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K. Kontturi[a]; P. Forssell[a]; A. Ekman[a]
[a] DEPARTMENT OF CHEMISTRY, HELSINKI UNIVERSITY OF TECHNOLOGY, FINLAND

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Separation of Ions Using Countercurrent Electrolysis in a Thin, Porous Membrane

K. KONTTURI, P. FORSSELL, and A. EKMAN

HELSINKI UNIVERSITY OF TECHNOLOGY
DEPARTMENT OF CHEMISTRY
SF-02150 ESPOO 15, FINLAND

Abstract

Separation of ions in a thin, porous membrane using countercurrent electrolysis has been studied both theoretically and experimentally. A set of differential equations which describes the separation process is presented. These equations are solved numerically. The separation has been verified in the ternary systems NaCl–HCl–H_2O and NaBr–KBr–H_2O.

INTRODUCTION

Countercurrent electrolysis has been used to separate ions with different mobilities (*1, 2*). Long capillaries; columns that are packed with sand, glass beads, etc.; packs of diaphragms; and slit chambers with or without diaphragms are examples of different cell designs which have been described in the literature (*3–10*). In these cells very high separation factors are obtained even with isotopes, but only small amounts of electrolytes can be processed. Further disadvantages of the process are that it is very slow and it cannot be operated continuously. This means, in practice, that countercurrent electrolysis with the cell designs presented in the literature can be utilized only for analytical and preparative purposes.

If a cell that has a thin, porous membrane is used instead of long capillaries, packed columns, etc., the following advantages are gained: the separation process can be arranged so as to be continuous, large amounts of electrolytes can be treated, and the process is considerably more rapid. These advantages are obtained at the cost of the separation efficiency that could be accomplished in the light of the magnitude of the separation factor. This is not a problem in many cases, especially if we are not dealing with isotopes. On the other hand, the process can be repeated several times in order to achieve the enrichment desired.

THEORY

Transport processes in the membrane can be treated in the same way as in long capillaries, packed columns, etc., except that the ionic flows with respect to the membrane are not zero.

This complicates the mathematical solution of the transport problem. The transport of ions in the membrane is governed *locally* by

$$-j_i = \sum_{l=1}^{n} \nu_{il} \sum_{j=1}^{n} D_{ij} \frac{dc_j}{dx} - t_i \frac{I}{z_i F} - c_i v; \qquad i = 1, 2, \ldots n \qquad (1)$$

where j_i is the ionic flow, t_i is the transport number, z_i is the charge number, and c_i is the concentration of ion i, c_j is the concentration and D_{ij} are the diffusion coefficients of component j, ν_{il} is the stoichiometric coefficient of ion i, F is the Faraday constant, I is the electric current density, and v is the velocity of the solvent flow through the membrane (which is referred to as convection in this text). Quantities j_i and v are expressed in reference to the membrane.

In thin membranes the ionic flows j_i are constant. By intergrating Eqs. (1) over the membrane, the functions that are obtained for ionic flows are dependent on the electric current density, the convection, and the boundary concentrations on both sides of the membrane. However, this is not feasible, except in a few cases, because the dependencies of the diffusion coefficients and transport numbers on concentrations in multicomponent systems are not known (*11*). Therefore Eqs. (1) are approximated by Nemst-Planck Eqs. (2):

$$-j_i = \frac{\lambda_i c_i}{z_i^2 F^2} \left[RT \frac{d}{dx} (\ln c_i) + z_i F \frac{d\phi}{dx} \right] - c_i \nu; \quad i = 1, 2, \ldots, n \quad (2)$$

where λ_i is the molar conductivity of ion i and ϕ is the so-called electric potential. Equations (2) are solved by eliminating $d\phi/dx$ with the aid of the electroneutrality condition:

$$\sum_{i=1}^{n} z_i c_i = 0 \qquad (3)$$

and the relation between electric current density and ionic fluxes:

$$\sum_{i=1}^{n} z_i j_i = \frac{I}{F} \tag{4}$$

Although the quantities in Eqs. (2) are usually known, the closed form solution is rarely obtained and we have to use numerical methods (*12*). The solution of the problem depends on $3n - 1$ parameters, where n is the number of the ionic species; in other words, it depends on the electric current density, convection, ionic flows, and $2n - 2$ boundary concentrations. The set of differential Eqs. (2) together with Eqs. (3) and (4) determine n functional dependencies among these parameters of which $n - 1$ parameters can be solved when $2n$ parameters are given. However, the lack of an analytical solution makes it difficult to analyze the general behavior of the membrane process, even though the numerical solution has made the study of any particular situation possible.

In a ternary system of strong electrolytes with two univalent cations, which are denoted by subscripts 1 and 2, and one common anion, denoted by subscript 3, the following equations are obtained by eliminating $d\phi/dx$ from Eqs. (2) and by using Eqs. (3) and (4):

$$\begin{aligned}\frac{dy}{dX} &= \frac{1}{2}\left(\frac{l_3}{l_1} - \frac{l_3}{l_2}\right)v_3 y_1 + \frac{1}{2}\left(1 + \frac{l_3}{l_2}\right)v_3 y \\ &\quad + \frac{1}{2}\left[\left(1 + \frac{l_1}{l_3}\right)K_1 + \left(1 + \frac{l_2}{l_3}\right)K_2 - I_r\right] \\ \frac{dy_1}{dX} &= -\frac{1}{2}\left(\frac{l_3}{l_1} - \frac{l_3}{l_2}\right)v_3\frac{y_1^2}{y} + \frac{1}{2}\left[\left(1 - \frac{l_1}{l_3}\right)K_1\right. \\ &\quad \left. + \left(1 + \frac{l_1}{l_3}\right)K_2 + I_r\right]\frac{y_1}{y} + \frac{1}{2}\left(2\frac{l_3}{l_1} - \frac{l_3}{l_2} + 1\right)v_3 y_1 - K_1\end{aligned} \tag{5}$$

The above dimensionless forms were obtained by making the following substitutions:

$$y(X) = c_3(x)/c_0$$

$$y_1(X) = c_1(x)/c_0$$

$$y_2(X) = c_2(x)/c_0 = y(X) - y_1(X)$$

$$v_3 = vl/l_3RT = vl/D_3 = \dot{V}l/AD_3$$

$$K_i = j_il/c_0D_i, \qquad i = 1, 2, 3$$

$$I_r = Il/Fc_0D_3$$

$$X = x/l$$

In these equations $l_i = \lambda_i/z_i^2F^2$ and is called the ionic mobility, and $D_i = l_iRT$ and is called the ionic diffusion coefficient. The thickness of the membrane is l, and c_0 is the scaling concentration, normally $c_0 \simeq c_3(l)$.

Even in this simple ternary case we are not able to achieve a closed form solution. We have eight parameters, two of which can be solved if six parameters are given. In many cases we want to obtain either the ionic flows for the cations or the electric current density and convection when the other six parameters are given. This leads us to a problem in which we have to solve the two-point boundary value problem. If we want to determine the boundary concentrations on the other side of the membrane when the other parameters are given, we have an initial value problem which is much easier to solve numerically than the boundary value problem. In our experience with the numerical solution of the transport problems we have noticed that by using the shooting method as described in Ref. *12* we have gotten good results. The values obtained from the Goldman constant field approximation (*13*) have been used as the initial guesses for the parameters to be iterated by the shooting method. We have been able to determine the solution in almost every case considered. With very high values of electric current density and/or convection the calculation routine fails, and we have to use more sophisticated or suitable methods such as multiple shooting and finite differences.

Upon studying the dimensionless parameters I_r, v_3, and K_1, K_2, a very important fact can be deduced. Suppose that we fix the value of the selectivity ratio (S):

$$S = y_1(1)y_2(0)/y_1(0)y_2(1) \tag{6}$$

(S is defined so that $S > 1$) and change the thickness of the membrane. We can easily conclude that if l increases, v, I and j_1, j_2 decrease and vice versa. This is a result of the fact that if S is constant, the dimensionless (variables) v_3, I_r, and K_1,K_2 are also constant. This in reality means that the thicker the membrane, the slower the process. That's why it is reasonable to make the membrane as thin as possible. Then, of course, the practical aspects have to be taken into account: the increase in ionic flows demands an increase also in the electric current density and convection, and therefore the membrane may be so thin that the heat generated by the high electric current and voltage spoils the membrane or causes disturbances in the transport phenomenon (boiling, etc.). The membrane must be thick enough so that the stirring in the bulk phases does not stir the whole porous membrane. The convection must not be so big that the flow in the pores of the membrane is turbulent.

To get an idea of how the selectivity ratio (S) depends on convection, we consider a limiting case in which the flows of cations are nearly zero, i.e., $j_i \simeq j_2 \simeq 0$. After integrating Eqs. (2) over the membrane, we obtain the following dimensionless form for S:

$$S = \exp\left[\left(\frac{l_3}{l_1} - \frac{l_3}{l_2}\right)v_3\right] \tag{7}$$

Equation (7) points out clearly that the selectivity ratio is exponentially dependent on convection when the cation flows are small enough. Actually it can be shown by numerical calculation and by experiments that although the cation flows are not zero, similar dependencies are obtained. This fact leads us to conclude that in practice it is reasonable to use as high a convection as possible and as thin a membrane as possible. Notice that the convection and the selectivity ratio determine the value of the electric current density for that particular situation.

EXPERIMENTAL

The first aim of the experiments presented in this paper was to verify the exponential relation between the selectivity ratio and the convection (Eq. 7). The membrane constant A/l (A is the effective area of the membrane and l is its thickness) is obtainable in the same experiments made in the ternary system NaCl–HCl–H_2O.

The measurements were done by feeding a solution with the concentrations c^0_{NaCl}, c^0_{HCl} and volume flow $\dot{V}^0$ into compartment α. When the stationary state was reached a solution with composition c^α_{NaCl}, c^α_{HCl} and volume flow $\dot{V}^\alpha$ flowed out of compartment α (see Fig. 1). Boundary concentrations, convections, and electric current were chosen so that, according to the calculations, zero fluxes for cations were obtained, i.e., we should have $c^\alpha_{NaCl} = 2c^0_{NaCl}$; $c^\alpha_{HCl} = 2c^0_{HCl}$, when $\dot{V}^\alpha = \frac{1}{2}\dot{V}^0$.

The second aim of the experimental work was to test the actual separation process in the ternary system NaBr–KBr–H_2O. The flows of potassium and sodium and the selectivity ratio were determined with a constant concentration ratio of NaBr and KBr in compartment β and with a constant sum of the fluxes of K^+ and Na^+ while varying the electric current density and convection through the membrane. Pure water with a volume flow $\dot{V}^0$ is fed into compartment α, and the enriched solution (relative to the more rapid cation, here K^+) flows out of compartment α with volume $\dot{V}^\alpha$ (see Fig. 1).

The apparatus was made of Plexiglas. The porous membrane was Millipore SC with pore size 8.0 μm. The solution flows were regulated by peristaltic pumps (DeSaga 132100 and Ismatec ip-12) and the flow rates were determined by weighing the solution volumes. The electric current was kept constant with the aid of Potentiostat Type 120 by Sycopel Scientific Ltd. Hydrogen ion was analyzed by titration, sodium and potassium by flame photometry, and bromide and chloride by ion selective electrodes.

RESULTS

The first quantity that was determined was the value of the membrane constant *A/l*. It was measured according to the method described by Rastas et al. (*14*), and the result was *A/l* = 200 cm. It is almost the same as the value proposed by Hashitani and Tamamushi (*15*). The membrane constant that they obtained for the Millipore type membrane was the same as the calculated from the ratio of the geometrical area to the thickness of the membrane. By using their calculation method the value of *A/l* in the

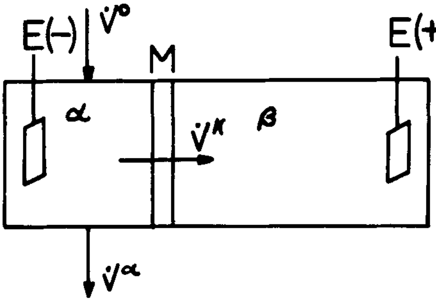

FIG. 1.Schematic drawing of the cell. Thin porous membrane (M) divides the cell into two compartments α and β. The volume of compartment β is so large compared to the volume of compartment α that the concentrations in compartment β remain constant during the measurements. The solutions in the compartments α and β are well mixed. E(−) is cathode and E(+) is anode, and they are reversible to the common anion i.e. AgCl/Ag electrode for $NaCl-HCl-H_2O$ system and AgBr/Ag electrode for $NaBr-KBr-H_2O$ system. By pumping the solution with constant rate ($\dot{V}^0$) to compartment α, the convection through the porous membrane ($\dot{V}^k = \dot{V}^0 - \dot{V}^\alpha$) can be easily regulated because this compartment is closed.

particular case is 3.14 $cm^2/0.015$ cm = 210 cm. After obtaining a value for A/l we can calculate the values of real physical parameters from the dimensionless parameters given by the mathematical model.

System NaCl–HCl–H_2O

The results obtained in the ternary system NaCl–HCl–H_2O in the case where $j_{Na^+} \simeq j_{H^+} \simeq 0$ are shown graphically in fig. 2. In Table 1 we have listed the results in dimensionless form. The exponential dependence of the selectivity ratio on convection is evident. With the aid of Fig. 2 we can estimate the value of the membrane constant A/l from the measurements. Equation (7) gives us the relation

$$\frac{A}{l} = \frac{D_2 - D_1}{D_1 D_2 \cdot 2.303K}$$

where K is the slope of the line $\lg S = K v_3$. The value that was obtained for K was 0.408 cm^3/s and gives $A/l = 196$ cm, which is in excellent agreement with the value 200 cm that was obtained in the separate measurement.

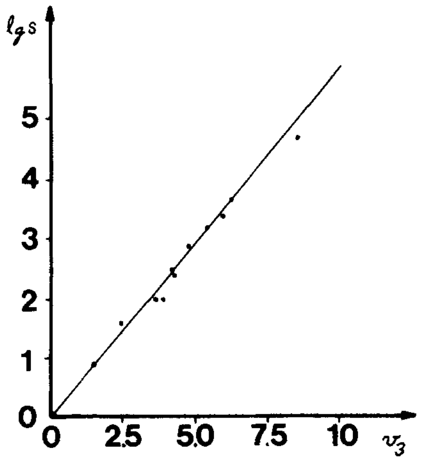

FIG. 2. The experimentally obtained relationship between the logarithm of the selectivity ratio (S) and the convection (v_3) through the membrane in the system NaCl–HCl–H_2O when the cation fluxes are vanishingly small.

TABLE 1

Experimental Results in the System NaCl–HCl–H_2O[a]

$-I_r$	v_3	$y^{\alpha}_{H^+}$	$y^{\alpha}_{Na^+}$	$y^{\beta}_{H^+}$	$y^{\beta}_{Na^+}$	K_{H^+}	K_{Na^+}	S
2.3	1.5	0.97	0.097	0.56	0.47	−0.023	−0.016	8.4
4.0	2.5	1.05	0.090	0.25	0.73	+0.025	+0.07	34
4.6	3.2	1.05	0.096	0.15	0.97	−0.034	+0.02	71
5.3	4.0	1.03	0.030	0.36	1.20	+0.046	−0.01	110
6.2	5.0	1.10	0.004	0.24	0.80	−0.009	+0.008	920
6.3	4.5	0.95	0.060	0.05	0.90	+0.048	−0.000	290
6.8	5.7	1.00	0.004	0.014	0.87	+0.10	+0.009	1,550
7.5	6.2	0.98	0.005	0.078	1.00	+0.027	+0.005	2,500
9.5	6.6	1.10	0.004	0.056	1.00	−0.14	−0.04	4,900
12.9	8.95	1.10	0.00015	0.155	1.00	+0.11	−0.002	47,000
13.6	9.3	1.06	0.00005	0.036	1.00	−0.12	−0.0007	59,000

[a] The measured concentrations and fluxes are presented as a function of electric current and convection. Dimensionless values for parameters are calculated from the experimental ones by taking $A/l = 200$ cm, the scaling concentration $c_0 = 0.01$ mol/dm^3, and the ionic mobilities in infinitely dilute solution $l_{H+} = 349.81$, $l_{NA+} = 50.10$, $l_{Cl-} = 76.50$ Ω^{-1}cm^{2}mol^{-3}. ($K_i = J_i l/l_i RTc_0$, $I_r = Il/c_0 F l_{Cl}-RT$, $v_3 = \dot{V}l/Al_{Cl}RT$.)

System NaBr–KBr–H_2O

In Table 2 we have listed results in the system NaBr–KBr–H_2O. The values for parameters were chosen so that total concentration in the α compartment remained constant. In Fig. 3 we have plotted the logarithm of selectivity ratio (S) against convection (v_3) and again we can see the exponential dependence of S on convection. The intercept of the lg S axis corresponds to the system where convection vanishes and the transport of electrolytes is due to the electrical conduction and diffusion. In that case $S \simeq 1.5$, which can be predicted by calculations.

CONCLUSIONS

The mathematical model presented predicts the exponential dependence of the selectivity ratio on convection when the fluxes of ions to be separated (here cations) are zero. When the cation fluxes have nonzero values it is not possible to obtain an analytical relationship between selectivity ratio and convection. However, we can study the dependence of the selectivity ratio on electric current density, convection, and concentrations by numerical methods. If electric current density and convection are chosen so that the

TABLE 2

Experimental Results in The System NaBr–KBr–H_2O[a]

$-I_r$	v_3	$y^{\alpha}_{K^+}$	$y^{\alpha}_{Na^+}$	$-K_{K^+}$	$-K_{Na^+}$	S
11.2	3.61	0.63	0.33	1.51	1.23	1.91
15.1	5.86	0.66	0.29	1.58	1.08	1.28
19.7	8.06	0.67	0.27	1.60	1.01	2.48
24.5	10.4	0.70	0.25	1.67	0.93	2.80
30.0	13.2	0.74	0.21	1.77	0.78	3.52

[a] The measured concentrations and fluxes are presented as a function of electric current and convection. Dimensionless values for parameters are calculated from experimental ones by taking $A/l = 200$ cm, the scaling concentration $c_0 = 0.01$ mol/dm^3, and the ionic mobilities in infinitely dilute solution $l_{Na^+} = 50.10$, $l_{K^+} = 73.50$, $l_{Br^-} = 78.14$ Ω^{-1}cm^{2}mol^{-1}. Concentrations in the β compartment are $y^{\beta}_{Na^+} = y^{\beta}_{K^+} = 0.5$. ($K_i = J_i l/l_i RTc_0$, $I_r = Il/c_0Fl_{Br^-}RT$, $v_3 = \dot{V}l/Al_{Br^-}RT$.)

total concentration is constant in the α compartment in different cases, we obtain an exponential relationship.

The ternary system NaCl–HCl–H_2O was used to verify experimentally the exponential relationship of the selectivity ratio on convection up to a value of about 60,000 when the cation fluxes are approximately zero. Continuous separation was studied in the system NaBr–KBr–H_2O by

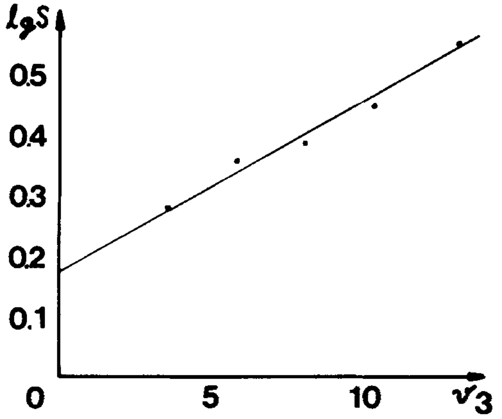

FIG. 3. The experimentally obtained relationship between the logarithm of the selectivity ratio (S) and the convection (v_3) through the membrane in the system NaBr–KBr–H_2O. The detailed data are given in Table 2.

keeping the total concentration and the sum of cation fluxes constant while varying the electric current density and convection. Also in this case the increase in convection causes the exponential increase in selectivity ratio.

The theoretical model and experiments predict that separation increases rapidly with increased convection, but in practice the lability of the system increases at the same time. This lability is due to the steep concentration profiles at high convections, and it sets practical limits for separation by this method.

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