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Countercurrent Electrolysis in a Cell Where Porous Membranes Have Been Connected in Series with Ion-Exchange Membranes. Part 1. Method

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Abstract

A new cell arrangement for countercurrent electrolysis in a porous membrane is presented. In this cell, where porous membranes are connected in series with ion-exchange membranes, much better separations are obtained compared to the procedure where the membrane is made thicker. However, separation is less than if convection is increased, but power consumption is also less. An iterative method is presented for solving convection as well as the concentrations in different compartments, when electric current, outflow rate, and concentrations of the product stream are specified.

INTRODUCTION

Basic research work to study the use of countercurrent electrolysis in a porous membrane as a separation method for electrolytes has continued for several years in our laboratory. In these studies both strong electrolytes (*1*–*4*) and weak electrolytes (*5*) as well as the effect of membrane thickness (*6*) have been considered. We have solved the theoretical model which leads to a set of convective electrodiffusional equations using two different approaches. One approach combines the shooting method (*7*) and the variational approach (*8*), and the other is the finite difference method as given by Aquilella (*9*). The method applied by Aquilella et al. is more accurate than ours because it takes into account the deviations from the condition of electroneutrality. However, in the most interesting cases where the differences in mobilities of the ions to be separated are small, the deviations from the electroneutrality are small as well. We have also compared the Nernst-Planck equations to the Miller's LN approximation to check the validity of the Nernst-Planck equation as a theoretical model (*10*).

It has been shown that the greater the difference of the mobilities of the ions, the better is the separation efficiency (*2*, *3*), and that increasing convection increases separation exponentially (*3*, *4*). When the membrane is made thicker, the separation effect is increased at first, but the membrane thickness always reaches a limiting value of separation efficiency which cannot be exceeded while still keeping the convective flow constant. Furthermore, by making the membrane thicker, attainment of the stationary state lasts much longer (*11*), and at the same time power consumption increases because of higher ohmic losses. Consequently, the most reasonable choice for increasing separation efficiency from the practical point of view is to increase convection. In many cases this solution is not the ideal one because of increased power consumption and increased use of pure water. Therefore a compromise between making the membrane thicker and increasing convection is desirable. In this work a suitable compromise was found by connecting porous membranes in series with the aid of ion-exchange membranes, which in the case of cation separation are cation-exchange membranes.

By connecting porous membranes in series with ion-exchange membranes, the advantages of both increased convection and increased membrane thickness are achieved. Of course, the number of compartments is increased (higher ohmic losses), and current efficiency is slightly decreased due to the ion-exchange membranes, but the affirmative effect of the ion-exchange membranes on separation compensates these effects. Depending on electric current densities, ohmic losses across the ion-exchange membranes may become important, i.e., the higher the current density, the greater is the deviation from ohmic behavior (*12*). Countercurrent electrolysis in the porous membranes is responsible for a major part of the separation phenomenon, but by manufacturing tailor-made ion-exchange membranes, the separation phenomenon in the ion-exchange membranes further increases separation efficiency significantly.

CELL

In Fig. 1 we described schematically the cell for the separation of cations.

The separation of cations takes place mostly in porous membranes,

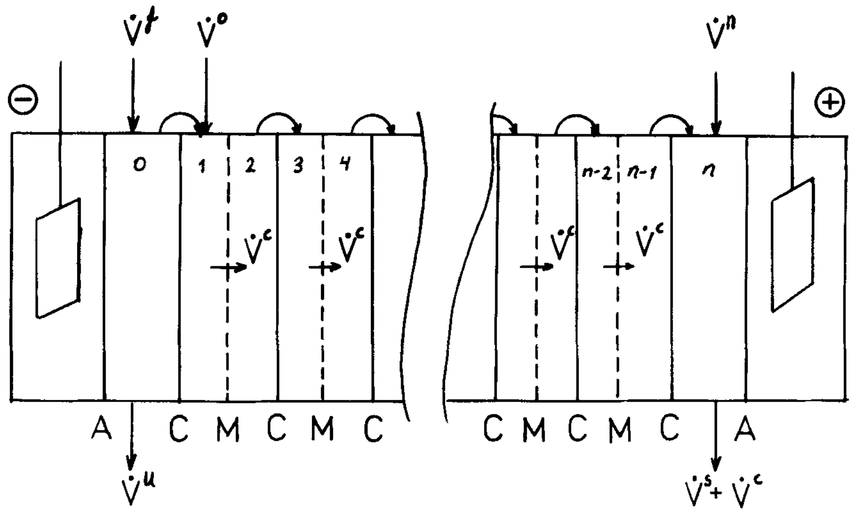

FIG. 1. Schematic drawing of the cell for cation separation. The electrode compartments (E) are separated from the rest of the system by anion-exchange membranes (A). The electrolyte solution to be separated is pumped at a constant rate $\dot{V}^s$ to Compartment n and thus the cations are forced to enter into the first separation unit—i.e., into Compartments $n - 1$ and $n - 2$ separated by a porous membrane (M)—through the cation-exchange membrane (C). Pure water is fed at a constant rate $\dot{V}^f$ into Compartment 0 and the product stream $\dot{V}^u$ is pumped out of compartment 0. The overflow from Compartment 0 to 1 is $\dot{V}^a = \dot{V}^f - \dot{V}^u$ and, of course, $\dot{V}^f \geqslant \dot{V}^u$. If one wants the convection $\dot{V}^c$ to be greater than $\dot{V}^a$, pure water ($\dot{V}^o$) is pumped into Compartment 1 and thus convection is $\dot{V}^c = \dot{V}^a + \dot{V}^o = \dot{V}^f - \dot{V}^u + \dot{V}^o$. The repeated separation unit consists of Compartments i and $i + 1$ separated by a porous membrane (M) and connected to the other separation units by cation-exchange membranes (C).

but the cation-exchange membranes also have selectivity. Fortunately, it appears that the cations that move fast in the aqueous solution are also quick in moving across the cation-exchange membrane, magnifying the separation efficiency. We have studied this selectivity of the cation-exchange membrane toward different cations with alkaline metals, and all the cations studied behave in the above manner. The problem of transport of ions across the ion-exchange membrane is difficult to treat theoretically because so many different phenomena are involved. We have come to the conclusion that the most important effects concerning the selectivity of ion-exchange membranes take place in the polarization layer. This fact was realized by studying the transport numbers and ionic mobilities inside the ion-exchange membrane (*13–15*): the selectivity could not be explained by the data obtained inside the membrane. Thus, selectivity is finally created in the polarization layer just adjacent to the ion-exchange membrane. However, no classical theories of concentration polarization can be used to describe this phenomenon, because the electric current densities in the polarization layer are always much greater than the classical theory allows. Attempts have been made to use different "classical models," e.g., water splitting, convective flow, etc., to explain the formation of the selectivity in the adjacent layer, but none of these explanations seems to be justified.

Rubenstein and Shtilman (*16*) presented an elegant theory that explains behavior in the polarization layer. Their approach is based on the breakdown of the conditions of electroneutrality which leads, for example, to current densities greater than those proposed by classical theory. Their approach can also be used to understand other cases (electrolysis in a dilute binary system). However, this model is so difficult to apply to our system that we decided to use experimental data. To obtain these data we performed experiments to measure the selectivity ratios in the cation-exchange membranes used while varying the concentration ratios of the cations chosen as a model system. Surprisingly, the results showed that the selectivity ratio was constant in the concentration range studied.

MASS BALANCES IN STATIONARY STATE

In the following treatment we examine a ternary electrolyte system consisting of a 1,1-electrolyte with a common anion. The concentrations of the cations are x_i and y_i, where the subscript denotes the department. The transport numbers, or perhaps it is preferable to speak of permeability constants, of the cations across the cation-exchange membrane are t_x^i and t_y^i, where the subscript denotes the cation and the superscript denotes the compartment. Note that the factor with the greatest effect on the values of t_x^i and t_y^i is the ratio of the concentrations of cations on the depleting side of the cation-exchange membrane. The electric current density is I, and the volume flows are as indicated in Fig. 1. The surface area of each porous membrane is A, and its thickness is l. The effect of electroosmotic flow through the ion-exchange membranes on the volume flow balances is so small that it can be neglected.

Compartment 0

The total concentration of electrolytes in Compartment 0 is

$$x_0 + y_0 = I/(\dot{V}^f F) \tag{1}$$

where F is Faraday's constant. The fluxes of the cations are

$$j_x = x_0 \dot{V}^u / A \tag{2}$$

$$j_y = y_0 \dot{V}^u / A \tag{3}$$

This means that the fluxes j_x and j_y are known as soon as the ratio x_0/y_0, I, and $\dot{V}^f$ are known. Because stationary state is assumed, the fluxes j_xA and j_yA have the same values throughout the cell. Furthermore, the total concentration in the product stream $\dot{V}^u$ and thus in Compartment 0 can be determined from the electric current density I and $\dot{V}^f$ alone.

Compartments *i* and *i* + 1; the Separation Unit

Because the separation unit is connected to the system by ion-exchange membranes, the selective effect it induces must be included in the mass balances. As mentioned earlier, measurements of selectivity ratio across the cation-exchange membrane showed that in the system studied the selectivity ratio is constant over a large range of concentration ratios. If this ratio is designated R_s, the transport numbers obtain the forms

$$t_x^i = \frac{x_i}{x_i + R_s y_i} \tag{4}$$

$$t_y^i = \frac{R_s y_i}{x_i + R_s y_i} \tag{5}$$

where ideal behavior is assumed, i.e., $t_x^i + t_y^i = 1$. Now the mass balances for Compartment $i + 1$ can be written

$$x_{i+1} = \frac{j_xA - t_x^{i+2} I/F}{\dot{V}^c} \tag{6}$$

$$y_{i+1} = \frac{j_yA - t_y^{i+2} I/F}{\dot{V}^c} \tag{7}$$

It is easy to see that the total concentrations in Compartments $i + 1$, when $i = 2, 4, 6, \ldots, n - 2$, remain constant, since $x_{i+1} + y_{i+1} = (j_xA + j_yA - I/F)/\dot{V}^c$. When the concentrations in Compartment $i + 1$ are known, the concentrations x_i and y_i on the other side of the porous membrane in Compartment i can be calculated using Nernst-Planck equations. This computation is relatively easily done because the problem to be solved is an initial value problem instead of a boundary value problem as solved in earlier papers (*7, 8*). We used the fourth-order Runge-Kutta method in the solution, and it appeared to be convenient in solving this problem.

Compartment *n*

If the concentrations of cations in the feeding solution ($\dot{V}^s$) are x_s and y_s, the concentrations in Compartment n, x_n and y_n, can be presented in the forms

$$x_n = \frac{\dot{V}^s x_s + j_x A}{\dot{V}^c + \dot{V}^s} \tag{8}$$

$$y_n = \frac{\dot{V}^s y_s + j_y A}{\dot{V}^c + \dot{V}^s} \tag{9}$$

These equations are obtained by subtracting the mass balance in Compartment n from that in Compartment $n + 1$.

SOLUTION PROCEDURE

By studying the mass balance it can be seen that an iterative procedure must be applied to obtain the solution of the problem. The most straightforward procedure is when the volume flows $\dot{V}^f$, $\dot{V}^u$, and $\dot{V}^s$, the electric current density I, the concentrations x_s and y_s, and the concentration ratio x_0/y_0 are given, to iterature $\dot{V}^c$ by changing the value $\dot{V}^o$, or if it is put equal to zero, to iterate the value for $\dot{V}^f$. The iterature is started from Compartment n, and it is continued compartment by compartment until Compartment 0 is reached. There a check can be made to see if the computed x_0/y_0 is the same as the given value. If the computed ratio is greater than the given one, the value of convection is increased and vice versa (y_i is the concentration of the faster moving cation). In this work all of these computations were done by a home microcomputer (Sinclair Spectrum). In our work this iteration was done by trial and error, but certainly more sophisticated methods can be applied.

The algorithm is as follows:

1. Values of the following quantities are given:
   a) $\dot{V}^f$, $\dot{V}^u$, and $\dot{V}^s$
   b) I, R_s, and the transport parameters (mobilities)
   c) x_s, y_s, and x_0/y_0 (this, in fact, means that we know the concentrations in the feeding solution, and we have decided what the concentration ratio in the product stream should be)
   $\rightarrow j_x$ and j_y are known.
2. We assume some proper value for $\dot{V}^o$, or if $\dot{V}^o = 0$, some proper value for $\dot{V}^f$
   $\rightarrow \dot{V}^c$ is known.
3. Mass balances
   a) Using Eqs. (8) and (9), x_n and y_n are determined
   b) By using eqs. (6) and (7) together with Eqs. (4) and (5), x_{n-1} and y_{n-1} are determined
   c) Integrating the set of differential equations derived from the Nernst-Planck equations (*2*) over the porous membrane by using x_{n-1} and y_{n-1} as initial values, x_{n-2} and y_{n-2} are obtained
   d) Analogously to b), x_{i+1} and y_{i+1} are obtained
   e) Analogously to c), x_i and y_i are obtained.
4. Continuing the calculation finally gives values for x_1 and y_1. The ratio x_1/y_1 is compared with the ratio x_0/y_0:
   a) If $x_0/y_0 = (1/R_s)\cdot x_1/y_1$, then go to 5
   b) If $x_0/y_0 > (1/R_s)\cdot x_1/y_1$, then the value assumed for $\dot{V}^o$ must be decreased, then go to 2
   c) If $x_0/y_0 < (1/R_s)\cdot x_1/y_1$, then the assumed value for $\dot{V}^o$ must be increased, then go to 2
5. The problem is solved. $\dot{V}^c$ is now known as well as the concentrations in the individual compartments.

This procedure is used in the simulation of the experimental results in a subsequent paper.

CONCLUSIONS

An iterative procedure is applied to solve the theoretical model of cell construction where porous membranes have been connected in series with ion-exchange membranes. This kind of cell construction has a smaller separation efficiency than construction where convection is increased, but it needs less power, because of lower electric current, and less pure water. Compared with the arrangement where the membrane is made thicker, the present method has a much better separation efficiency.

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