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Countercurrent Electrolysis in a Cell Where Porous Membranes Have Been Connected in Series with Ion-Exchange Membranes. Part 2. Experimental Verification

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Abstract

Countercurrent electrolysis in a cell wehre porous membranes have been connected in series with ion-exchange membranes has been studied experimentally for the ternary system NaCl-KCl-H_2O. The number of porous membranes was varied from one to four, and the effect of cationic fluxes on separation was also studied. A comparison between three different kinds of cell arrangements was made, and the present method was found to be the most attractive for practical purposes.

INTRODUCTION

We have studied the use of countercurrent electrolysis in a porous membrane experimentally as a separation method in several cases: separating alkaline metal and alkaline-earth metal halides (*1-3*), separating trace ions (*4*), and separations weak electrolytes (*5*). All of these experiments were performed using one thin porous membrane. These experiments also included studying the effect of convection on separation. We have further carried out experiments in which the porous membrane was made thicker (*6*). Now steps toward a more realistic

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cell design have been taken; the porous membranes are connected in series with the aid of ion-exchange membranes. With this kind of construction, power consumption can be reduced, but it must be realized that the quantitative improvement of power consumption remains unanswered because of poor cell design. We have constantly tried to improve the experimental set up, but at this moment the stack consisting of porous membranes, ion-exchange membranes, and spacers is still too thick to make any pertinent comparisons between different constructions. The main problem that has to be solved before the stack thickness can be reduced is to stir the separate compartments individually. Our experiments have clearly shown the need for stirring because otherwise both the separation and the electric current efficiency decrease considerably. We hope to overcome these difficulties in the near future and thus be able to make economic calculations.

ION-EXCHANGE MEMBRANES

As emphasized earlier (*6*), ion-exchange membranes have a selectivity of their own with respect to the different ions in a mixture. Because no theoretical approach is available for this problem (*7*), we performed a series of measurements to evaluate the permeability of different cations through ion-exchange membrane from mixtures of different compositions. These measurements were carried out in the ternary bulk solution system $NaCl–KCl–H_2O$. The total concentration was 10^{-2} mol/dm^3, and the concentration ratio of sodium to potassium was varied. The ratios studied were C_{Na^+}/C_{K^+} = 1:1, 1:2, 1:4, 1:8, 1:16, and 1:32. The electric current density was the same as in the separation measurements described later in this text, and the effect of electric current density as well as the effect of the total concentration of sodium and potassium chloride mixtures were not studied. The measurements were made with two different types of ion-exchange membranes (Ionics and Nafion).

As a preliminary experiment we measured the thickness of the stagnant layer just adjacent to the ion-exchange membrane in our experimental set-up. These measurements were made by the method of Indusekhar and Meares (*7*). The results clearly showed that in our measurements the electric current density was several times greater than the limiting current density according to the classical polarization theory of the stagnant layer.

Surprisingly, the selectivity ratio over the membrane was constant when the concentration ratio of sodium and potassium chlorides was varied. The values of

$$R_s = \frac{x_i}{y_i}\frac{(y_{i-1})}{(x_{i-1})}, \qquad i = 1, 3, 5, \ldots, n-1$$

obtained for the Ionics and Nafion cation-exchange membranes were $R_s = 1.39$ for Ionics 61 AZL 389 and $R_s = 1.45$ for Nafion 423.

Fortunately, the effect of these cation-exchange membranes is advantageous: the selectivity of cation-exchange membranes increases the separation effect, thus adding an important contribution to the separation efficiency of the whole process. In fact, this means that the ion-exchange membranes themselves can be used to achieve the separation of ions. Of course, separation is not as high as when countercurrent electrolysis is involved, but its effect is worth consideration in certain cases.

POROUS MEMBRANE

The same kind of porous membranes as described earlier (*6*) were used. These porous membranes were prepared by putting three sheets of filter paper (Mackerey-Nagel MN617) between two Millipore SC membranes whose thicknesses were ~0.15 mm each and whose pore size was 2 μm. Since it is quite obvious that this kind of a membrane has ion-exchange properties, adsorption, and surface diffusion, at least to some extent, an experimental method was devised to verify if these phenomena exist in our porous membrane. The method employed was the AC-impedance method and the determination was made by a procedure which will be considered later (*8*). The measurements clearly verified that our porous membrane has these characteristics. This fact explains why the mobilities of the cations are not the same as in the corresponding electrolyte solution. Fortunately, these relatively small deviations are in the positive direction, i.e., the difference in mobilities is greater in the porous membrane consdiered here than in the corresponding electrolyte solution. However, one must bear in mind that we are using the Nernst-Planck equations to model the transport process inside the porous membrane, and the difference in mobilities may be due to our model. However, according to our experience, the inaccuracy of this model does not explain the above-mentioned behavior.

SEPARATION EXPERIMENTS

The experimental set up was similar to those previously described (*6*), and the cell arrangement was according to Fig. 1 in Ref. *9*. In the present experiments $\dot{V}^o = 0$ and the values for electric current (I), the rate of feed solution ($\dot{V}^n$), the outflow from Compartment 0 ($\dot{V}^u$), and the water feed ($\dot{V}^f$), and thus the convection $\dot{V}^c$, were the same as in the experiments where the porous membrane was made thicker (*6*). Also, the membranes used (porous, anion exchange, and cation exchange) were the same as those in previous measurements. It is especially worth noting that the cation-exchange membranes used in these experiments were Nafion.

The experiments were carried out in the ternary system NaCl–KCl–H_2O. The total concentration of feeding solution ($\dot{V}^n$) was 0.2 mol/dm^3 and the concentration ratio was unity, i.e., $C_{K^+}/C_{Na^+} = 1$. In four experiments the convection and electric current were kept constant and the number of porous membranes connected in series with the cation-exchange membranes was varied from one to four. The electric current was calculated and set to have such a value that the total concentration in the outflow stream ($\dot{V}^u$) was $\sim 10^{-2}$ mol/dm^3.

The system was deduced to have reached the stationary state when the concentrations in the outflow stream $\dot{V}^u$ remained unchanged. Depending on the number of membranes, the time required to reach the stationary state varied from several hours to several days.

The cations sodium and potassium were analyzed by AAS, and potentiometric titration of the common anion chloride was used to check the AAS results.

The results are listed in Table 1. In this table we also present the theoretical values computed with the aid of the procedure given in a previous paper (*9*). The effect of outflow rate $\dot{V}^u$ also studied, i.e., the effect on separation of cationic fluxes across the membranes. These studies were made for four porous membranes connected in series with cation-exchange membranes. The results were as follows: When $\dot{V}^u$ was doubled, i.e., to $2\dot{V}^u$, the selectivity ratio was $S = 5.9$, and when $\dot{V}^u$ was halved to $\frac{1}{2}\dot{V}^u$, the selectivity ratio was $S = 140$. These results are in agreement with the behavior obtained earlier (*3*).

DISCUSSION AND CONCLUSIONS

In Fig. 1 we present graphically the results of three different cell arrangements:

a) The case where convection and electric current density are increased in a cell having one porous membrane.
b) The case where the number of porous membranes is increased by

TABLE 1

Experimental Results for the System NaCl-KCl-H_2O; $Y_{Na^+} = Y_{K^+} = 1$ in the Feeding Solution[a]

Number of membranes (n)	$-I_r/n$ (exptl)	$-I_r/n$ (theoret)	v^c/n (exptl)	v^c/n (theoret)	$-(K_{K^+} + K_{Na^+})/n$ (exptl)	$-(K_{K^+} + K_{Na^+})/n$ (theoret)	S
1	8.16	8.16	6.36	6.08	1.34	1.44	9.2
2	8.16	8.16	6.36	5.96	1.32	1.46	19.1
3	8.16	8.16	6.36	5.85	1.35	1.48	26.0
4	8.16	8.16	6.36	6.11	1.33	1.43	51.9

[a] Dimensionless parameters are electric current density $I_r = I/(A/l)C_0D_0F$, convection $v^c = \dot{V}^c/(A/l)D_0$, and ionic flux $K_i = J_i/(A/l)C_0D_0$, where the membrane constant $A/l = 10$ cm, scaling concentration $C_0 = 0.1$ mol/dm^3, scaling diffusion coefficient $D_0 = 2 \times 10^{-5}$ cm^2/s, and F is Faraday's constant. The theoretical values are obtained by using the procedure described in a previous paper (9) and the ionic mobilities of potassium and sodium were used in the calculations 88.1 and 50.1 Ω^{-1}cm^{2}mol^{-3}.

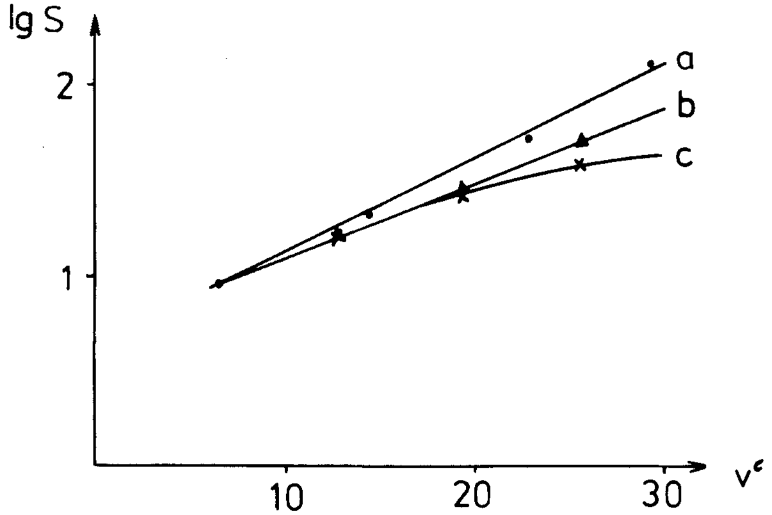

FIG. 1. The experimentally obtained relationship between the logarithm of the selectivity ratio (S) and the dimensionless convection v^c in the system NaCl–KCl–H_2O. Note that $v^c = \dot{V}^c/(A/l)D_0$ and that the number of membranes is included in the membrane constant A/l. Curve a: Increasing convection. Curve b: Increasing the number of porous membranes. Curve c: Making the porous membrane thicker.

connecting them in series with the aid of cation-exchange membranes while keeping the convection and electric current density constant.

c) The case where the porous membrane is made thicker while keeping the convection and electric current density constant.

It can be clearly seen that in Case b the advantages obtained by increasing convection and electric current (Case a) as well as by making the porous membrane thicker (Case c) are accomplished. It thus follows that for practical purposes the procedure where porous membranes are connected in series with ion-exchange membranes is the most attractive arrangement of the three studied. By using ion-exchange membranes the separation efficiency is further increased by the affirmative effect of the ion-exchange membranes on selectivity.

An important factor to be considered in the separation process is the current efficiency with respect to the ions to be separated (η_I^c), i.e.

$$\eta_I^c = \frac{(K_{K^+} + K_{Na^+})}{I_r} \tag{1}$$

where K_{K^+} and K_{Na^+} are the dimensionless ionic fluxes of potassium and sodium, respectively, and I_r is the dimensionless electric current density; $K_i = J_i/(A/l)C_0D_0$ and $I_r = I/(A/l)C_0D_0F$ (see Table 1 for the meaning of the different quantities).

The maximum value for η_I^c is, of course, unity. However, $\eta_I^c = 1$ can never be attained, and in the measurements presented in Fig. 1 the value calculated for η_I^c is 0.16 . . . 0.17, which can be regarded as a fairly high value. According to theoretical calculations, maintaining a reasonably high value for the selectivity ratio S, $\eta_I^c < 0.5$, is preferable. Future studies will concentrate on optimizing η_I^c and on decreasing ohmic losses.

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