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

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

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

To cite this Article Forssell, P. and Kontturi, K.(1983) 'Experimental Verification of Separation of Ions Using Countercurrent Electrolysis in a Thin, Porous Membrane', Separation Science and Technology, 18: 3, 205 — 214
To link to this Article: DOI: 10.1080/01496398308058331
URL: http://dx.doi.org/10.1080/01496398308058331

SEPARATION SCIENCE AND TECHNOLOGY, 18(3), pp. 205–214, 1983

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

P. FORSSELL and K. KONTTURI

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

Abstract

Countercurrent electrolysis in a porous membrane has been used to separate cations in systems LiCl–NaCl–H_2O, LiCl–$CaCl_2$–H_2O, LiCl–$BaCl_2$–H_2O, LiCl–KCl–H_2O, and LiCl–NaCl–KCl–H_2O. The experimental results confirm the relationship between the separation efficiency and the difference in ionic equivalent conductance. Furthermore, the dependence of the separation efficiency on the outflow of the enriched solution and on the convection through the membrane has been verified.

INTRODUCTION

In a previous paper (*1*) we described the method of separation of ions in a thin and porous membrane using countercurrent electrolysis. The treatment of this method is continued by verifying experimentally the dependence of separation efficiency on the difference in ionic equivalent conductance on the convection through the membrane and on the outflow rate of enriched solution.

Mathematical analysis of transport in porous membrane is done by the Nernst-Planck equations

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

where j_i is the flux of the ion i, λ_i is its molar conductivity, z_i is its charge number, c_i is its concentration, and v is the velocity of the solvent, i.e.,

0149-6395/83/1803-0205$3.50/0

convection in a fixed coordinate system. There is one Nernst-Planck equation for every ion, with each equation containing the common quantity, the derivate of the electric potential, $d\phi/dx$. These flux equations are used in the sense described in Refs. *2–4* to give approximate values for diffusion coefficients of components and for transport numbers of ions (ionic constituents). In practice this means that we eliminate $d\phi/dx$ from the set of differential equations (1) with the aid of the electroneutrality condition (*1*).

Let us consider a system where there are two electrolytes with a common ion and solvent. We define the selectivity ratio with

$$S = \left[\frac{c_1(x=l)}{c_1(x=0)}\right]^{1/z_1} \bigg/ \left[\frac{c_2(x=0)}{c_2(x=l)}\right]^{1/z_2} \tag{2}$$

where l is the thickness of the membrane, and subscript 1 denotes the slower and subscript 2 the faster moving ion to be separated. With the aid of definition (2), we can solve from Eqs. (1) the dependence of the selectivity ratio on the convection and on the ionic fluxes. Integrating the solution over the membrane gives

$$\ln S = \frac{F^2}{RT}\left(\frac{|z_1|}{\lambda_1} - \frac{|z_2|}{\lambda_2}\right)lv + \int_0^l \frac{F^2}{RT}\left(\frac{j_2|z_2|}{c_2\lambda_2} - \frac{j_1|z_1|}{c_1\lambda_1}\right)dx \tag{3}$$

As can be seen, the selectivity ratio depends exponentially on the convection and on an integral term which contains the ionic fluxes through the membrane.

Examining the special case where the ionic fluxes ($j_1 = j_2 = 0$) are zero, the selectivity ratio is an exponential function of the convection and of the difference of the inverses of the ionic equivalent conductance. In the case where the ionic fluxes are not zero we must calculate the integral term which is also a function of the convection. The selectivity ratio's dependence on the convection obtains such a complicated form that its solution is possible only by numerical methods.

APPARATUS

In Fig. 1 a countercurrent electrolysis cell is presented for the separation of cations. In the case of separation of anions, anion exchange membranes must be replaced by cation exchange membranes and, of course, anode and

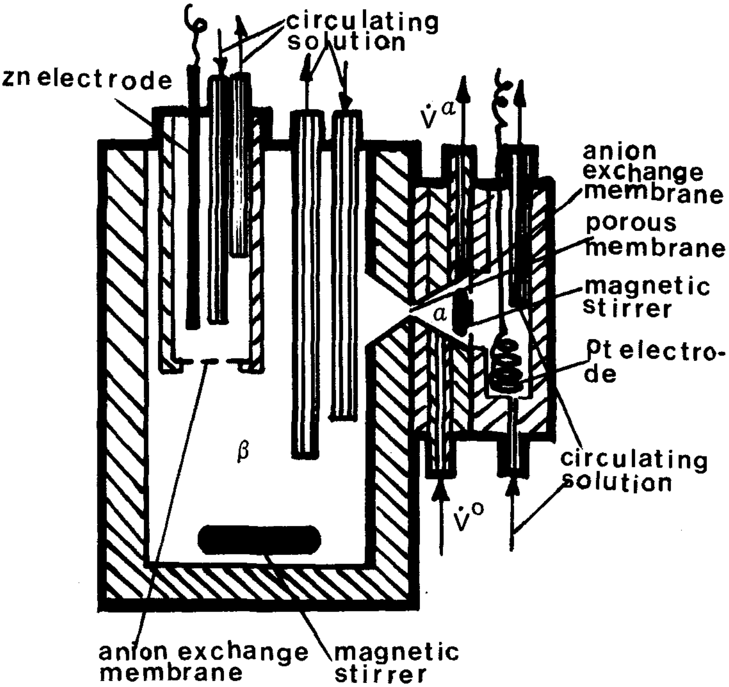

FIG. 1. Side view of the cell used for the experimental measurements.

cathode and the circulating solution in electrode compartments must be chosen properly.

The cell is made of Plexiglas and is divided into two compartments α and β with a porous membrane, Millipore SC, whose thickness is 0.1 cm, diameter 0.5 cm, and pore size 8 μm. Pure water is pumped (Ismatec ip -12) at a constant rate into compartment α and part of this flow is pumped out of the compartment ($\dot{v}^{\alpha}$) and the rest flows through the membrane (convection).

The cathode is a Pt wire and the anode is a Zn rod. Anion exchange membranes are used to separate the electrode compartments from the cell compartments α and β, thus preventing foreign ions from disturbing the separation process.

A potentiostat (PAR 173) is used to control the electric current through the cell, and a peristaltic pump (Desaga 132100) is used to circulate the solution in the cell.

ANALYSIS

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

MEASUREMENTS

The first set of experiments was carried out in four different systems: $LiCl-NaCl-H_2O$, $LiCl-CaCl_2-H_2O$, $LiCl-BaCl_2-H_2O$, and $LiCl-KCl-H_2O$. In these measurements the cation fluxes were zero ($\nu^\alpha = 0$). The concentrations in the β compartment were kept constant during the measurement, the total concentration was 10 mmol/dm^3, and the ratio of the convection of electrolytes was equal to one. The convection in all four systems was kept constant and the electric current was chosen so that the total concentration in α compartment was approximately 10 mmol/dm^3.

The second set of experiments was done in the same systems as the first but with nonzero cation fluxes. In these measurements both $\dot{\nu}^\alpha$ and the total concentrations in Compartments β and α were maintained constant and the concentration ratio of the electrolytes in Compartment β was equal to one.

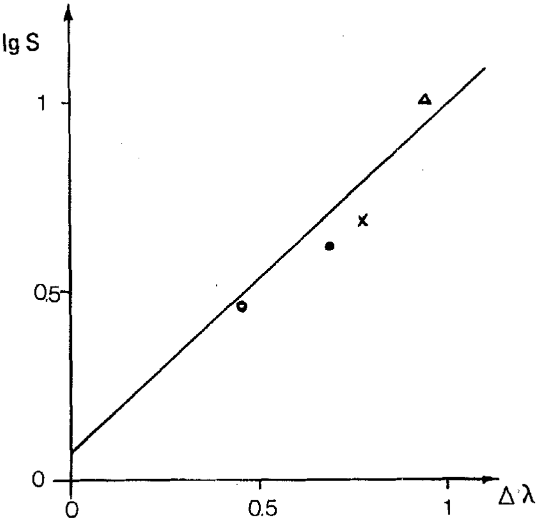

FIG. 2. The experimentally obtained relationship between the logarithm of the selectivity ratio (S) and the difference in the ionic equivalent conductance [$\Delta\lambda \equiv \lambda(Cl^-)/\lambda(Li^+) - \lambda(Cl^-)/\lambda(M^{z+})$] in systems where the cation fluxes are zero. The systems are $LiCl-NaCl-H_2O$ (○), $LiCl-CaCl_2-H_2O$ (●), $LiCl-BaCl_2H_2O$ (×) and $LiCl-KCl-H_2O$ (△), and the convection through the membrane is $\nu^k = 6.5$.

To check the stationary state of the system, the outflow (v^{α}) was analyzed. The selectivity ratio was measured at five different convections through the membrane for each of the four systems.

The third set of experiments was done in LiCl–KCl–H_2O system. The convection through the membrane was kept constant and the outflow rate (v^{α}), i.e., the cation fluxes, was varied. The selectivity ratio was determined at two different values of convection. In these experiments the total concentration was 10 mmol/dm^3.

The final set of experiments was done in a quaternary system LiCl–NaCl–KCl–H_2O. Both the total concentration in the cell and v^{α} were kept constant during the experiment. The concentrations of the three electrolytes in the β compartment were equal. Measurements were carried out in five different convections.

RESULTS

Equation (3) points out clearly that the selectivity ratio (S) is exponentially dependent on the difference in ionic equivalent conductances (λ_i/z_i) when cation fluxes are equal to zero. This was verified experimentally in four different ternary electrolyte systems, and the results can be seen in Fig. 2 and in Table 2. In Table 1 we have listed the dimensionless numbers used as well

TABLE 1
Definitions of Dimensionless Numbers

Electric current density	$I_r = Il/AFC_0D_0$
Convection	$v^k = \dot{V}^k l/AD_0$
Outflow rate	$v^{\alpha} = \dot{V}^{\alpha} l/AD_0$
Ionic flux	$K_i = J_i l/l_i RTC_0$
Selectivity ratio:	
(a) theoretical	$S = \left[\dfrac{c_1(x=l)}{c_1(x=0)}\right]^{1/z_1} \Big/ \left[\dfrac{c_2(x=0)}{c_2(x=1)}\right]^{1/z_2}$
(b) practical	$S^* = C_1(l)C_2(0)/C_1(0)C_2(l)$

Numerical values for parameters are as follows: Membrane constant $A/l = 8.5$ cm, $C_0 = 0.01$ mol/dm^3, $D_0 = 2.0 \times 10^{-5}$ cm^2/s, $F = 96{,}500 As/\text{mol}$, $R = 8.314$ $J/K \cdot \text{mol}$, $T = 298$ K, $l_{\text{Li}^+} = 38.7$, $l_{\text{Na}^+} = 50{,}1$, $l_{K^+} = 73.5$, $l_{Ca^{2+}} = 59.5$, $l_{\text{Ba}^{2+}} = 63.5$, $l_{\text{Cl}^-} = 76.4\ \Omega^{-1} \cdot \text{cm}^2/\text{mol}^3$, and $l_i = \lambda_i/z_i^2F^2$ (l_i is the so-called ionic mobility).

TABLE 2
Dependence of Separation Efficiency on Differences in Ionic Equivalent Conductances[a]

System	$\frac{\lambda_{Cl^-}}{\lambda_{Li^+}} - \frac{\lambda_{Cl^-}}{\lambda_{M^{2+}}}$	v^k	$-I_r$	S
$LiCl-NaCl-H_2O$	0.45	6.54	11.58	2.9
$LiCl-CaCl_2-H_2O$	0.69	6.70	23.16	4.0
$LiCl-BaCl_2-H_2O$	0.77	6.70	23.16	4.6
$LiCl-KCl-H_2O$	0.93	6.54	11.58	10.4

[a] In every measurement the total concentrations on both sides of the membrane, i.e., in Compartments α and β, were kept constant (0.01 mol/dm^3), the concentration ratio in Compartment β was equal to one, and cation fluxes $K_{Li^+} = K_{M^{z+}} = 0$.

as the numerical values for relevant parameters.

The separation process that is of practical importance is a continuous process, i.e., the fluxes of ions to be separated deviate from zero. We studied the continuous separation processes in four ternary systems by varying the convection and the electric current density while keeping the outflow rate constant. The results of these measurements are presented in Fig. 3 and in

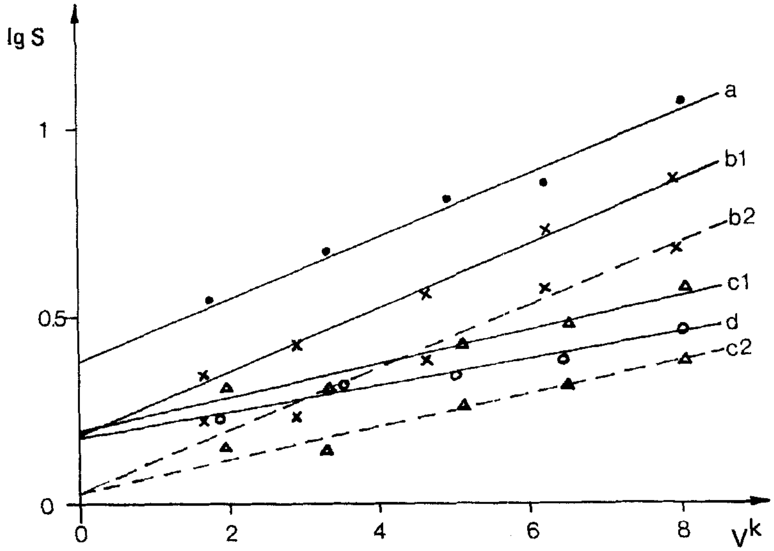

FIG. 3. The experimentally obtained relationship between the logarithm of the selectivity ratio (S) and the convection (V^k) in the systems (a) $LiCl-KCl-$, (b) $LiCl-BaCl_2-$, (c) $LiCl-CaCl_2-$, and (d) $LiCl-NaCl-H_2O$. The relationship of the practical selectivity ratio (S^*) and the convection is also shown in the figure (b2 and c2).

TABLE 3

Measured Fluxes and Selectivity Ratios as a Function of Electric Current and Convection in Various Ternary Systems[a]

System	v^k	$-I_r$	S	S^*	$-K_{Li^+}$	$-K_{M^{z+}}$
LiCl–NaCl–H_2O	8.01	24.4	2.9		0.3	0.9
	6.42	18.9	2.4		0.3	0.8
	4.98	15.2	2.2		0.4	1.0
	3.50	11.0	2.1		0.4	0.9
	1.86	6.10	1.7		0.4	0.7
LiCl–$CaCl_2$–H_2O	8.06	55.5	2.4	3.7	0.4	1.4
	6.50	42.7	2.1	3.0	0.4	1.1
	5.08	32.9	1.8	2.6	0.5	1.3
	3.32	25.0	1.4	2.0	0.6	1.2
	1.96	15.8	1.4	2.1	1.0	1.0
LiCl–$BaCl_2$–H_2O	7.88	55.5	4.8	7.2	0.2	1.4
	6.19	42.7	3.7	5.4	0.3	1.3
	4.58	34.1	2.4	3.6	0.4	1.4
	2.86	28.0	1.7	2.6	0.6	1.5
	1.65	13.4	1.7	2.2	0.5	1.1
LiCl–KCl–H_2O	8.02	24.4	11.8		0.1	1.4
	6.19	18.9	7.0		0.2	1.4
	4.89	14.6	6.4		0.2	1.4
	3.30	10.7	4.7		0.3	1.2
	1.73	5.49	3.3		0.3	1.0

[a] In every measurement the total concentrations on both sides of the membrane, i.e., in Compartments α and β, were kept constant (0.01 mol/dm^3) and the concentration ratio in Compartment β was equal to one. The outflow rate v^α was constant in every measurement and its value was 1.5.

Table 3. The exponential dependence of the selectivity ratio on convection can be seen, but the slope of the line lg $S = Kv^k$ differs from the slope obtained when the fluxes are zero. In each case the nonzero fluxes give a smaller value for the slope.

To confirm that the behavior is the same in more complicated systems, we did analogous measurements in the quaternary system LiCl–NaCl–KCl–H_2O and the results are presented in Fig. 4 and in Table 4. It is clearly evident that the behavior in this quaternary system is of the same kind as in the ternary systems.

Intuitively, it is clear that the greater the outflow rate, the smaller the separation efficiency. This was verified experimentally by keeping the convection constant and varying the outflow rate (v^α). The results are shown in Fig. 5 and in Table 5. From these experiments we can also see the exponential dependence of the selectivity ratio on the convection in the case where the cation fluxes are zero.

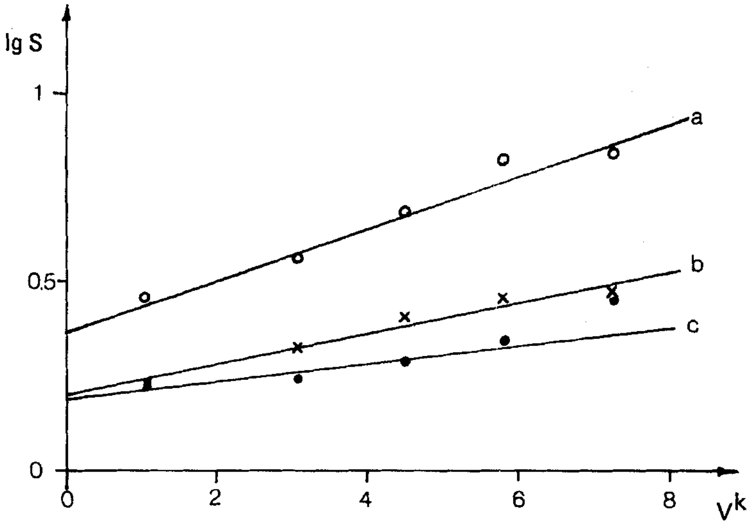

FIG. 4. The experimentally obtained relationship between the logarithm of the different selectivity ratios (S) and the convection (v^k) in the system LiCl–NaCl–KCl–H_2O. The selectivity ratios are (a) K^+/Li^+, (b) K^+/Na^+, and (c) Na^+/Li^+.

TABLE 4

Measured Fluxes and Selectivity Ratios as a Function of Electric Current and Convection in Quaternary System LiCl–NaCl–KCl–H_2O[a]

v^k	$-I_r$	$S(Na^+/Li^+)$	$S(K^+/Na^+)$	$S(K^+/Li^+)$	$-K_{Li^+}$	$-K_{Na^+}$	$-K_{k^+}$
7.23	23.5	2.3	3.0	6.8	0.2	0.4	1.3
5.80	18.2	2.2	2.9	6.8	0.2	0.4	1.2
4.53	14.1	1.9	2.6	4.9	0.2	0.4	1.1
3.14	10.3	1.8	2.1	3.7	0.2	0.4	0.9
1.16	5.3	1.7	1.7	2.9	0.2	0.4	0.6

[a] In every measurement the total concentrations on both sides of the membrane, i.e., in Compartments α and β, were kept constant (0.01 mol/dm^3) and the concentrations of electrolytes were equal in Compartment β. The outflow rate v^α was constant in every measurement and its value was 1.5.

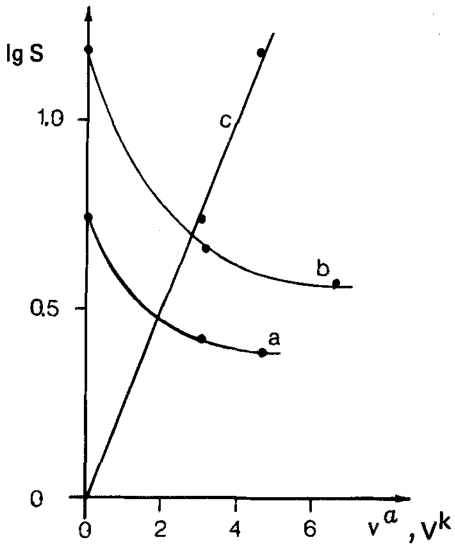

FIG. 5. The experimentally obtained relationship between the logarithm of the selectivity ratio and outflow rate v^{α} (Curves a and b) and the convection (v^k) (Curve c) in the system LiCl–KCl–H_2O. The value of the convection is $v^k = 3.0$ (a) and $v^k = 4.6$(b).

TABLE 5

Measured Effect of Outflow Rate v^{α} for Separation Efficiency in Ternary System LiCl–KCl–H_2O[a]

	v^{α}	$-I_r$	S
$v^k = 3.0$	4.7	13.9	2.44
	3.1	12.8	2.64
	0	7.3	5.44
$v^k = 4.6$	6.6	23.8	3.7
	3.2	17.7	4.5
	0	11.0	14.7

[a] In every measurement the total concentrations on both sides of the membrane, i.e., in Compartments α and β, were kept constant (0.01 mol/dm^3) and the concentration ratio in Compartment β was equal to one.

CONCLUSIONS

In countercurrent electrolysis in a thin porous membrane, the ionic equivalent conductance determines the order in which the ions can be separated. This means that the ions with greater equivalent conductance can be enriched from the mixture of different electrolytes; the faster moving ions travel more quickly against the convection. Of course, the condition of electroneutrality is fulfilled at all times.

The outflow rate of the product has a significant effect upon the selectivity ratio. When the outflow rates are fairly large, the effect is small, i.e., the selectivity ratio remains almost constant. But when outflow rates are small, the effects are quite large so that the selectivity ratio decreases rapidly with an increased outflow rate.

The fact that the separation is dependent on ionic equivalent conductance and not on molar conductance makes the separation of ions with different charge numbers unfeasible. This is due to the fact that there are easier and better ways to separate ions with different charge numbers (e.g., ion exchange).

Countercurrent electrolysis in a thin porous membrane seems to be worthy of consideration as a separation process when the ions have the same charge numbers and when they are difficult to separate by other means. The separation effect in the present method can be considerably enlarged by connecting porous membranes in series with the aid of ion-exchange membranes and also by using thicker porous membranes. These studies are in progress.

REFERENCES

1. K. Kontturi, P. Forssell, and A. Ekman, *Sep. Sci. Technol., 17,* 1195 (1982).
2. A. Ekman, S. Liukkonen, and K. Kontturi, *Electrochim Acta, 23,* 243 (1978).
3. A. Ekman, P. Forssell, K. Kontturi, and G. Sundholm, *J. Membr. Sci., 11,* 65 (1982).
4. K. Kontturi, P. Forssell, and A. Sipilä, *J. Chem. Soc. Faraday Trans. 1,* In Press.

Received by editor October 5, 1982