This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The Effect of Membrane Thickness on Countercurrent Electrolysis in a Thin, Porous Membrane

K. Kontturi[a]; H. Pajari[a]
[a] DEPARTMENT OF CHEMISTRY, HELSINKI UNIVERSITY OF TECHNOLOGY, ESPOO, FINLAND

To cite this Article Kontturi, K. and Pajari, H.(1986) 'The Effect of Membrane Thickness on Countercurrent Electrolysis in a Thin, Porous Membrane', Separation Science and Technology, 21: 10, 1089 — 1099
To link to this Article: DOI: 10.1080/01496398608058399
URL: http://dx.doi.org/10.1080/01496398608058399

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, 21(10), pp. 1089-1099, 1986

The Effect of Membrane Thickness on Countercurrent Electrolysis in a Thin, Porous Membrane

K. KONTTURI and H. PAJARI

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

Downloaded At: 13:18 25 January 2011

Abstract

The effect of membrane thickness on countercurrent electrolysis in a porous membrane is studied and compared with the increase of convection. It was verified both theoretically and experimentally that the separation efficiency increases considerably when the membrane is made thicker. When the fluxes of ions to be separated deviate from zero, no simple relationship between the logarithm of selectivity ratio and convection could be found. Both computed and measured results showed that $\lg S = f(v^c)$ is strictly nonlinear. Results show that in the light of separation efficiency it is more useful to use higher convections than thicker membrane. This is, of course, done at the cost of increased power consumption. Therefore, in practice the most reasonable approach is a compromise between increased convection and making the membrane thicker.

INTRODUCTION

It has been shown that countercurrent electrolysis in a thin, porous membrane can be used to separate ions of different mobilities both in systems consisting of strong electrolytes (*1-3*) and weak electrolytes (*4*). In the latter case, however, the dissociation constants make significant contributions to the separation in addition to the differences in mobilities (*4*). A special multi-ion case, binary system with trace ions, has also been studied (*5*). In this paper we investigate how the separation is influenced by the membrane thickness. It must, however, be remembered that in any case the membrane thickness will be orders of magnitude smaller than in conventional cell construction for countercurrent electrolysis; for a

Copyright © 1986 by Marcel Dekker, Inc. 0149-6395/86/2110-1089$3.50/0

review, see Ref. 6. This, in fact, means that the actual separation process is still basicly a stationary process and not a nonstationary one.

Using the theoretical model described in our previous papers (*1, 7, 8*), it can be shown that from the point of view of separation efficiency it is better to increase convection than to make the membrane thicker. However, there are limitations which prevent us from increasing convection beyond a certain value, namely, the lability of the system at high convections and the disturbances (boiling, thermodiffusion, etc.) due to the heat generated by the high electric current (as a result of high convection) and by the high voltage. Of course, power consumption is one of the practical aspects which speaks on behalf of making the membrane thicker. That is why it is reasonable in many cases to use a thicker membrane to decrease both convection and electric current, even though the separation efficiency is decreased at the same time.

Downloaded At: 13:18 25 January 2011

THEORY

Let us first examine a ternary case where the ionic fluxes are zero, i.e., $J_1 = J_2 = 0$. Using the results derived in our earlier paper (*2*) we have*

$$S = \left[\frac{c_1(x = l)}{c_1(x = 0)}\right]^{1/z_1}\left[\frac{c_2(x = 0)}{c_2(x = l)}\right]^{1/z_2} \tag{1}$$

and

$$\ln S = \frac{F^2}{RT}\left(\frac{|z_1|}{\lambda_1} - \frac{|z_2|}{\lambda_2}\right)lv \tag{2}$$

where S is the selectivity ratio ($S \geqslant 1$), λ_i is the molar conductivity of ion i, z_i is its charge number, c_i is its concentration, l is the thickness of the membrane, and v is the velocity of the solvent in a fixed coordinate system. In dimensionless form, Eq. (2) reads

$$\ln S = \left[\frac{D_0}{|z_1|D_1} - \frac{D_0}{|z_2|D_2}\right]v^c \tag{3}$$

where D_0 is the scaling diffusion coefficient, D_1 and D_2 are the ionic diffusion coefficients ($D_i = l_iRT = \lambda_iRT/z_i^2F^2$), and v^c is the dimensionless convection defined as $v^c = vl/D_0 = Vl/AD_0$.

*Note the typographical error in Ref. *2* in Eq. (2) and in Table 1.

Considering Eq. (3), it can be easily seen that the right-hand side of this equation has the same value if either the value of $\dot{V}$ or the value of l is made n times bigger. In other words, according to this relationship the same value for the selectivity ratio S is obtained if, e.g., either $\dot{V}$ is doubled or l is doubled. However, it must be kept in mind that the ionic fluxes are zero, i.e., $J_1 = J_2 = 0$, and, therefore, doubling the quantities only gives indication that both methods have a similar limiting behavior.

Let us define the selectivity ratio (S_1) in the case where $\dot{V} = \dot{V}_b$ and $l = l_b$ as

$$S_1 = \exp\left[\frac{D_0}{|z_1|D_1} - \frac{D_0}{|z_2|D_2}\right] v_b^c \tag{4}$$

where $v_b^c = \dot{V}_b l_b / AD_0$. Now, if either $\dot{V}$ or l is made n times bigger, i.e., $l = nl_b$ or $\dot{V} = n\dot{V}_b$ we obtain, using Eq. (4),

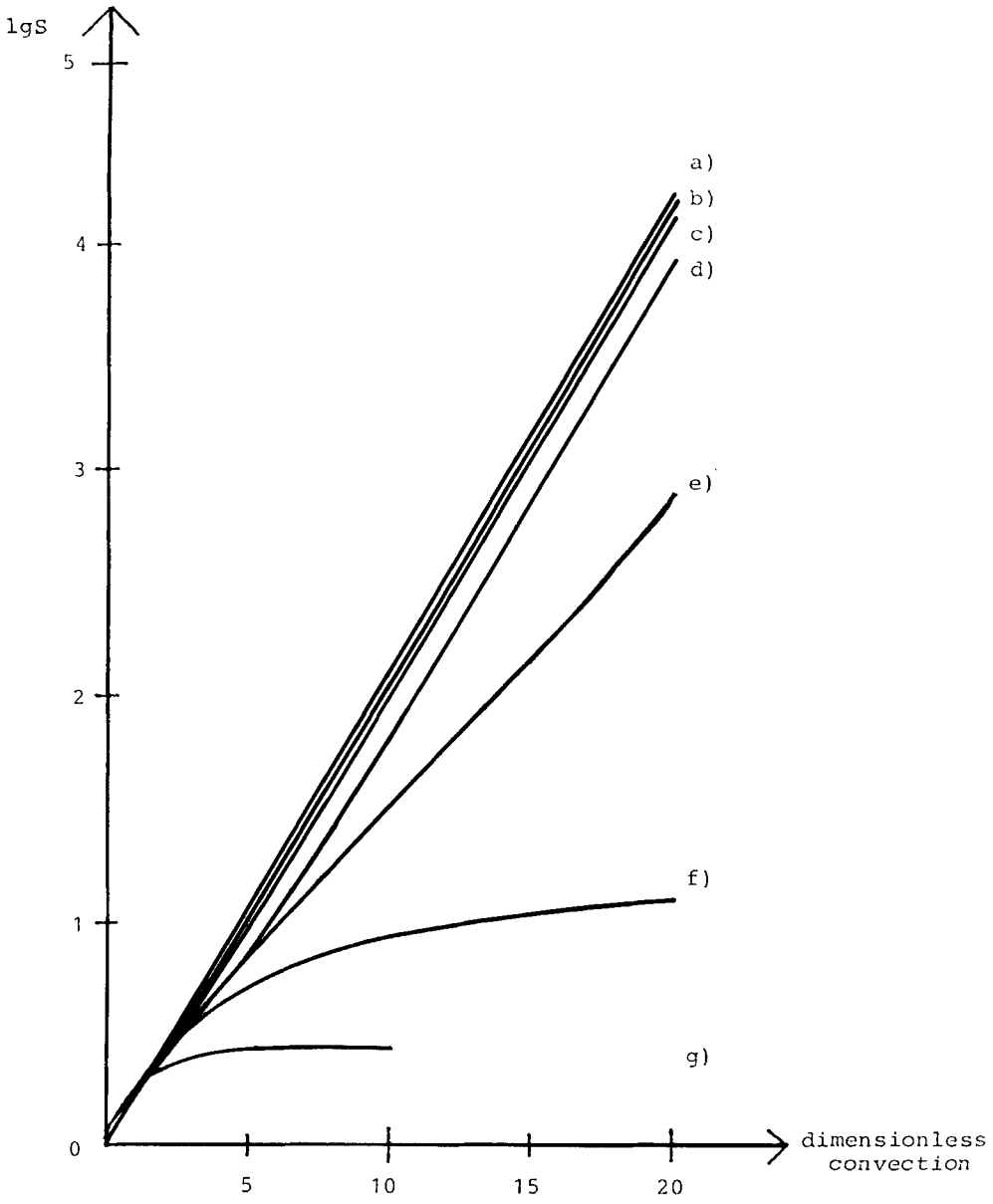
$$S_n = S_1^n \tag{5}$$

where the subscript n, of course, denotes either the number of membranes or the quantity $\dot{V}/\dot{V}_b$.

Equation (5) is important since it offers us an approximate way to estimate how much the selectivity ratio increases when the number of membranes is increased. As can be seen, the number of membranes has a drastic effect on the selectivity ratio because of its exponential dependence on n. Equation (5) has another important application. If several membranes are put together to form a stack, it is known that the effective thickness of this stack is not obtained by summing up the thicknesses of the individual membranes. This is due to the fact that the hydrodynamic situation for each of the membranes is not the same any more. Therefore Eq. (5) can be used to evaluate the "real" number of membranes as referred to some well-defined case where S_1 is known.

In the case of nonzero ionic fluxes the selectivity ratio's dependence on convection reaches such a complicated form that its solution is possible only by numerical methods. In order to elucidate the behavior of the transport process when making l's value n times bigger or when making $\dot{V}$'s value n times bigger, we performed numerical calculations in the system NaCl-KCl-H_2O. Some examples of these calculations are presented in Fig. 1 and in Tables 1 and 2. It can be clearly seen that increasing convection $\dot{V}$ has a much better effect on increasing the separation efficiency than if the equivalent number of membranes is increased. It must be remembered that as the convection is increased, the electric current also strives to increase. On the one hand, electric power

Downloaded At: 13:18 25 January 2011



Downloaded At: 13:18 25 January 2011

FIG. 1. Calculated relationships between the logarithm of the selectivity ratio and the convection or the number of membranes (the thickness of the membrane) in the system NaCl-KCl-H_2O. a): lg S vs convection or the number of membranes when the cationic fluxes are zero (cf. Eq. 3). b), c), and d): lg S vs convection when the sum of the cationic fluxes is constant (cf. Table 1). e), f), and g): lg S vs the number of membranes when the sum of the cationic fluxes is constant (cf. Table 2). The sum of the cationic fluxes in d) and g) is

TABLE 1

Calculated Results for the System NaCl-KCl-H_2O When Convection Is Increased and the Sum of the Cationic Fluxes Is Constant.[a] $Y_{Cl^-}(\bar{x} = 0) = Y_{Cl^-}(\bar{x} = 1) = 1$; $Y_{Na^+}(\bar{x} = 1) = Y_{K^+}(\bar{x} = 1) = 0.5$; $K_{K^+}/K_{Na^+} = Y_{K^+}(\bar{x} = 0)/Y_{Na^+}(\bar{x} = 0) = S$

	$-(K_{K^+} + K_{Na^+}) = 0.138$ (Curve 1b)		$-(K_{K^+} + K_{Na^+}) = 0.276$ (Curve 1c)		$-(K_{K^+} + K_{Na^+}) = 0.689$ (Curve 1d)	
v^c	$-I_r$	S	$-I_r$	S	$-I_r$	S
1	2.55	1.66	2.86	1.69	3.78	1.72
2	4.72	2.60	5.02	2.55	5.94	2.41
3	6.80	4.08	7.11	3.88	8.03	3.40
5	10.8	10.2	11.1	9.29	12.1	7.10
7.5	15.8	33.5	16.1	29.7	17.0	20.4
10	20.7	112	21.0	99.0	21.9	64.8
20	41.0	15,100	41.3	13,100	42.2	8410

[a]Definitions of dimensionless parameters: $v^c = \dot{V}^c/(A/l)D_0$; $I_r = I/(A/l)FD_0c_0$; $K_i = j_i/(A/l)D_0c_0$; $Y_i = c_i/c_0$; $\bar{x} = x/l$, where F is Faraday's constant. A/l, c_0, and D_0 were chosen to be 10 cm, 0.1 mol/dm^3, and 2×10^{-5} cm^2/s, respectively.

TABLE 2

Calculated Results for the System NaCl-KCl-H_2O When the Number of Membranes (the thickness of the membrane) Is Increased and the Sum of the Cationic Fluxes Is Constant.[a] $Y_{Cl^-}(\bar{x} = 0) = Y(\bar{x} = 1) = 1$; $Y_{Na^+}(\bar{x} = 1) = Y_{K^+}(\bar{x} = 1) = 0.5$; $K_{K^+}/K_{Na^+} = Y_{K^+}(\bar{x} = 0)/Y_{Na^+}(\bar{x} = 0) = S$

	$-(K_{K^+} + K_{Na^+})/n = 0.138$ (Curve 1e)		$-(K_{K^+} + K_{Na^+})/n = 0.276$ (Curve 1f)		$-(K_{K^+} + K_{Na^+})/n = 0.689$ (Curve 1g)	
n	$-I_r/n$	S	$-I_r/n$	S	$-I_r/n$	S
1	2.55	1.66	2.86	1.69	3.78	1.72
2	2.51	2.55	2.82	2.45	3.74	2.19
3	2.47	3.72	2.79	3.25	3.73	2.46
5	2.42	7.20	2.74	5.00	3.70	2.68
7.5	2.37	15.1	2.70	6.90	3.71	2.70
10	2.35	31.3	2.69	8.52	3.71	2.70
15	2.33	145	2.67	10.8	—	—
20	2.32	780	2.67	12.2	—	—

[a]Definitions of dimensionless parameters: $v^c = \dot{V}^c/(A/l)D_0$; $I_r = I/(A/l)FD_0c_0$; $K_i = j_i/(A/l)D_0c_0$; $Y_i = c_i/c_0$; $\bar{x} = x/l$, where F is Faraday's constant. A/l_b, c_0, and D_0 were chosen to be 10 cm, 0.1 mol/dm^3, and 2×10^{-5} cm^2/s, respectively.

five times and in c) and f) two times greater than in b) and e). This sum is equal in b) and e). Notice that the change in the *dimensionless* convection $v^c = \dot{V}^c/(A/l)D_0$ is the same if the convection ($\dot{V}^c$, the volumetric rate) or the number of membranes (l, membrane thickness) is changed in the same ratio.

Downloaded At: 13:18 25 January 2011

consumption is directly proportional to the square of electric current, while on the other hand, thickening the membrane increases the power consumption approximately linearly (assuming as a first approximation that the membrane behaves as a linear resistance). Therefore, in practice a compromise is necessary between making the membrane thicker and increasing the convection. Of course, this compromise is greatly dependent on the construction of the experimental setup.

APPARATUS

The cell construction (*2*) used so far has been a typical one for laboratory purposes. Now an approach toward a more practical setup was done. The cell was chosen to be of the filter-press type. The experimental setup for the separation of cations is schematically described in Fig. 2.

Downloaded At: 13:18 25 January 2011

The porous membrane was 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. Thus the thickness of the porous membrane as a whole was relatively large, ~0.8 mm. This relatively tight membrane made the stirring of each compartment possible by circulating the solution with the aid of a peristaltic pump (Ismatec ip-12).

In measurements with thicker membranes, similar porous membranes were separated from each other with a stirred compartment in order to obtain an integer value for n, i.e., for the equivalent "number" of the membrane. The surface area of the membranes was 2.0 cm^2.

Pure water is pumped (Ismatec ip-12) at a constant rate into Compartment 0, and a part of this flow is pumped out of Compartment 0 ($\dot{V}^u$) and the rest overflows to Compartment 1, forming the convection ($\dot{V}^c = \dot{V}^f - \dot{V}^u$) through the porous membrane. The solutions from which the cations are enriched is fed into Compartment n ($\dot{V}^n$).

Cathode and anode are Pt plates. The anolyte is 0.1 mol/dm^3 $NaSO_4$ solution and the catholyte is 0.1 mol/dm^3 KCl solution, and their concentrations are kept constant by circulating these solutions. Anion exchange membranes (Neosepta AFN, Tokuyama Soda Co.) are used to separate the electrode compartments from the cell Compartments 0 and n. Cation-exchange membranes (Nafion) are used to be able to control the separation process more effectively. The first cation-exchange membrane (C1) enables the determination of the sum of cationic fluxes since the total concentration in Compartment 0 is fixed by the electric current and by $\dot{V}^f$. With knowledge of $\dot{V}^u$, the sum of these fluxes can be

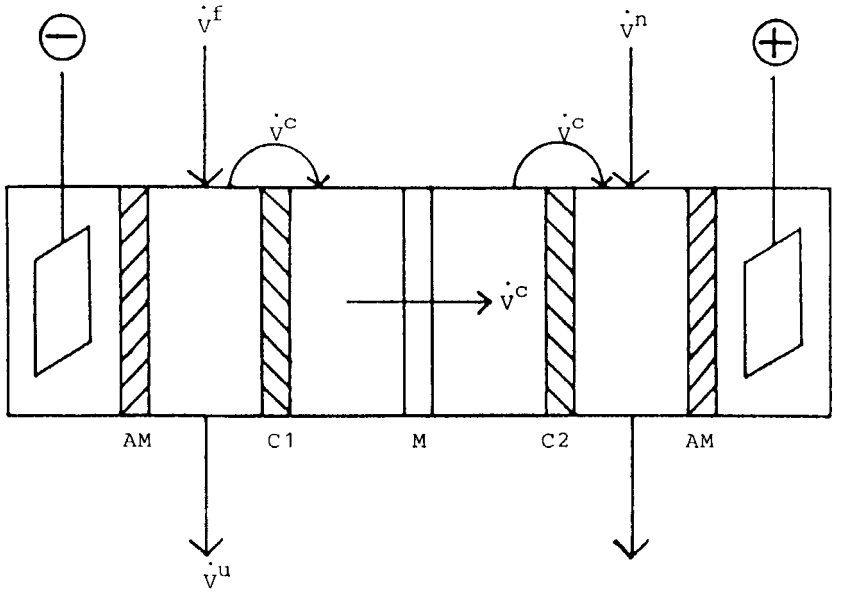


FIG. 2. Schematic drawing of the cell. For details, see the text.

Downloaded At: 13:18 25 January 2011

determined. The second cation-exchange membrane (C2) governs the concentrations in the output stream $\dot{V}^c + \dot{V}^n$ because of the electrodialytic nature of Compartment *n*.

A potentiostat (PAR 173) is used to control the electric current through the membranes.

ANALYSIS

The cations were analyzed both by flame photometry and by AAS. The potentiometric titration of the common anion was used to check the results of flame photometry and AAS.

MEASUREMENTS

The experiments were carried out in the ternary system NaCl-KCl-H_2O. The total concentration of the 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 of the

experiments the convection and electric current were kept constant and the number of membranes was varied from 1 to 4. The electric current was calculated and set at have such a value that the total concentration in the outflow stream ($\dot{V}^u$) was about 10^{-2} mol/dm^3. A set of experiments employing one membrane but at higher convections was carried out to elucidate that the increase of convection has a much more advantageous effect on separation than making the membrane thicker. These experiments were equivalent to those in which the membrane was thicker in the sense that the sum of the cationic fluxes and the dimensionless convections were the same (compare with Tables 1 and 2).

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 stationary state varied from several hours to several days.

Downloaded At: 13:18 25 January 2011

RESULTS

The results obtained in the ternary system NaCl–KCl–H_2O are shown graphically in Fig. 3. Table 3 lists the results in dimensionless form. The functional dependence of the selectivity ratio on the membrane thickness and on convection resembles the computed behavior in Fig. 1. As can be seen, the separation efficiency is better when the convection is increased than if the membrane is made thicker. This experimental behavior again indicates the validity of the theoretical model used. We tried to explain the results obtained by using a theoretical model based on the Nernst-Planck equations and on mass balances. This theoretical model was not able to predict the experimental results. The deviation from theoretical behavior was especially significant when separation is weak. Experimentally and theoretically, we were able to show that this deviation was mainly due to the cation-exchange membranes C1 and C2. Furthermore, we have shown that the mobilities of sodium and potassium ions are almost equal in the cation-exchange membrane (*9, 10*). However, because of the polarization phenomenon on the surface of ion-exchange membranes, quite large separations can be obtained due to the diffusion process taking place in the polarization layer. The effect of this layer will be considered later on, since this effect is of minor interest in the present study.

As mentioned earlier, the time needed to reach a stationary state is relatively long when the membrane is thick. In practice, this means that disturbances in feeding increase the duration of the process. The effect of membrane thickness on the time required to reach a stationary state will be studied in a subsequent paper (*11*).

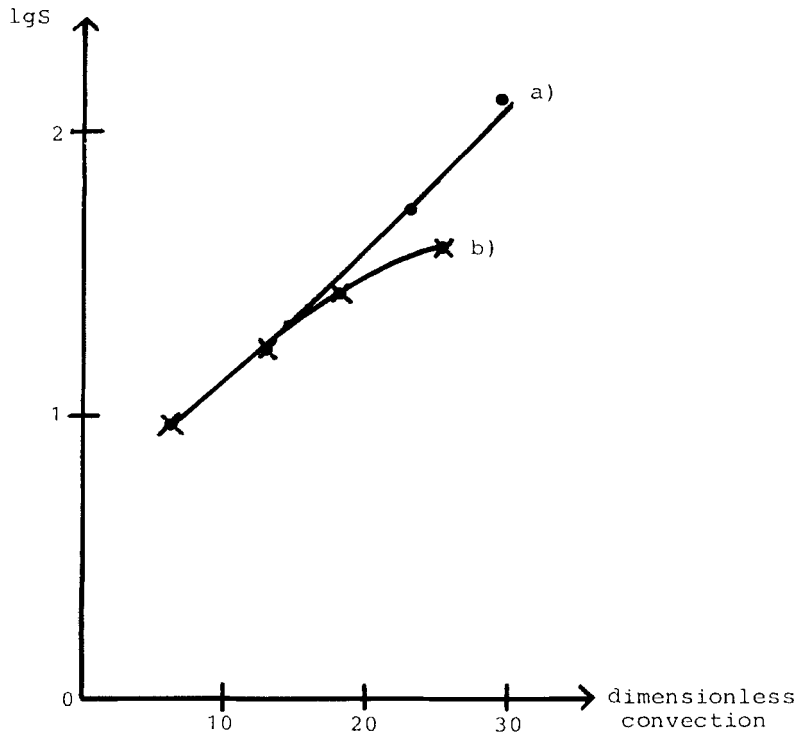


FIG. 3. Experimentally obtained relationships between the logarithm of the selectivity ratio and the convection and the number of membranes when the sum of the cationic fluxes is constant. a) lg S vs convection. b) lg S vs the number of membranes.

Downloaded At: 13:18 25 January 2011

The filter-press type cell construction worked well in the measurements described in this paper.

CONCLUSIONS

In countercurrent electrolysis in a thin, porous membrane, thickening of the porous membrane increases the separation efficiency considerably. In the case of zero cationic fluxes, a closed form solution of the exponential type (cf. Eq. 5) is obtained. Even though a stationary state is reached much slower when the membrane is made thicker and the separation efficiency is worse than in the case where the convection is increased, the system's advantage is a smaller consumption of electric power.

Downloaded At: 13:18 25 January 2011

TABLE 3
Experimental Results for the System NaCl-KCl-H_2O; $Y_{Na^+} = Y_{K^+} = 1$ in the Feeding Solution[a]

Increase of convection (one membrane) (Curve 2a)						Increase of the number of membranes (V^c = constant) (Curve 2b)					
v^c	$-I_r$	$10^3 Y^0_{K^+}$	$10^3 Y^0_{Na^+}$	$-(K_{K^+} + K_{Na^+})$	S	n	$-I_r/n$	$10^3 Y^0_{K^+}$	$10^3 Y^0_{Na^+}$	$-(K_{K^+} + K_{Na^+})/n$	S
6.36	0.816	92	11.0	0.134	9.2	1	0.816	92	11.0	0.134	9.2
14.3	1.63	99	4.75	0.135	20.8	2	0.816	96	5.60	0.132	17.1
22.8	2.45	100	1.90	0.132	52.6	3	0.816	97	3.60	0.131	26.8
29.2	3.27	100	0.75	0.131	133	4	0.816	100	2.82	0.147	39.0

[a]Definitions of dimensionless parameters: $v^c = \dot{V}^c/(A/l)D_0$; $I_r = I/(A/l)FD_0c_0$; $K_i = j_i/(A/l)D_0c_0$; $Y_i = c_i/c_0$, where F is Faraday's constant. A/l_b, c_0, and D_0 were chosen to be 10 cm, 0.1 mol/dm^3, and 2×10^{-5} cm^2/s, respectively.

Studies of a new kind of system in which the porous membranes are connected in series with the aid of ion-exchange membranes are in progress.

Acknowledgment

The Academy of Finland is thanked for financial support.

REFERENCES

1. K. Kontturi, P. Forssell, and A. Ekman, *Sep. Sci. Technol., 17,* 1195 (1982).
2. P. Forssell and K. Kontturi, *Ibid., 18,* 205 (1983).
3. A. Ekman, P. Forssell, K. Kontturi, and G. Sundholm, *J. Membr. Sci., 11,* 65 (1982).
4. K. Kontturi, T. Ojala, and P. Forssell, *J. Chem. Soc., Faraday Trans. I, 80,* 3379 (1984).
5. K. Kontturi, *Sep. Sci. Technol., 21,* 591 (1986).
6. K. Wagener, H. D. Freyer, and R. A. Bilal, *Sep. Sci., 6,* 483 (1971).
7. A. H. Sipilä, A. Ekman, and K. Kontturi, *Finn. Chem. Lett.,* p. 97 (1979).
8. K. Kontturi and A. H. Sipilä, *Ibid.,* p. 97 (1983).
9. K. Kontturi, A. Ekman, and P. Forssell, *Acta Chem. Scand., A39,* 273 (1985).
10. P. Forssell, K. Kontturi, and A. Ekman, *Ibid., A39,* 278 (1985).
11. K. Kontturi and A.-K. Kontturi, To Be Published.

Received by editor February 11, 1986

Downloaded At: 13:18 25 January 2011