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Abstract

A simplified design model for a chromatographic ion exclusion column is developed in which the flxed bed of resin is dividl~d into a number of perfectly mixed equilibrium stages and the liquid Aow rate is constant. The model is represented by the following dimensionless differential equation which results from the combination of a material balance about the rth stage and a second-degree phase equilibrium relationship: (1 /h}(f, - 1/;,-1l + K (clf,/dT) + M>/;, (df,/dT) = 0, where K and Mare dimensionless groups while 1 /his the number of equilibrium stages. 1/; and T are dimensionless concentration and time, respectively. The numerical solutions of this E~quation for single, square wave inputs are presented for different values of the dimension·less groups, feed volumes, and number of stages. The resulting calculated elution curves and experimentally determined curves are compared. Design applications are discussed.

Disciplines

Catalysis and Reaction Engineering | Complex Fluids | Other Chemical Engineering

Comments

SIMPLIFIED DESIGN MODEL FOR AN ION EXCLUSION COLUMN

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A simplified design model for a chromatographic ion exclusion column is developed in which the fixed bed of resin is divided into a number of perfectly mixed equilibrium stages and the liquid flow rate is constant. The model is represented by the following dimensionless differential equation which results from the combination of a material balance about the rth stage and a second-degree phase equilibrium relationship: $(1/h)(\psi_r - \psi_{r-1}) + K (d\psi_r/d\tau) + M\psi_r (d\psi_r/d\tau) = 0$, where K and M are dimensionless groups while $1/h$ is the number of equilibrium stages. ψ and τ are dimensionless concentration and time, respectively. The numerical solutions of this equation for single, square wave inputs are presented for different values of the dimensionless groups, feed volumes, and number of stages. The resulting calculated elution curves and experimentally determined curves are compared. Design applications are discussed.

ON exclusion is a method of separation based on the different sorption characteristics which ion exchange resins have for different types of solutes where no actual ion exchange is involved. It was first reported by Wheaton and Bauman (*13*) for the separation of ionic and nonionic solutes. Later these investigators found that it could also be used for the separation of two or more nonionic solutes (*12*). It was subsequently applied commercially for the separation of salt and glycerol in aqueous solutions (*5*).

The process of ion exclusion is usually carried out by washing a batch of the solute mixture through a fixed resin bed, so that in effect it is a type of elution chromatography. Both kinetic models and equilibrium models have been proposed for the simulation of chromatography columns (*2*). As an initial step toward the development of a kinetic model, Vassiliou and Dranoff (*11*) and Tayyabkhan and White (*10*) investigated the kinetics of ion exclusion.

The plate theory of chromatographic columns was proposed by Martin and Synge (*3*) and expanded by Mayer and Tompkins (*4*). Their model utilized a linear sorption isotherm and was based on a discontinuous equilibration process. This model was applied by Simpson and Wheaton to the analysis of an ion exclusion column (*9*). Plate models based on continuous fluid flow were proposed by Glueckauf (*1*) and Said (*6, 7*).

In the work described below, the equilibrium plate model utilizing a second-order equilibrium isotherm is developed and compared with some experimental results. The application of this model for the analysis and design of ion exclusion columns is also discussed.

Mathematical Model

To develop a simple design model it was assumed that the fixed bed of resin is divided into a number of perfectly mixed equilibrium plates or stages. The liquid flows through the bed continuously at a constant rate. A single solute material balance over the rth stage of the column provides the following differential equation:

$$Vc_{r-1} - Vc_r = HS \left(\alpha \frac{dc_r}{dt} + \beta \frac{dq_r}{dt} \right)$$

This can be combined with a second-order equilibrium expression of the form

$$q = Ac + Bc^2$$

and upon substituting the following dimensionless variables

$$h = \frac{H}{L}, \quad \psi = \frac{c}{c_0}, \quad \tau = \frac{tV}{(\alpha + \beta)SL}$$

the dimensionless equation below is obtained.

$$\frac{1}{h} (\psi_r - \psi_{r-1}) + \left(\frac{\alpha + \beta A}{\alpha + \beta} \right) \frac{d\psi_r}{d\tau} + \left(\frac{2\beta Bc_0}{\alpha + \beta} \right) \psi_r \frac{d\psi_r}{d\tau} = 0$$

The two dimensionless groups appearing in the last equation represent constant parameters for any given run through a particular column. Hence, the equation can be simplified somewhat by letting K and M represent the two groups, respectively,

$$K = \frac{\alpha + \beta A}{\alpha + \beta}, \quad M = \frac{2\beta Bc_0}{\alpha + \beta}$$

When these substitutions are made, the dimensionless differential equation becomes

$$\frac{1}{h} (\psi_r - \psi_{r-1}) + K \frac{d\psi_r}{d\tau} + M\psi_r \frac{d\psi_r}{d\tau} = 0$$

This equation together with the initial condition constitutes the design model. The equation can be numerically integrated for single square wave inputs to yield single, dimensionless elution curves.

Initially it is assumed that the solute concentrations in the column are zero. The input function is based on the feed concentration and volume. The latter is introduced in dimensionless form by relating it to the empty column volume as follows:

$$\nu = \frac{F}{SL}$$

Thus ν becomes the third dimensionless parameter which is invariant for any given run in a particular column. Fixing the four parameters—K, M, ν, and the number of theoretical plates —completely determines the shape and size of a particular elution curve plotted in terms of the dimensionless coordinates.

Of the four parameters only two are independent, since it is possible to transform the differential equation into one with a single dimensionless group, M/K, providing the dimensionless time variable is redefined as τ/Kh. The four parameters have been retained in this work because the resulting dimensionless variables have greater physical significance and are easier to visualize. Thus, τ as used here represents the number of times the liquid content of the column has been displaced and it is independent of the sorption isotherm and the number of equilibrium plates.

Numerical Method of Solution

The numerical solution is based upon replacing the differential equation with one involving finite differences. Since ψ and the derivative can be approximated by these expressions,

$$\psi_\tau = \frac{1}{2}\left(\psi_{\tau,s} + \psi_{\tau,s-1}\right)$$

$$\frac{d\psi_\tau}{d\tau} = \frac{1}{k}\left(\psi_{\tau,s} - \psi_{\tau,s-1}\right)$$

$$\left(\psi_\tau - \psi_{\tau-1}\right)\big|_s = \left(\psi_{\tau,s} - \psi_{\tau-1,s}\right)$$

they can be substituted into the differential equation to obtain the following finite difference equation:

$$\psi_{\tau,s} = -\left(\frac{K}{M} + \frac{k}{hM}\right) +$$

$$\sqrt{\left(\frac{K}{M} + \frac{k}{hM}\right)^2 + 2\left[\frac{k}{hM}\,\psi_{\tau-1,s} + \frac{K}{M}\,\psi_{\tau,s-1} + \frac{1}{2}\,\psi_\tau{}^2{}_{,s-1}\right]}$$

Although ideally the feed input to the column should be represented by a square wave, this results in a double valued function at the beginning and end of the wave which is inconsistent with the method of finite differences. Hence, a rounded, flat-topped, symmetrical wave was used to represent the feed input. Both the leading and trailing edges are represented by the expression

$$\int d\psi = \int f(\tau)d\tau$$

where the following function was chosen so that the first three derivatives are zero at both $\tau = 0$ and $\tau = \delta$:

$$f(\tau) = a\tau^3(\delta - \tau)^3$$

This function produces a leading edge having an elongated S shape. The concentration rises from zero to the maximum feed value over a period of time, δ. The constant, a, is evaluated by integrating the expression

$$\int_0^1 d\psi = \int_0^\delta f(\tau)d\tau$$

In this work δ was arbitrarily made equal to $5k$, which was from 4 to 9% of the total width of the input function, depending upon the feed volume. Reducing δ to k while holding all other conditions constant had little effect on the elution curve. Concentrations for the leading edge were calculated from the following:

$$\int_0^\psi d\psi = \frac{140}{\delta^7} \int_0^{nk} \tau^3(\delta - \tau)^3 \, d\tau$$

where n represents the number of time increments from time zero.

The numerical solution can be carried out with a digital computer using a small but arbitrary time increment size which
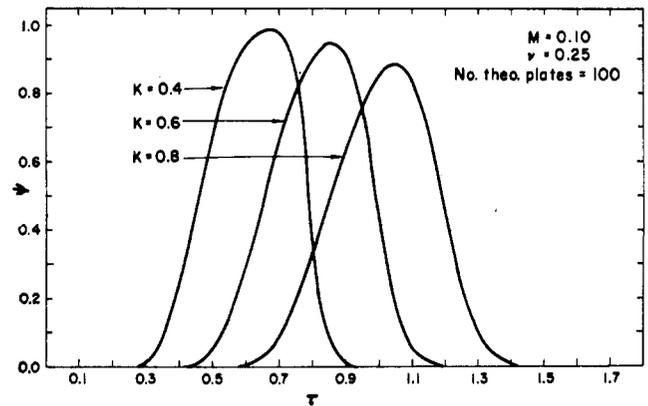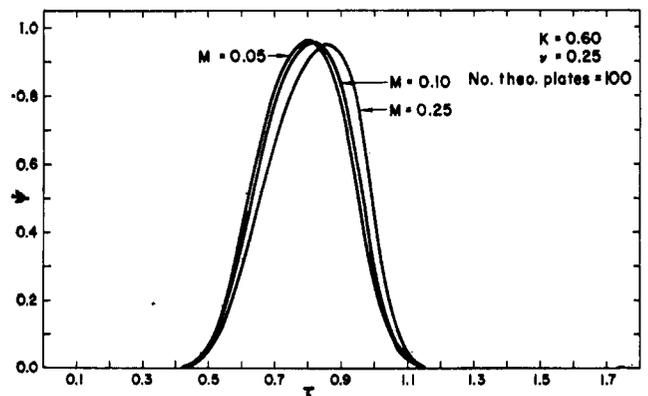

Figure 1.   Effect of K on elution curve

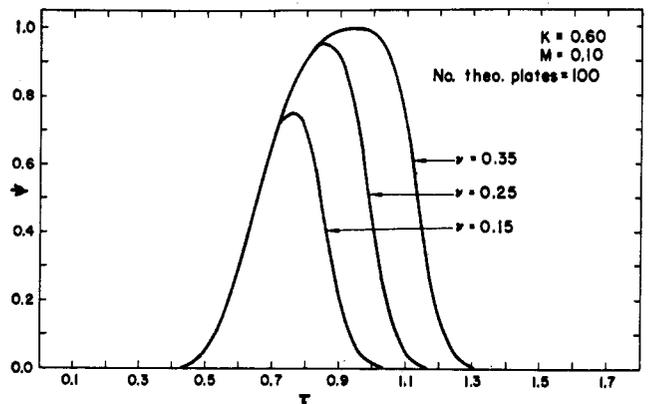Figure 2.   Effect of M on elution curve

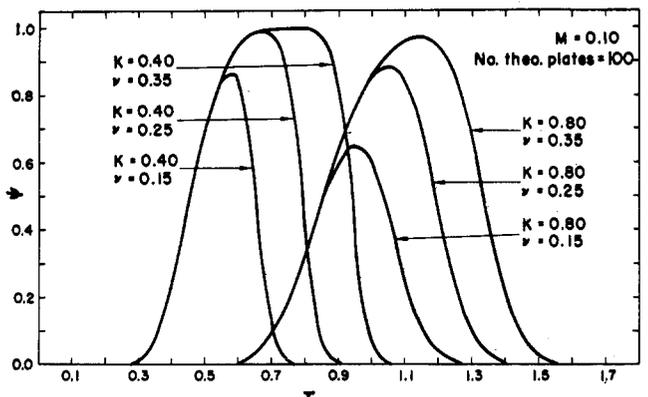Figure 3.   Effect of ν on elution curve

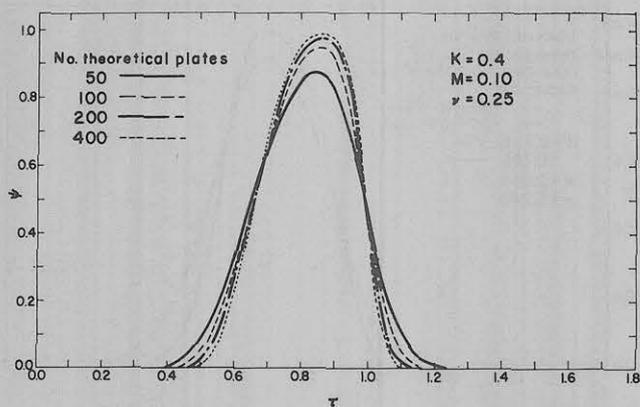Figure 4.   Effect of ν on degree of separation between components

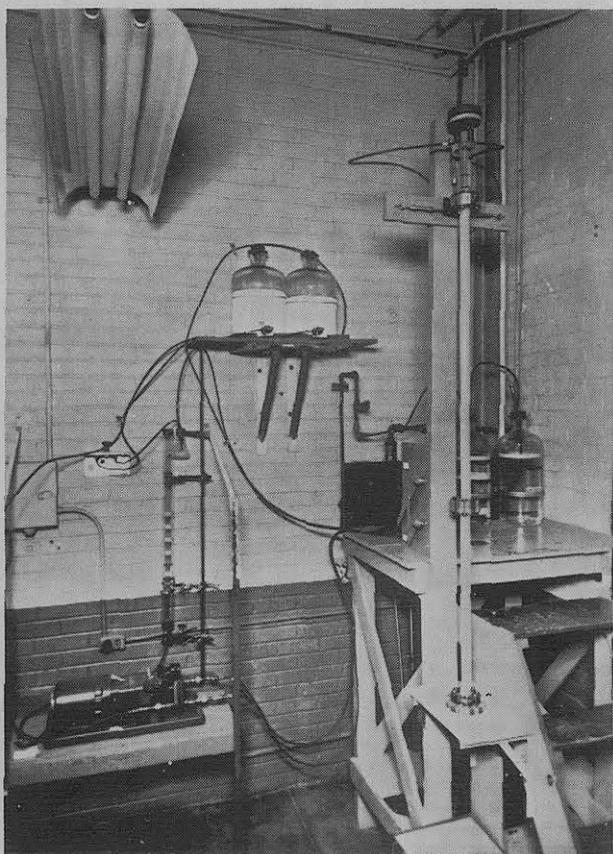Figure 5. Effect of number of theoretical plates on elution curve

Figure 6. Experimental apparatus

will ensure convergence. When k was varied over the range of 0.001 to 0.016, the resulting family of elution curves appeared to converge fairly rapidly for values of k less than 0.004. The latter was used for all calculated curves shown here. The program took about 2 minutes per 100 theoretical plates to run on an IBM 7074 computer.

Typical Solutions

The mathematical model was used to predict elution curves for typical values of the four dimensionless parameters K, M, ν, and the number of theoretical plates. The results are presented in Figures 1 to 5.

Figure 1 demonstrates the effect of varying K while holding M, ν, and number of plates constant. It shows that an increase in K causes the elution curve to shift markedly to the right

while at the same time broadening the curve slightly and reducing the maximum concentration somewhat. In other words, the principal effect of increasing K is to cause the concentration wave to appear later at the column outlet.

Figure 2 shows that increasing M skews the elution curve to the right while not producing any noticeable changes in the width and peak height. For the range of parameter values investigated, changes in M have much less effect than changes in K. As the value of M approaches zero, the model approaches one based on a linear sorption isotherm. This can occur when the solute concentration is very small as well as when the effect of the second-order term of the sorption isotherm is small.

Figure 3 demonstrates the effect of varying the dimensionless feed volume, ν. It shows that an increase in ν increases both the width and peak height markedly but does not affect the time when the concentration wave begins to appear at the outlet.

For the design engineer ν is the most important of the four dimensionless parameters because he can vary it over a wide range, while he has practically no control over K and M. Increasing ν will increase column throughput per pass but decrease the degree of separation between components. The latter is illustrated by Figure 4, where two families of curves are plotted corresponding to two different components having $K = 0.4$ and 0.8, respectively. For $\nu = 0.35$ there is considerable overlapping of the two elution curves representing the two different components. However, as ν is decreased, the degree of overlapping diminishes and it is rather small for $\nu = 0.15$. Obviously complete separation could be obtained by making ν small enough but, of course, feed throughput per unit volume of column would be small. Now the designer can make ν small by increasing column length or diameter as well as by decreasing the actual feed volume.

The effect of the number of theoretical plates is shown in Figure 5. Thus the elution curves become less spread out and the peak height increases as the number of plates increases for fixed values of the other parameters. Since the family of curves appears to converge rather rapidly as the number of plates increases beyond 100, it appears that this may be a practical limit which it would not pay to exceed. This being the case, the designer could predict limiting elution curves even in the absence of information concerning the height equivalent to a theoretical plate.

Experimental

Apparatus and Procedure. The equipment shown in Figure 6 was used for obtaining experimental elution curves. The heart of the apparatus was the packed column, details of which are shown in Figure 7. The column was made of 1.0-inch inside diameter Plexiglas tubing and it had a floating piston head which was kept pressed against the top of the resin bed so as to eliminate any void space above the resin. The column was filled with Dowex 50W-X8 cation exchange resin in the sodium form by pouring a slurry of the resin into the water-filled column. The resin was allowed to settle freely and the bed was not backwashed or tamped.

The column feeding arrangement is shown in Figure 8. A duplex, Zenith gear pump with a Zero-Max variable speed drive was used for pumping and metering either distilled water or feed solution to the column at a controlled rate. The two three-way valves between the pump and the column were linked together mechanically, so that one fluid was simply recycled while the other was being pumped to the column.

In preparing for a run an excess of feed solution was placed in the standpipe and distilled water was pumped through the column for about half an hour to wash the resin. At the start of the run both three-way valves were thrown and this interrupted the flow of distilled water and started the flow of feed solution to the column. The feed was introduced at a metered
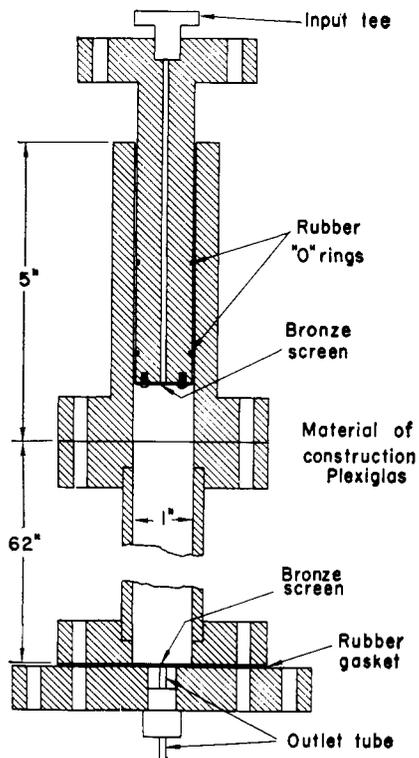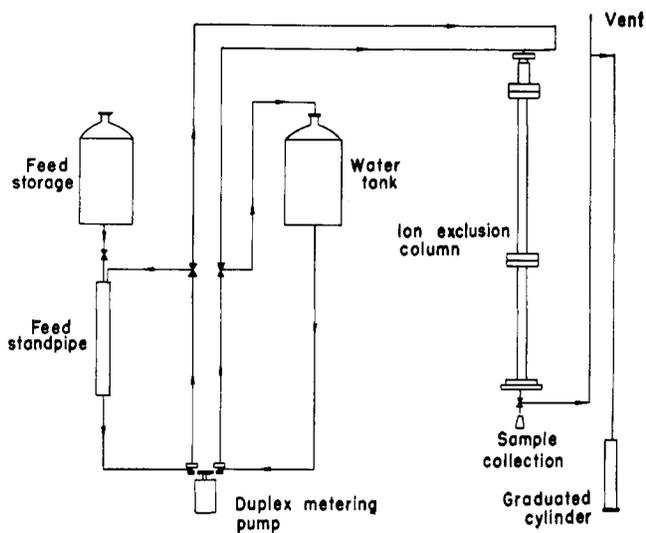
Figure 7. Details of experimental column
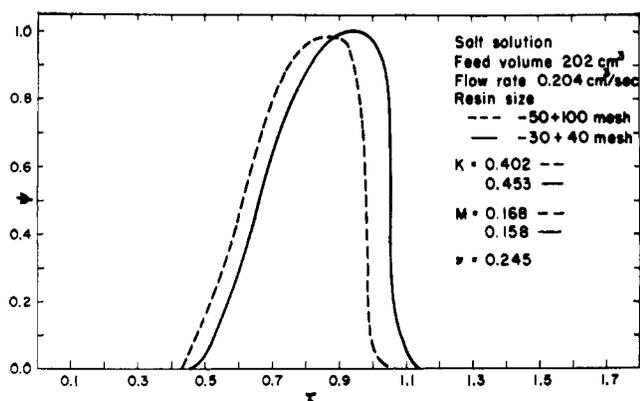

Figure 8. Flow sheet

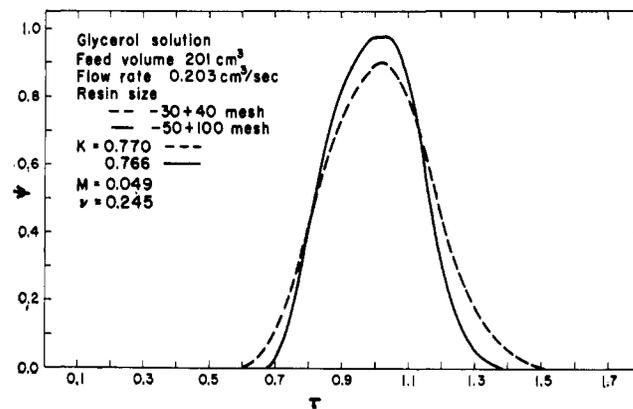Figure 9. Effect of resin size on sodium chloride curve

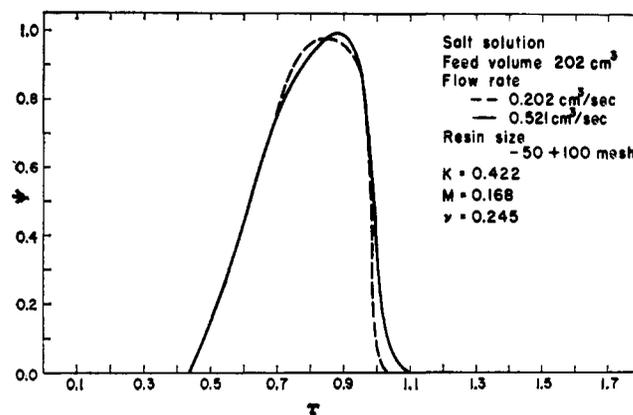Figure 10. Effect of resin size on glycerol curve

Figure 11. Effect of flow rate on sodium chloride curve
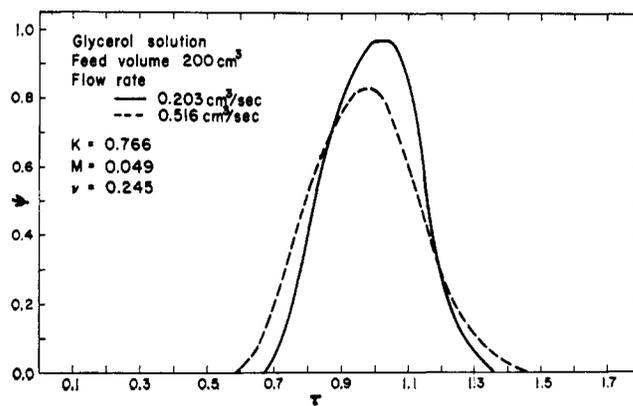

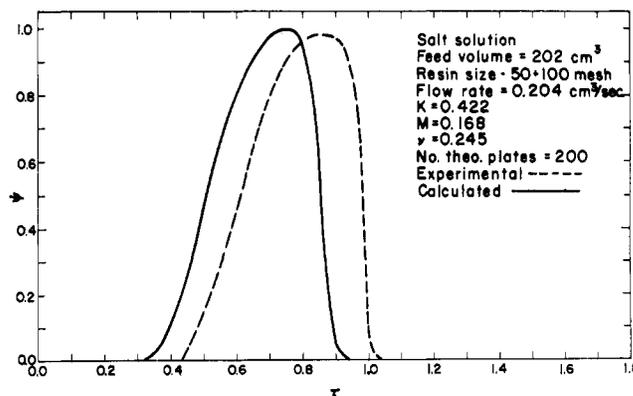Figure 12. Effect of flow rate on glycerol curve

Figure 13. Comparison of calculated and experimental sodium chloride curves
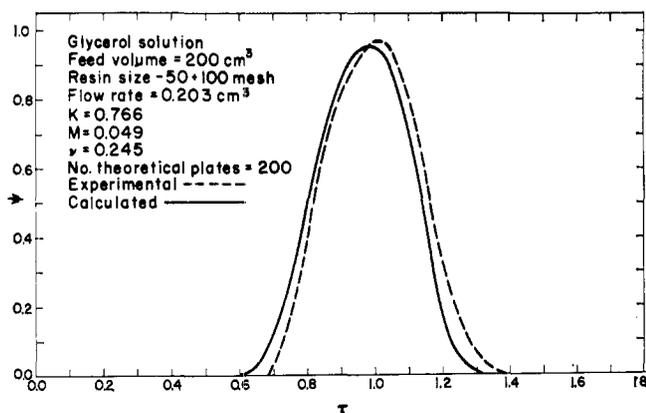
Figure 14. Comparison of calculated and experimental glycerol curves

rate for a measured time interval and then the three-way valves were returned to their former positions so that distilled water instead of feed solution was metered to the column. Thus, as the composition of the fluid entering the column was changed from water to feed solution and back to water, there was no interruption in flow through the column. Intermittent sampling of the column effluent was started before the solute began to appear and was continued until the concentration wave had passed. At low feed rates the effluent was collected for the first 5 seconds of every minute and at high feed rates for the first 5 seconds of every half minute. Concentrations were determined by measuring the refractive index with a Bausch and Lomb refractometer.

After completing a series of runs made with a particular solute and particular resin size, both the void fraction and occluded fraction of the bed were determined. Air saturated with water vapor was passed into the top of the column and the water in the interstices was blown out, collected, and weighed. The volume of water collected divided by the volume of the column was the void fraction. All of the moist resin was removed from the column and weighed and its moisture determined. The occluded fraction was the ratio of the volume of water in the moist resin to the volume of the column.

Results. Experimental elution curves were determined at room temperature for the binary solutions, 10 weight % sodium chloride–water and 10 weight % glycerol–water. These components were chosen because of the availability of published phase equilibrium data (8). Two sizes of Dowex 50W-X8 resin were used and the observed bed properties corresponding to these are tabulated below.

Resin Size Screen Mesh	Salt		Glycerol	
	α	β	α	β
−50 + 100	0.27	0.39	0.32	0.38
−30 + 40	0.29	0.38	0.32	0.37

The void fraction, α, appeared low when compared with a value of 0.38 reported by others (5), so it was checked by a mercury intrusion method and a value of 0.27 was obtained for −50 + 100-mesh resin after a 10% sodium chloride solution had been eluted. Since the column used in this investigation did not permit free expansion of the resin bed, the resulting void fraction may have been smaller than usual. The occluded fraction, β, agreed well with the value of 0.37 reported for −50 + 100-mesh Dowex 50-X8 resin (5).

The resin size and liquid flow rate were varied over the ranges which might be used in commercial columns (5) to see whether the kinetic effects might be highly significant. Figures 9 and 10 show that varying the resin size produced relatively minor changes in the elution curves for salt and glycerol, respectively. The shift in the curve for sodium chloride would

more likely result from an abnormal void fraction or some other source of experimental error than from a kinetic effect. On the other hand, the broadening of the glycerol curve and lowering of the peak height when the resin size increased are expected consequences of a finite rate of mass transfer. Changing the flow rate produced similar effects. Figure 11 shows that doubling the flow rate had practically no effect on the sodium chloride curve. However, it did broaden the glycerol curve and lower the peak height (Figure 12). Thus in the case of a highly mobile solute such as sodium chloride the kinetic effects appeared negligible while for the less mobile glycerol they appeared small.

Elution curves for sodium chloride and glycerol were calculated on the basis of the observed bed properties and the equilibrium data of Shurts and White (8) and the results are compared with the experimentally determined curves in Figures 13 and 14. For salt the calculated curve had about the same size and shape as the experimentally observed curve but was shifted to the left. It is suspected that this discrepancy may have resulted from a temporary increase in bed void fraction when the band of salt solution passed through the column. This could happen if the resin contracted in volume more than the bed did as the salt passed through. Moreover, much better agreement would have been obtained had the calculated curve been based on a void fraction of 0.38 instead of 0.27. The agreement was about as good when 100 theoretical plates were used as when 200 were used.

The agreement between the calculated and experimental curves was fairly good in the case of glycerol. For this case the experimental curve matched the calculated curve based on 200 plates a little better than the one based on 100 plates.

Extension and Application

The equilibrium plate model incorporating a nonlinear sorption isotherm appears to offer a promising means for predicting elution curves for ion exclusion systems. Since the model can be used to relate the degree of separation between components with the feed throughput per pass and, column dimensions, it should prove useful for designing and analyzing chromatography columns. Even without knowing the height equivalent to a theoretical plate, the model can be used to predict limiting separations for an arbitrarily large number of equilibrium stages. Since the effect of the number of plates decreases rapidly above 100, it appears that this may be a practical limit for large-scale separations. Where there is a large interaction between solutes, the model can be extended by using separate material balances for each solute and an equilibrium expression which accounts for the interaction.

Nomenclature

A = coefficient in equilibrium relation, dimensionless
a = constant, dimensionless
B = coefficient in equilibrium relation, cc./gram
c = concentration of mobile phase, grams/cc.
c_o = concentration of feed, grams/cc.
F = feed volume, cc.
H = height of theoretical plate, cm.
h = length increment, dimensionless
k = time increment, dimensionless
K = dimensionless parameter
L = column length, cm.
M = dimensionless parameter
n = time increment number, dimensionless
q = concentration of stationary phase, grams/cc.
r = stage number from top of column, dimensionless
s = time increment position, dimensionless

S = cross-sectional area of column, sq. cm.
t = time, sec.
V = volumetric flow rate, cc./sec.
α = void fraction of bed
β = occluded fraction of bed
δ = time period for feed to reach maximum concentration
ν = dimensionless feed volume
τ = dimensionless time
ψ = dimensionless concentration of mobile phase

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SEPARATION OF SOME INORGANIC SALTS IN AQUEOUS SOLUTION BY FLOW, UNDER PRESSURE, THROUGH POROUS CELLULOSE ACETATE MEMBRANES

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The experimental results illustrate the general applicability of this separation technique for aqueous inorganic solutions, the possible predictability of the separation and flow characteristics of porous cellulose acetate membranes, and the concept that separations are similar for ions of the same valency.

THE separation of inorganic salts in aqueous solution by flow, under pressure, through porous cellulose acetate membranes is of wide engineering interest. The physical chemistry of ion-selective membranes, and the various mechanisms of membrane separation, are extensively discussed in the literature (*1–3, 5, 7, 8, 11, 12, 14–16, 22–24*). Based on the Gibbs adsorption equation, a mechanism was recently postulated for this separation process (*18*). The negative adsorption of the solute at the liquid-solid interface, together with the flow of the preferentially sorbed interfacial liquid through the film containing pores of size equal to or less than a critical diameter characteristic of the system, constitutes the essence of this mechanism.

Such a postulate offers a new approach to the subject. Two consequences are of practical interest. First, it is clear that an appropriate chemical nature of the film surface in contact with the solution, together with the existence of pores of appropriate size on the area of the porous film at the interface, are indispensable twin requirements for the success of this separation technique. Further, the rate of production of desalted water can be increased, without affecting the degree of separation under the given operating conditions, by simply increasing the number of pores of appropriate size on the film surface. Thus the degree of separation and the rate of production of desalted water are two independent characteristics of the membrane.

From an industrial standpoint, the application of the above technique for a given separation problem involves essentially the problem of choosing the appropriate chemical nature of the film surface and developing techniques for making films containing the largest number of pores of the required size on the area of the film at the interface. This approach formed the basis of the successful experiments described earlier on the development of porous cellulose acetate films capable of giving both high flow rates and high degrees of demineralization of aqueous sodium chloride solutions (*9*). The reported upswing (*4*) in the studies on the above separation technique for saline water conversion is largely a direct result of this approach.

Scope of This Work

The possible development of this separation technique for sea water conversion is of tremendous engineering significance. Even more significant is the possibility of developing it as a general process for the separation of any substance in solution (*19*). This work forms part of a wider program of investigations to explore the latter possibility. In particular, the object of this paper is to report three major experimental observations of general significance with respect to the separation of inorganic salts in aqueous solution using porous cellulose acetate membranes.