentration of hydrogen ions is above 0.01 M. (▫) r_0 = 0.0198 cm, no salt present, $D_H = 7.2 \times 10^{-6}$ cm²/sec. (⊙) r_0 = 0.0198 cm, in 0.17 M saline, $D_H = 6.9 \times 10^{-6}$ cm²/sec. (△) r_0 = 0.0335 cm, in 0.019 M saline, $D_H = 6.7 \times 10^{-6}$ cm²/sec.

of the model [4]. The rate of adsorption of alkali by carboxylic acid resins fits similar rate expressions at the higher concentration level [8], and the reaction is assumed to be analogous to that discussed here. The next stage will then be an attempt to predict the kinetics of salt adsorption by mixed beds of weak electrolyte ion-exchange resins.

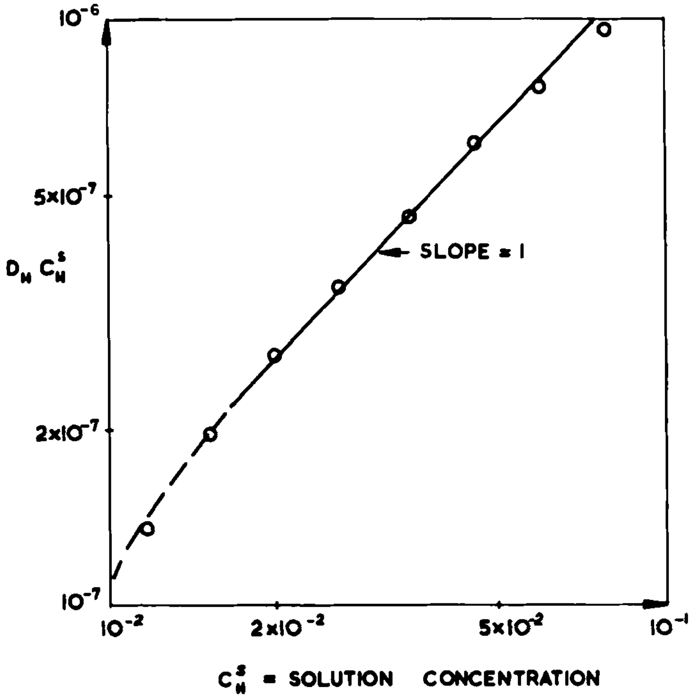

Fig. 5. Test of the dependence of the adsorption rate of hydrochloric acid by Amberlite IRA-93 on the concentration of hydrogen ions.

$$D_H C_H^S = \frac{dF}{dt}\,\frac{Cr_0^2}{3}\left[(1 - F)^{-1/3} - 1 + k + \frac{D_H \delta}{D_{HCl} r_0}\right]$$

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