

Kinetics of Sorption of Aliphatic Acids by Oleophilic Anion Exchange Resins in Toluene

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Synopsis

The rate of sorption of toluene by dry oleophilic anion exchange resins in the hydroxide state was measured both by direct weight measurements and also by the visual observation of the rate of movement of a refractive index gradient between unreacted and reacted zones. The rate of sorption of carboxylic acids from solution in toluene was also measured by beads swollen in toluene, both by direct chemical analysis of the solution and by the visual method. Diffusion coefficients of acids in the resins were calculated using three different theories for diffusion in gels coupled with chemical reactions, and reasonable agreement between theory and experiment was found.

INTRODUCTION

Conventional ion exchange resins are of little utility in nonaqueous solvents, particularly in those of low dielectric constant where the small degree of swelling of these resins makes diffusional processes too slow for practicality.¹ The oleophilic resins have similar sulfonic or quaternary ammonium exchange groups, but they also contain substituent groups which have the same cohesive energy density as these solvents, causing the resins to swell normally.²⁻⁶ Anion exchange resins containing the *N,N*-dimethyldodecylbenzylammonium group and cross linked with 1% DVB were prepared by Shida and Gregor⁵ and characterized by their swelling in mixed polar and nonpolar solvents.

This study was undertaken to characterize more fully the reactions of these oleophilic quaternary ammonium resins by the rate of uptake of aliphatic acids, in particular, the sorption and kinetics of acetic acid uptake by the hydroxide form of the resin. Additional kinetic experiments were performed with myristic and stearic acids. Equilibrium sorption and swelling measurements were made with these acids and also with capric acid.

THEORETICAL

Many authors have studied ion exchange processes in the presence of a chemical reaction. The monograph of Helfferich⁷ is an excellent introduction to the subject; Helfferich⁸ also treated systems quite similar to those under

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consideration here. Similarly, Dana and Wheelock⁹ studied coupled exchange-reaction processes and employed a shell-core mechanism in their interpretation of the data.

The rate of uptake of acetic acid provides a good illustration of how one can treat data for a system which demonstrates a strong degree of sorption and extract a fairly accurate solute diffusivity. The Weisz⁷ model provides a generalized solution to Fick's second law while accounting for strong or weak sorption by the introduction of the Langmuir isotherm to describe equilibria between mobile and immobilized solute molecules.

The Langmuir isotherm for the system can be given by

$$C_a = CC_{at}/[(1/K) + C]$$

where C is the concentration of mobile, nonsorbed species, the subscript a refers to adsorbed molecules, C_{at} is the concentration at saturation, and K is the equilibrium constant. If one defines⁷ $1/K = C_i$, a dimensionless form of the isotherm is attained:

$$C_a/C_{at} = (C/C_i)/[1 + (C/C_i)]$$

where $C_i = C$ when $C_a = 0.5C_{at}$ or when half-saturation of sites occurs.

For the diffusion of species within the bead, Fick's second law is written:⁷

$$\frac{\partial(C + C_a)}{\partial t} = \frac{\partial C'}{\partial t} = \nabla D \nabla C \quad (1)$$

where D is the diffusion coefficient in the solid phase.

This latter equation was solved by Weisz; his tabulated values of generalized half-sorption parameters for spherical geometry and for weak and strong sorption can be used to determine values for D from kinetic and sorption data.

For our system, the concentration in the resin phase of diffusing species $C = [\text{HA}]$ is low ($<0.03M$) when compared to those of the fixed reactive sites $[\text{R}_4\text{N}^+\cdot\text{OH}^-]$, which are $0.5\text{--}1M$. Since the reaction to produce $\text{R}_4\text{N}^+\cdot\text{A}^-$ goes nearly to completion at all times except for a very short initial period we find that in regions where C is appreciable, C_a (equal to $[\text{R}_4\text{N}^+\cdot\text{OH}^-]$) is very much larger than C , making use of the notation of Weisz.⁷ In fact, $C_a \cong C_{at}$ for all saturated regions, because of the nature of the reaction since $K \gg 1$. Under these circumstances we can set $d(C + C_a) \cong dC$ because C_a is nearly constant.

We can now make use of the treatment of Dusek¹⁰ who pointed out that for a system where D is a function of C only, one can employ the Boltzmann (1894) transform $\zeta = rt^{-1/2}$ and make Fick's second law into an ordinary differential equation:

$$\frac{d^2C}{d\zeta^2} + \frac{dC}{d\zeta} \left(\frac{2}{\zeta} + \frac{\zeta}{2D} \right) + \frac{dD}{dC} \frac{1}{D} \left(\frac{dC}{d\zeta} \right)^2 = 0. \quad (2)$$

In the Dusek model, the locus of constant concentration is the locus of constant ζ . This "moving boundary" approach requires that the boundary between unreacted and reacted zones within the bead moves at a rate such that the radius of the unreacted core increases at a rate proportional to $t^{1/2}$, the radius being measured from the bead periphery.

In the unreacted core model of Kunii and Levenspiel,^{11,12} the reaction occurs first at the outer skin of the solid particle and then moves into the solid while

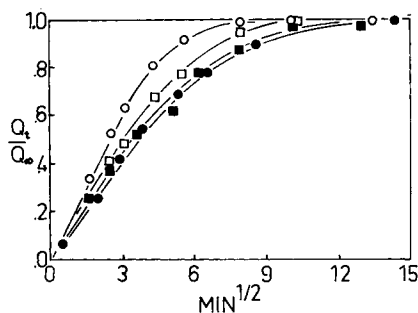


Fig. 1. Sorption of acetic acid from 0.010M (solid symbols) and 0.023M (open symbols) solutions (initial concentrations) in toluene by hydroxide form resin beads of diameter 0.39–0.47 mm (O) and 0.47–0.56 mm (□).

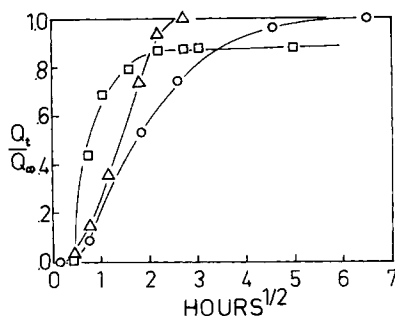


Fig. 2. Sorption of myristic acid from 0.010M (Δ) and 0.030M (\square) solutions in toluene by 0.47–0.56 mm diameter hydroxide form resin beads; sorption of stearic acid from 0.0026M (O) solution in toluene by 0.39–0.59 mm diameter beads of same resin.

leaving behind a completely converted zone. Where diffusion through the converted zone controls, the radius of the unreacted core takes the form

$$t/\tau = 1 - 3(r_c/r_0)^2 + 2(r_c/r_0)^3 \quad (3)$$

where r_0 is the initial particle radius, r_c is the radius of unreacted core measured from the center, τ is the time it takes for the particle to be completely converted, and t is elapsed time. For this model, τ is given by

$$\tau = \rho_B r_0^2 / 6bDC^0 \quad (4)$$

where ρ_B is the molar density of reaction sites in the bead in moles/ml, b is the number of moles of diffusing species which are fixed by one mole of site, r_0 is the particle radius in cm, and C^0 is the concentration of reactant in the external solution in moles/ml.

A means for evaluating D of mobile species in different solvents has been developed by Wilke¹³ using the Stokes–Einstein equation. This expression takes the approximate analytical form (for dilute solutions)

$$D = 7.4 \times 10^{-8} (\Psi_1 M_1)^{1/2} T / \eta \bar{V}_2^{0.6} \quad (5)$$

of a solute (2) in a solvent (1), where D is the diffusion coefficient of a solute (2) in cm^2/sec , \bar{V}_2 is the molar volume in $\text{cm}^3/\text{g-mole}$, η is the solution viscosity in

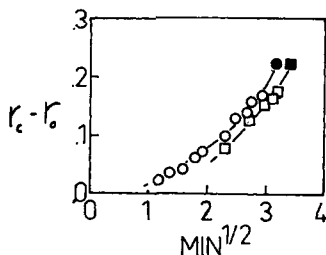


Fig. 3. Boundary radius R_t in mm for sorption of toluene by partially dry hydroxide beads 0.224 mm (O) and 0.226 mm (□) in radius. The solid points of maximum R_t values represent the end of the process.

centipoises, M_1 is the molecular weight of the solvent, and Ψ_1 is an "association parameter" for the solvent which takes the value 2.6 for water, 1.9 for methanol, 1.5 for ethanol, and 1.0 for benzene, ether, heptane, and other unassociated solvents.

EXPERIMENTAL

The oleophilic anion exchange resin used in this study was prepared by aminating crosslinked polystyrene (1% DVB) beads with *N,N*-dimethyldodecylamine after about 50% chloromethylation. The resin was converted to the hydroxide form with aqueous sodium hydroxide and washed free of excess base with water and then finally with methanol made absolute by treatment with magnesium turnings, followed by distillation. The hydroxide-form resin had a capacity of 2.1 meq/g. It was washed with methanol and then converted to the toluene state by repeated washings with toluene which had been distilled after treatment with Linde type 4A molecular sieves.

The following chemicals were also used: myristic acid, Eastman Org. Chem.; stearic acid, Fisher Reagent, mp 68–69.5°C; glacial acetic acid, Baker and Adamson Reagent, 99.8% minimum; sodium methoxide, Fisher, purified. These were dried and used without further purification. Ground glass-stoppered vessels were used throughout for all resin containers.

Rate of sorption experiments were carried out by conventional procedures. To the hydroxide form resin in toluene was added a known amount of acid in toluene solution and the flask shaken vigorously at room temperature (24–26°C). Solution samples taken periodically were diluted 1:5 with methanol and titrated with approximately 0.081*N* sodium methoxide in methanol. A 0.04% bromthymol blue solution was used as indicator. The sodium methoxide solution was standardized against purified benzoic acid in toluene or with recrystallized myristic acid in toluene.

The rates of both solvent and acid uptake could also be followed microscopically. Single resin beads (0.3–0.6 mm in diameter) were viewed using a Spencer microscope with a 10× eyepiece and a 1.8× objective lens. A calibrated millimeter scale fitted into the eyepiece and allowed for direct bead size measurements. Beads were observed first in the dry state and then in 1 ml solution. No noticeable size distortion resulted from viewing these particles in air or in solution. Unbroken spherical particles were used for this study, selected from the

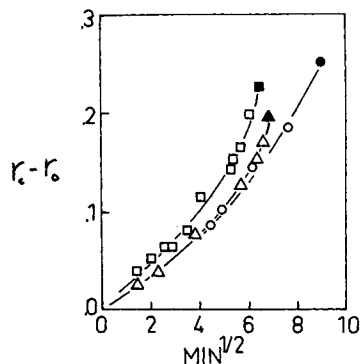


Fig. 4. Boundary radius R_s for sorption of acetic acid (0.0139M in toluene) by hydroxide form of resin previously swelled to equilibrium in toluene, for beads of initial (in toluene) diameters of 0.502 mm (○), 0.448 mm (□), and 0.390 mm (△).

sieved hydroxide form resin partially in the toluene state. Sphericity was determined by visual examination and selection of beads after rolling them down an incline. Particles in the $-34 + 40$ and $-40 + 45$ U.S. mesh sizes were used. To keep the system dry, the entire microscope assembly (except for the eyepiece) was placed in a plastic glove bag purged with nitrogen.

Two kinds of experiments were performed. In one, a partially dry (23% solvent) bead was placed into the container, 1 ml pure toluene was added, and the diameter was measured as a function of time. The beads were transparent in the toluene solution but opaque when dry, so a well-defined boundary inside the bead could be observed.

In other experiments, the resin particle was preswollen to swelling equilibrium in toluene and the excess toluene was removed with suction followed by rapid blotting with filter paper, which left but a minute amount of toluene around the bead, which was negligible compared to the 1 ml of approximately 0.014N acid solution added to start the experiment. The acid added was in large excess compared to the capacity of the resin bead. Acetic acid, 0.0139N, and 0.015M myristic acid in toluene were used. Here, as before, the course of the sorption process was followed by measuring the dimensional changes of the moving boundary inside the bead. Since the bead also swelled, the outer diameter was also measured as a function of time. The sorption of acetic acid by a preswollen bead was evidenced by a swelling of the particle as well as by the visible moving boundary. However, the sorption of myristic acid at that concentration by a preswollen particle brought about spalling of the particle at its outer edge after a short time. This was due, apparently, to strains resulting from the sorption of the larger chain species with its concomitant strong swelling.

RESULTS AND DISCUSSION

The results of the batch kinetic experiments given as Q_t/Q_∞ versus $t^{1/2}$ for the sorption of acetic acid from toluene is given in Figure 1, where Q is the moles of acid sorbed at time t and at infinite time. There was no obvious breakage of resin particles at the end of these experiments; this was also observed to be the case with microscopic observations of the same process. In these experiments, about

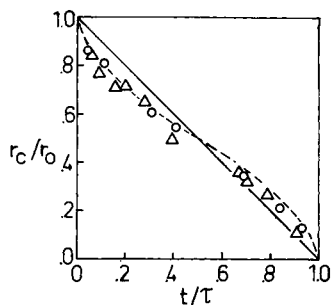


Fig. 5. Sorption of acetic acid by hydroxide form beads with r_c (radius of unreacted core at time t), r_0 (radius at zero time), τ (elapsed time when r_c is zero). All values of r measured from center of bead. For 0.391-mm-diameter beads (O), $\tau = 47.1$ min; for 0.447-mm-beads (Δ), $\tau = 41.0$ min. Dashed line is plot of eq. (3).

0.2 g of resin was treated with from 75 to 150 ml of the 0.023*M* or 0.010*M* solution, so that the resin capacity was about 60% of the acid originally in the solution. Figure 1 shows that resin size is a more important factor in these processes occurring in the more concentrated 0.023*M* solutions and of little significance when concentrations are at the 0.01*M* level.

The sorption of a myristic acid from 0.010*M* and 0.030*M* solutions (150 and 100 ml, respectively) in toluene by about 0.08 g of the hydroxide form resin is shown in Figure 2. Here, about 20% of the acid originally in solution was sorbed. Figure 2 also shows the reaction of 0.14 g of the resin with 120 ml 0.0026*M* stearic acid, where 74% of the acid originally present in solution was sorbed. There was much spalling of the resins during these experiments, which resulted in abnormally shaped rate curves; no interpretation of this datum is attempted.

When toluene was added to the partially dry hydroxide resin, a visible boundary moved through the bead, one where the phase boundary between the swollen polymer and "nearly glass phase polymer" was defined by the boundary radius r_c . After the resin was completely swollen in toluene, either acetic or myristic acid in toluene was added and a new visible phase boundary designated by r_c could be observed.

Figure 3 shows $r_0 - r_c$ versus $t^{1/2}$, which would be linear if the conditions of eq. (2) and the attainment of a boundary of constant composition were fulfilled, because if $r_c = r_0$ at $t = 0$, then $r = r_0 - kt^{1/2}$. The data give curves that are not linear and have a short time lag in that they do not extrapolate linearly to the origin, indicating that these assumptions are but approximate here. Several other partially dry beads of about the same particle size were placed in toluene. The visible boundary reached their centers in about 10 min, as did the boundary in the experiments of Figure 3. However, swelling equilibrium as measured by weight took one to three days, probably due to the slow relaxation of polymer chains in highly crosslinked beads. Thus, there was a relatively rapid diffusive process involving only low molecular weight species (solvent and solute), which in turn gave rise to a change in swelling pressures and a slow relaxation of highly crosslinked and entangled polymer chains.

The data for acetic acid diffusing into and reacting with hydroxide beads are shown in Figure 4. If we assume that the rate of the acid-base reaction was more rapid than the diffusion rate, then a boundary of nearly constant concentration

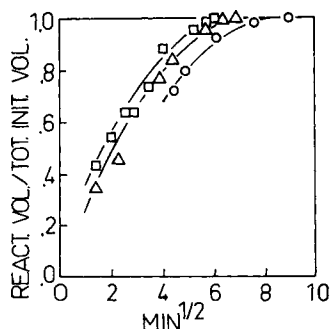


Fig. 6. Sorption of 0.0139M acetic acid in toluene by hydroxide form beads of diameter 0.447 mm (\square), 0.391 mm (Δ), and 0.502 mm (\circ).

moved through the bead. In such a situation, eq. (2) should be valid. From Figure 4 we see a nonlinear relationship, but the curves extrapolate linearly to the origin.

When myristic acid diffused into the beads for times up to 7 min, a linear relationship was indeed observed, but since outer portions of the bead began to break off at that point, an analysis of the data was considered of but limited value.

The data of Figure 4 can be fitted to the Kunii-Levenspiel model. Figure 5 shows this plot and the corresponding value of τ . Similarly, the ratio Q_t/Q_∞ can be calculated from the volume of the reacted zone to that of the entire particle; plots similar to those of Figure 1 are obtained and are shown in Figure 6.

One can now calculate diffusion coefficients for acetic acid based upon the various models. First, the straightforward application of Fick's law without regard to the sorption process gives $D = (0.3-3) \times 10^{-8}$ cm²/sec. When the Weisz treatment is employed with the assumption of a linear isotherm ($C_a = kC + b$), $D = 6 \times 10^{-7}$. However, when the Langmuir expression is employed, the expressions of Weisz lead to $D = 1.81 \times 10^{-5}$. This latter value should be compared with the calculated value of Wilke, $D = 2.6 \times 10^{-5}$, and the value he measured for the diffusion of acetic acid in toluene, $D = 2.26 \times 10^{-5}$. One also can apply the Kunii-Levenspiel treatment to microscopic observations and calculate $D = 1.38 \times 10^{-5}$. The agreement between the two methods is good, considering that that data of sorption from solution were used in the Weisz treatment and microscopic observations of reaction zone boundaries were used in the Kunii-Levenspiel treatment. Their mathematical bases are identical, but the experimental parameters are quite different.

According, there is a reasonable agreement between the two calculated values and the measured one by Wilke. Since effective diffusion coefficients in open gels of high solvent volume fraction (where tortuosity is not a factor) are approximately equal to the solvent volume fraction (0.82 for our systems) times the value of the diffusion coefficient in pure solvent, one should compare theoretical values with 1.89×10^{-5} cm²/sec calculated from the experimental value of D in free solution. On this basis, the Kunii-Levenspiel treatment leads to agreement within about 25%, and the Weisz treatment differs only by about 5%. The value of D for stearic acid as calculated by Wilke (corrected for volume fraction) is 5.7×10^{-6} cm²/sec, while Weisz treatment applied to the data of Figure 2 leads to 8.2×10^{-6} cm²/sec, quite reasonable agreement.

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