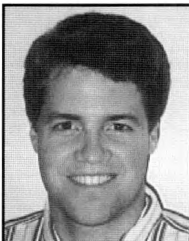


ION EXCHANGE CHROMATOGRAPHY LABORATORY

Experimentation and Numerical Modeling

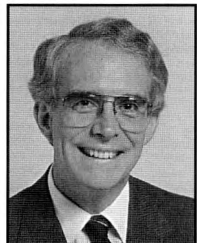
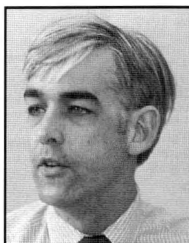
MARK R. ANKLAM, ROBERT K. PRUD'HOMME, BRUCE A. FINLAYSON*
Princeton University • Princeton, NJ 08544

After four years of contact with highly structured courses and laboratories, undergraduate students may be left with the impression that mathematical modeling and experimentation are mutually exclusive. At Princeton we have found that a series of short experiments run by the students outside the normal class hours is a good way to teach and reinforce concepts. An example that we have used effectively in an elective upper-division bioseparations course is fixed-bed ion exchange. We have developed an experiment coupled with a numerical simulation using a teaching program developed at the University of Washington.



Mark R. Anklaam is a graduating PhD student in chemical engineering at Princeton University. He received his BS from Stanford University in 1991. His research focuses on the flow and stability of emulsions.

Robert K. Prud'homme is a professor in the Department of ChE at Princeton University. He received his BS at Stanford University, his PhD at the University of Wisconsin-Madison, and spent a year in a special studies graduate program at Harvard University. His research interests are transport phenomena involving polymer, surfactants, and complex fluids.



Bruce A. Finlayson is the Rehnberg Professor of Chemical Engineering at the University of Washington. He received his BA and MS degrees from Rice University and his PhD from the University of Minnesota. He has taught at the University of Washington for 29 years and is currently chairman of the Department. His research focuses on numerical methods applied to chemical engineering problems.

* Address: University of Washington • Seattle, WA 98195

Fixed-bed ion-exchange is an ideal process for this mixed-mode approach. It is easy to motivate the problem using examples in biotechnology, water purification, soil and groundwater pollution, or chromatography.^[1] The mathematical analysis of the process can be presented at a variety of levels depending on the class, from straightforward presentations such as Cussler's^[2] or Sherwood, Pigford, and Wilkes^[3] classic (and excellent) presentation to more mathematically rich presentations such as Rhee, Aris, and Amundson^[4] or Helfferich and Klein.^[5]

These presentations alone, even the straightforward ones, are most often opaque to the students. Giving an undergraduate the solution for the frontal motion from Rhee, *et al.*,^[4]

$$c(\xi, \eta) = e^{-\beta\xi - (\eta - \xi)} I_0 \left[2\sqrt{\beta\xi(\eta - \xi)} \right] + e^{-\beta\xi - (\eta - \xi)} e^{-\eta - \xi} \int_0^{\eta - \xi} e^{-\eta''} I_0 \left[2\sqrt{\beta\xi\eta''} \right] d\eta'' \quad (1)$$

does not ensure illumination! On the other hand, seeing a blue front of copper sulfate move through the ion exchange column and register as a breakthrough curve makes the concepts concrete for the student.

The problem with doing a great number of experiments to understand phenomena is that great numbers of experiments take great amounts of time. Furthermore, with interacting and nonlinear phenomena it is often difficult for the students to extract general principles from specific experiments. These disadvantages can be avoided by numerical simulation. Once the students are comfortable seeing the phenomena in the experiment, they become comfortable duplicating the phenomena in the simulation. Running the simulation for a range of parameter values then becomes a much more effective way for them to learn and generalize.

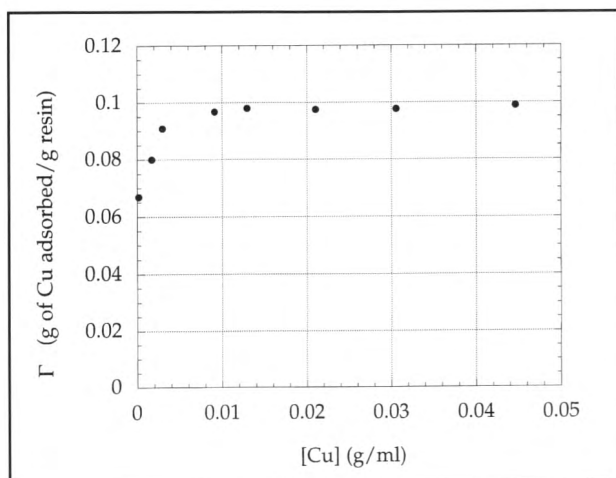


Figure 1. Adsorption isotherm for Cu^{++} adsorption on 200-400 mesh Dowex beads. Used 1 g of particles for 15 to 17 g of solution for each data point.

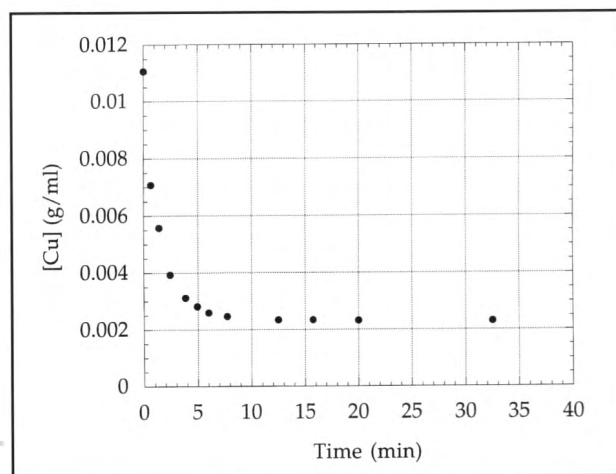


Figure 2. Kinetics of adsorption for Cu^{++} ions on 20-50 mesh Dowex beads. $[\text{Cu}^{++}]$ is 0.0110 g/ml, the initial mass of solution is 156.43 g, and the mass of particles is 18.58 g. Absorption measured at 660 nm.

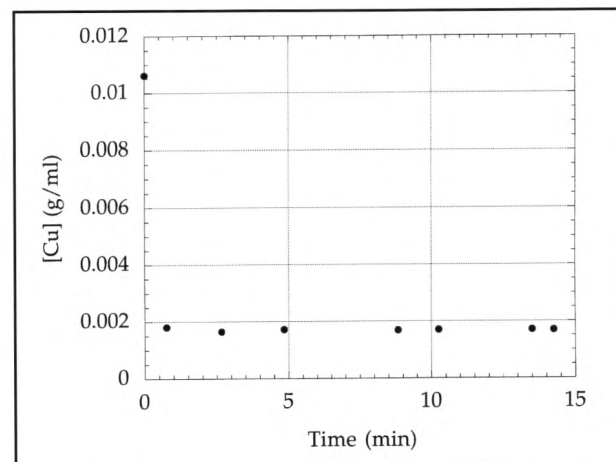


Figure 3. Kinetics of adsorption of Cu^{++} ions on 200-400 mesh Dowex beads. $[\text{Cu}^{++}]$ is 0.0104 g/ml, the initial mass of solution is 167.93 g, and the mass of particles is 18.17 g.

In this article we will first summarize the simple ion-exchange experiment that we have implemented. Measurements from a batch-adsorption experiment are used to predict the results from the fixed-bed experiment. Next, we present an overview of the computer simulation that Finlayson has developed as a companion to his text^[6] on numerical analysis. The program, which runs on Macintosh computers, allows the students to investigate several numerical schemes for solving the governing equations and lets them explore the stability of the numerical solutions. For this laboratory, where ion exchange is the focus, we prescribe the numerical scheme and suggest step sizes. The parameter values for the simulation come from the batch-experiment results, so the students have a sense of actually modeling a real process. And finally, the results of the experiment can be compared with the simulations.

EXPERIMENTAL

The following is a summary of the experimental method. A detailed laboratory handout and equipment list is available upon request from

prudhomm@princeton.edu

and the computer program, a companion to the Finlayson text, is available on the internet at

<http://www.halcyon.com/ravenna/>.

Although any one of a number of solutes could be used, cupric sulfate (Sigma) was chosen because it is relatively safe, it is inexpensive, and its blue color allows visualization of the moving front as it passes through the ion exchange column. Concentrations are measured with a spectrophotometer at 660 nm. Two Dowex 50W-X8 cationic exchange resins are used: a 20-50 mesh (290-840 μm) and a 200-400 mesh (37-74 μm) available from Bio-Rad or J.T. Baker. The two sizes are used to compare the effects of particle size on adsorption kinetics and dispersion in the fixed bed. The resins are originally in the acid (*e.g.*, H^+) form, and after ion exchange they can be regenerated by washing with excess 1.0 to 2.0 N HCl.

The experimental portion consists of two sets of experiments: batch- and fixed-bed ion exchange. The batch experiments consist of mixing a known amount of cupric sulfate solution with a known amount of resin in a small vial and determining the final equilibrium ion concentration in solution. By a mass balance the amount of copper adsorbed is calculated. The adsorption isotherm, shown in Figure 1, is generated from a series of these experiments with various copper ion concentrations. Initially, one or two batch experiments are performed on a larger scale to measure the kinetics of adsorption as shown in Figures 2 and 3. The larger

particles (20-50 mesh) take on the order of fifteen minutes to reach equilibrium, whereas smaller particles (200-400 mesh) reach equilibrium in less than one minute. This allows the students to estimate how long the batch isotherm experiments take to reach equilibrium and establishes a reference point for a discussion on how fast or slow the solute flow rate should be in the fixed-bed experiment to assure the front is in "equilibrium."

The column experiments involve measuring breakthrough curves for a fixed-bed ion exchange column. The system consists of a peristaltic pump (Watson-Marlow), a glass chromatography column (Omnifit Columns from Alltech), and a flow-through, low-volume cuvet (Fisher) for the spectrophotometer. Of course, a UV/VIS chromatography detector could be used to monitor concentration if one is available. The glass column allows observation of the front.

One important feature of the column is that it needs to have adjustable end frits so that the volume of ion exchange resin in the bed can be varied for studies with different ionic strengths of cupric sulfate. Otherwise, experiments at low ionic strength take forever because the volume of dilute cupric sulfate solution that it takes to saturate the bed is very large, and the time is long because flow rates must be kept low to minimize mass transfer resistance.

The analog output from the spectrophotometer is read by a data acquisition board on a Macintosh computer (Strawberry Tree ACM2 Analog Connection with T21 terminal panel) driver by WorkBenchMac software (Strawberry Tree). We find the WorkBenchMac graphical data acquisition interface

... we have found that a series of short experiments run by the students outside the normal class hours is a good way to teach and reinforce concepts. An example that we have used effectively in an elective upper-division bioseparations course is a fixed-bed ion exchange experiment coupled with a numerical simulation using a teaching program developed at the University of Washington.

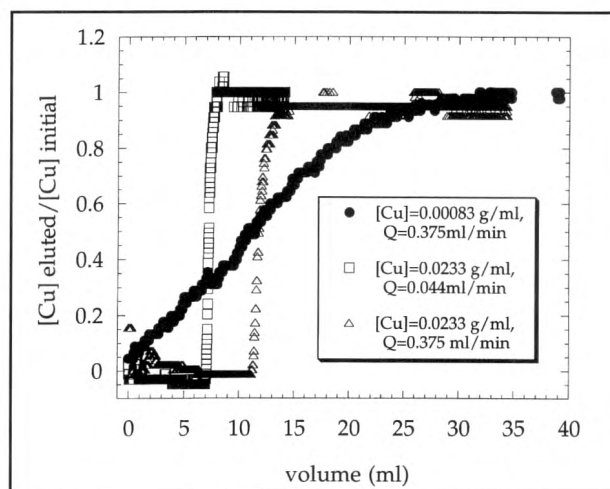


Figure 4. Eluted relative concentration versus volume eluted. Eluted volume for the sample of lower concentration is adjusted to display comparisons of plot profiles and is not the actual volume eluted for the front to come through the packed bed. Bed depth was 1.4 cm for the low-concentration sample, 3.1 cm for the low-flow-rate sample, and 5.2 cm for the higher flow-rate sample; the bed diameter was 0.9 cm. When the eluted volume was adjusted for bed volume (volume eluted/bed volume) the curves from the higher concentration samples superimposed (not shown). The 200-400 mesh resin was used.

easier to use than a strip chart recorder and the students have the data already in the computer for graphing and analysis.

Figure 4 shows relative Cu^{++} concentration as a function of eluted volume for different flow rates and initial concentrations. In the figure, the volumes have been arbitrarily shifted along the x-axis for clarity. The shape of the front is relatively insensitive to flow rate for the small 200-400 mesh particles since mass transfer is rapid. At higher flow rates, broadening due to dispersion and non-equilibrium mass transfer would be observed.

As concentration is lowered from the plateau region to the linear adsorption region, a broadening of the front can be seen that the students are asked to explain after they have run the numerical simulation. The students also need to think about the relationship between the front profile from the computer simulations (concentration as a function of position at a particular time) and the elution measurements (concentration as a function of eluted volume at the column exit) and to understand how they are related.

COMPUTER SIMULATION

The computer simulation aspect of the laboratory uses parameters from the adsorption isotherm and batch kinetics experiments to model the performance of the fixed-bed adsorption experiment. The simulation and the actual results can be compared and the students are led to understand issues involved in equilibrium and non-equilibrium exchange and the effects of linear and nonlinear adsorption isotherms. The simulation package has the advantages of being menu driven and of having integrated graphics so that

the results can be easily interpreted by the students. There are two simulation programs: ADSORPTION and LANGMUIR. Both solve the convective diffusion equations for solute transport in a fixed bed, but with different limiting assumptions.

Linear Adsorption Isotherm with Dispersion

ADSORPTION solves for the solute concentrations in the fluid phase and the stationary phase with the inclusion of dispersion or diffusion terms, but for the case of a linear adsorption isotherm. The differential equations for the concentration in the fluid phase, c , and in the solid phase, n , are

$$\phi \frac{\partial c}{\partial t} + \phi v \frac{\partial c}{\partial z} + (1 - \phi) \frac{\partial n}{\partial t} = D_1 \frac{\partial^2 c}{\partial z^2} \quad (\text{fluid}) \quad (2)$$

$$\frac{\partial n}{\partial t} - k(\gamma c - n) = D_2 \frac{\partial^2 n}{\partial z^2} \quad (\text{solid}) \quad (3)$$

where

v fluid velocity

ϕ porosity

k rate constant for adsorption

γ linear adsorption coefficient (*e.g.*, $n = \gamma c$)

D_1, D_2 effective diffusion or dispersion coefficients in the liquid or solid phase, respectively.

The initial conditions are

$$c(z, 0) = f(z) \quad \text{and} \quad n(z, 0) = h(z) \quad (2)$$

and the boundary condition is

$$c(0, t) = g(t) \quad (5)$$

For the purposes of this adsorption experiment, the student inputs a short concentration profile in the bed (first line in Figure 5) equivalent to

$$\begin{aligned} c(z = 0) &= 1 & t &\geq 0 \\ c(z > 0) &= 0 & t &= 0 \\ n(z) &= 0 & t &= 0 \end{aligned} \quad (6)$$

and specifies the inlet boundary condition as a constant solute concentration. The boundary condition at $z=0$ is rigorous if Pe_1 is infinite (no dispersion), and it is a good approximation for the case with dispersion when the inlet condition is a step change and does not change thereafter (so that the diffusive flux at the inlet is zero after a short time). The equations are non-dimensionalized by taking

$$\xi = \frac{zk}{v}, \quad \eta = kt, \quad Pe_1 = \frac{Vz}{D_1}, \quad Pe_2 = \frac{V^2}{D_2 k^2} \quad (7)$$

to obtain

$$\frac{\partial c}{\partial \eta} + \frac{\partial c}{\partial \xi} + \frac{1 - \phi}{\phi} (\gamma c - n) = \frac{1}{Pe_1} \frac{\partial^2 c}{\partial \xi^2} \quad (\text{fluid}) \quad (8)$$

$$\frac{\partial n}{\partial \eta} - (\gamma c - n) = \frac{1}{Pe_2} \frac{\partial^2 n}{\partial \xi^2} \quad (\text{solid}) \quad (9)$$

It should be noted that k and v are incorporated into the dimensionless time and distance, so students need to put some thought into how changes in these two parameters will affect the flow front. It should also be noted that the dispersion in the solid phase is generally small compared to dispersion in the liquid phase. Therefore, for all simulations we drop the terms in Eq. (9) involving Pe_2 , and the mass-transfer resistance in the solid phase is represented by a lumped mass-transfer coefficient, k . The program menu lets the student select among several solution techniques (finite difference with upstream weighting, Galerkin method, Random Choice method, Taylor-Galerkin method with Taylor-finite differencing, MacCormack method with flux-correction, or the Euler-Lagrange method). The text by Finlayson presents parallel calculations using all of these techniques to demonstrate numerical stability and numerical dispersion effects. For this laboratory, we specify that the students use the MacCormack method with flux-correction. Figures 5, 6, and 7 (next page) show the effects of Peclet number on a front moving through a packed bed.

We should note here that when the problem is non-linear and shocks form, the MacCormack method must be formulated differently than is done under APPLICATIONS. Poulain and Finlayson^[7] show that the front speed is calculated correctly by the random choice method in APPLICATIONS, however. Even that method requires mesh refinement keeping $\Delta t / \Delta x$ fixed to validate the results.

Analytical solutions and approximations are possible for the above system of equations. When diffusion is neglected, the solution for c may be found using the J or Bessel function.^[3] With the inclusion of diffusion, approximations using the J function also exist.^[8] Instructors should comment on the existence of analytical solutions and may wish to include a discussion of how these solutions and approximations compare to the numerical results.

Langmuir Adsorption Isotherm with Solid-Fluid Equilibration

The program LANGMUIR solves the governing equations (Eqs. 2 and 3) for the case in which the rate of adsorption is very fast (*e.g.*, k is very large) and the solid and liquid phases are in equilibrium. Rather than a linear adsorption isotherm, a Langmuir adsorption isotherm is assumed:

$$n = f(c) = \frac{\gamma c}{1 + Kc} \quad (10)$$

This allows the student to explore “favorable” and “unfavor-

able” isotherms and the “shock” formation. The program omits the dispersion terms in Eq. (2) so that the equation for the fluid phase becomes

$$\phi \frac{\partial c}{\partial t} + \phi v \frac{\partial c}{\partial z} + (1 - \phi) \frac{\partial n}{\partial t} = 0 \quad (\text{fluid}) \quad (11)$$

If the solid and fluid phases are in equilibrium, then

$$\frac{\partial n}{\partial t} = \frac{df}{dc} \frac{\partial c}{\partial t} \quad (12)$$

and the governing equation is

$$\phi \frac{\partial c}{\partial t} + \phi v \frac{\partial c}{\partial z} + (1 - \phi) \frac{df}{dc} \frac{\partial c}{\partial t} = 0 \quad (13)$$

which in dimensionless form is

$$\left(1 + \frac{1 - \phi}{\phi} \frac{df}{dc} \right) \frac{\partial c}{\partial \eta} + \frac{\partial c}{\partial \xi} = 0 \quad (14)$$

The program gives the same range of techniques to solve Eq. 2, and the text^[6] gives example solutions. For these experiments, we took approximate values of K and γ from the batch adsorption experiments and generated the results in Figures 8 and 9. Figure 8 uses a concentration above $1/K$ that results in the formation of a shock front, whereas Figure 9 uses a value in the linear region. The sharpening of the front for high solute concentration seen in the experiments (Figure 4) is also seen in the simulation in Figure 8, whereas at concentrations in the linear adsorption regime, the front does not sharpen. The students are then asked to relate the simulation results at low concentration from this simulation to the simulation results with the linear adsorption isotherm, but with added dispersion.

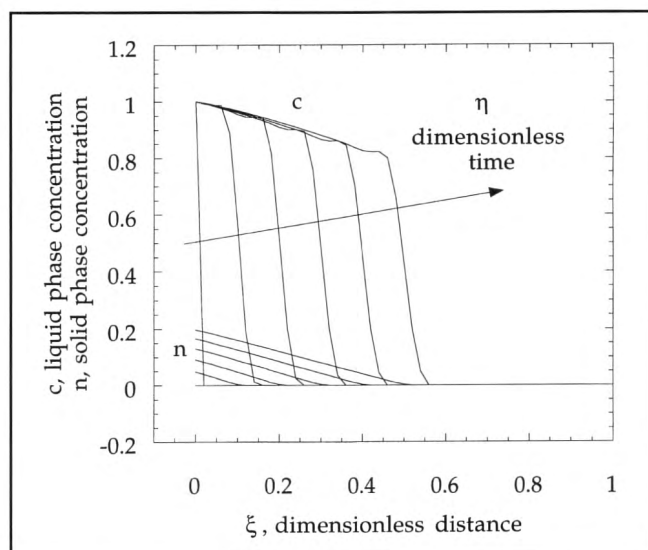


Figure 5. Moving concentration front during adsorption. Simulation performed using linear adsorption with $\gamma=0.5$, $\phi=0.485$, initial concentration of $c=1$ and $n=0$, $\Delta\eta=0.01$ (10 steps between plots, $\Delta\xi=0.02$, and with the diffusion term neglected (Pe_1 is infinitely large).

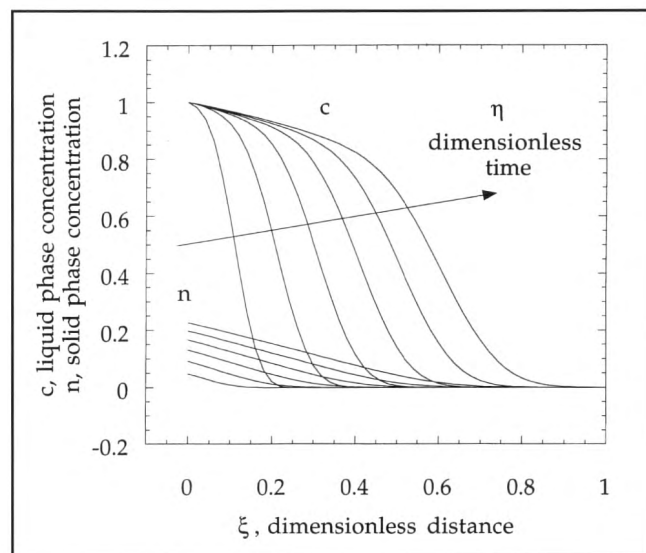


Figure 6. Moving concentration front during adsorption. Simulation performed using linear adsorption under the same conditions as in Figure 5 except $Pe_1=100$.

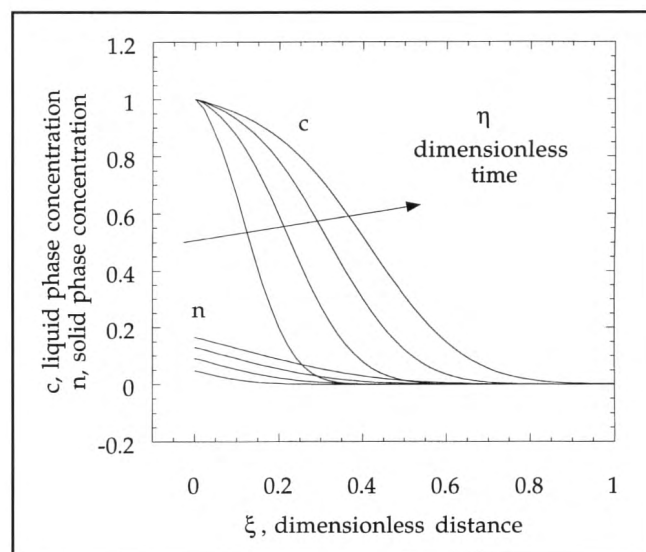


Figure 7. Moving concentration front during adsorption. Simulation performed using linear adsorption under the same conditions as in Figure 5 except $\Delta\eta=0.005$ (20 steps between plots) and $Pe_1=25$.

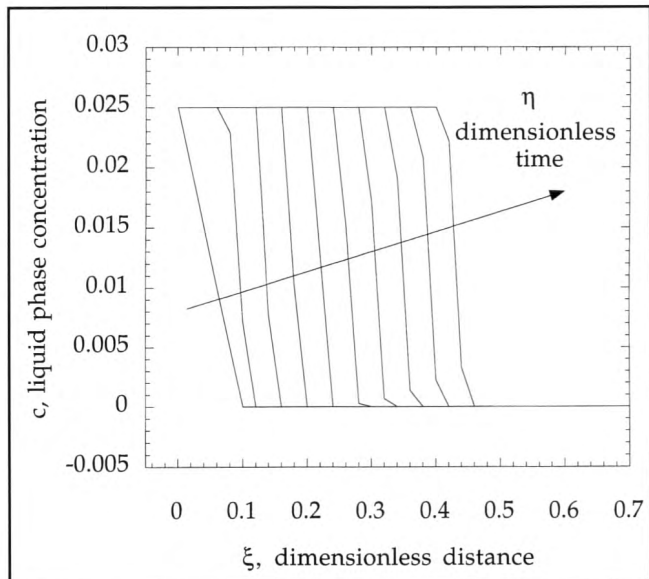


Figure 8. Moving concentration front during adsorption. Simulation performed using Langmuir isotherm with $K=500$, $\gamma=50$, $\phi=0.485$, $c=0.025$, $\Delta\eta=0.01$ (10 steps between plots), and $\Delta\xi=0.02$. Note that a triangular concentration profile is used as the initial condition for Figures 8 and 9.

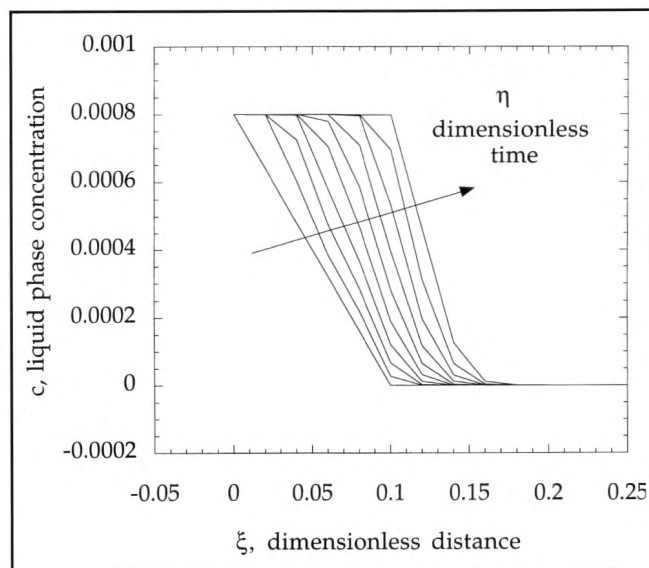


Figure 9. Moving concentration front during adsorption. Simulation performed using Langmuir isotherm with $K=500$, $\gamma=50$, $\phi=0.485$, $c=0.0008$, $\Delta\eta=0.01$ (30 steps between plots), and $\Delta\xi=0.005$.

Analytical results for Eq. (14) can be obtained using the method of characteristics^[3] and some discussion of this method with the students may prove useful. In particular, the characteristic lines may help clarify some of the observed effects, including broadening and sharpening of fronts. An example illustrating the method of characteristics is given in reference 7.

CONCLUDING REMARKS

The ion exchange experiment and simulation provides a way to effectively teach concepts in mass transfer and separations to students at a number of levels. The experiment and simulation reinforce the learning experience. The experiments are straightforward in their execution, but lead to discussions about diffusion length scales, internal and external mass-transfer control, and dispersion versus diffusion.

For undergraduates, the simulation package frees the students from becoming enmeshed in the details of numerical analysis so that they can focus on the concepts and results. For more advanced students, the package provides a way to teach and compare numerical methods.

While we have described and given examples of the most rudimentary problem of a step change in solute-free concentration, the experiment and simulation can also be used to investigate desorption and regeneration of beds, pulse injection chromatographic separations, and dispersion in porous media without adsorption.

ACKNOWLEDGMENTS

The authors would like to acknowledge financial support at Princeton University from the NSF Undergraduate Laboratory Instrumentation Program.

REFERENCES

1. Anderson, Robert A., "Ion Exchange Separations," in *Handbook of Separation Techniques for Chemical Engineers*, Philip A. Schweitzer (ed.), McGraw-Hill, New York, NY, 1-359 (1979)
2. Cussler, E.L., *Diffusion, Mass Transfer in Fluid Systems*, Cambridge University Press, New York, NY (1984)
3. Sherwood, Thomas K., Robert L. Pigford, and Charles R. Wilke, *Mass Transfer*, McGraw-Hill Company, New York, NY, Chap. 10 (1975)
4. Rhee, H.K., R. Aris, and N.R. Amundson, *First-Order Partial Differential Equations: Vol. I, Theory and Application of Single Equations*, Prentice Hall, Englewood Cliffs, NJ (1986)
5. Helfferich, F., and G. Klein, *Multicomponent Chromatography: Theory of Interference*, Marcel Dekker, Inc., New York, NY (1970)
6. Finlayson, Bruce A., *Numerical Methods for Problems with Moving Fronts*, Ravenna Park Publishing, Seattle, WA, Chap. 9 (1992)
7. Poulain, C.A., and B.A. Finlayson, "A Comparison of Numerical Methods Applied to Non-Linear Adsorption Columns," *Int. J. Num. Methods Fluids*, **17**, 839 (1993)
8. Ruthven, Douglas M., *Principles of Adsorption and Adsorption Processes*, John Wiley & Sons, New York, NY, Chap. 8 (1984) □