Separations of Ions by Ion-Exchange Membranes

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The separation of ions by ion-exchange membranes using a counter-current cell assembly is presented. Experimental verification was carried out using sodium and potassium ions and ions cation-exchange membranes whose permeability properties with respect to these ions are known from earlier work. The results obtained show that when the overall electric current efficiency was allowed to decrease, the separation efficiency increased rapidly and that an increase in the number of the cation-exchange membranes raised the separation efficiency in an exponential manner. Using a simple theoretical model based on the measured separation ratio we were able to predict satisfactorily the behaviour of the cell.

Membrane processes provide a promising technique for the separation of ions from mixtures of electrolytes, as their energy consumption is modest. From the point of view of a separation process, membrane processes are particularly appealing since neither high temperatures nor a transformation into another state of aggregation is required. Furthermore, continuous operation is achieved since electric current continuously regenerates the ion-exchange membranes.

Electrolytic separation of ions by ion-exchange membranes is, of course, based on the different permeabilities of the ions through the membrane system consisting of the membrane itself and the stagnant layers just adjacent to the membrane surface. Schlögl1 defines the separation ratio $S$ as

$$S = \frac{(J_1/J_2)}{(C_1/C_2)}$$

where $J_1$ and $J_2$ are the fluxes through the membrane and $C_1$ and $C_2$ are the concentrations on the depleting side of the membrane; subscripts 1 and 2 denote the countercations. According to Gurskii and Moskvin,2 the separation ratio $S$ is dependent on the functional groups in the membrane but is independent of the stirring conditions and electric current density over a wide range. These independences are in contradiction to our own studies, which showed that the stirring conditions and electric current density affected the separation ratio. This in fact means that according to our result the stagnant layers play an important role in the separation phenomenon. We have recently presented results3 which indicate that the separation ratio for sodium and potassium remained constant while changing the concentration ratio of these ions in the bulk solution. It should be noted that the mobilities of these ions inside the membrane do not have a constant value for alkali metal ions,4 a fact which lends support to stagnant layer control. The constancy of the separation ratio enables the construction

![Fig. 1. Schematic drawing of the cell for ion 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 $\dot{V}$ to compartment n. Pure water is fed at a constant rate $\dot{V}'$ into compartment 1 and the product stream $\dot{V}_1$ is pumped out of compartment 1. The outflows are $\dot{V}_1 = \dot{V}_1 - \dot{V}_n$ and, of course, $\dot{V}_n > \dot{V}_1$. The cation-exchange membranes are denoted by C. The flow balances are not significantly affected by the electroosmotic flows across the membranes since the magnitude of electroosmotic flow is orders of magnitude lower than flow rates $\dot{V}_0$, $\dot{V}_n$ and $\dot{V}$.](image)
branes. The separation of isotopes has also been tried, e.g., by using a membrane in the form of a rod or a strip.\textsuperscript{9} Hara has separated amino acids by using ion-exchange membranes.\textsuperscript{10,11} A characteristic feature of all these suggested cell constructions is the tendency to maintain the efficiency with respect to electric current as high as possible, usually near the value unity. However, because of the relatively low price of electricity this is not necessary and in many practical applications certainly not reasonable. The present study verifies that when the current efficiency is allowed to decrease a considerable increase in the separation efficiency is achieved.

**Cell**

In Fig. 1 the cell for the separation of cations is presented. The cell used was of the filter-press type. The active surface area of the ion-exchange membranes was ca. 2.0 cm\(^2\) and the thickness of the compartments was ca. 2 mm. As cation-exchange membranes we used IONICS 61AZL389, and as anion-exchange membranes IONICS 103 FZL-389. Stirring of the compartments was achieved out by circulating the solution with the aid of a peristaltic pump. Stirring in this manner resembles channel-flow conditions, and the thickness of the stagnant layer was measured to be ca. 0.25 mm. The latter measurement was made as described by Indusékhar and Meares.\textsuperscript{12}

Pure water is pumped at a constant rate \(\dot{V}^0\) into compartment 1, and a part of this flow is pumped out of compartment 1 and the rest overflows to the rest of the cell, forming \(\dot{V}^c = \dot{V}^0 - \dot{V}^o\). The solution from which the cations are enriched is fed into compartment \(n\) (\(\dot{V}^o\)), the cathode and anode being Pt plates. The anolyte is 0.03 mol dm\(^{-3}\) Na\textsubscript{2}SO\textsubscript{4} solution and the catholyte is 0.03 mol dm\(^{-3}\) NaCl solution, and their concentrations are kept constant by circulating these solutions. A potentiostat (PAR 173) is used to control the electric current through the membranes. The flow rates were determined by weighing.

Since the separation ratio \(S\) differs from unity, the mixture on passing through the cation exchange membrane from compartment \(n\) to \(n-1\) becomes enriched. Without the overflow \(\dot{V}^o\) the enrichment should run out in compartments \(1, 2, \ldots, n-2\), but because of the overflow the separation takes place cumulatively in every cation exchange membrane. The entropy production, as well as common sense, manifests that the smaller the product flow \(\dot{V}^o\) the greater is the total separation factor \(S^*\)

\[
S^* = \frac{(C_1/C_2)}{(C_1^*/C_2^*)} \quad (2)
\]

where the subscripts denote the cations 1 and 2 and the superscripts denote the compartments; both \(S\) and \(S^*\) are defined to be equal or greater than unity.

In the present process we have two kinds of fluxes: the product fluxes \((N_1, N_2)\) and the fluxes through the ion-exchange membranes \((J_1, J_2)\). They are defined as follows:

\[
N_i = -C_i^1 \dot{V}^o / A; \quad N_2 = -C_i^2 \dot{V}^o / A \quad (3)
\]

and

\[
J_i = ISC_i / [F(SC_i + C_i)]; \quad J_i^* = IC_i^* / [F(SC_i^* + C_i)];
\]

\[
i = 2, 3, \ldots, n
\]

where \(I\) is the electric current density, \(A\) is the exposed surface area of the membrane and \(F\) is Faraday constant. In eqn. (4) the ideal behaviour of the cation-exchange membrane has been assumed. The efficiency \(\eta_i\) with respect to electric current of the whole separation process can now be expressed as

\[
\eta_i = (N_1 + N_2) / (J_1 + J_2) = (C_1^1 + C_2^1) \dot{V}^o F / (IA) \quad (5)
\]

Since the total concentration in compartment 1 obtains the form

\[
C_1^1 + C_1^2 = IA / (\dot{V}^o F) \quad (6)
\]

the current efficiency \(\eta_i\) can now be written as

\[
\eta_i = \dot{V}^o / \dot{V}^o; \quad (\dot{V}^o < \dot{V}^o) \quad (7)
\]

Eqn. (7) clearly demonstrates how the product stream is related to the rate of water feed into compartment 1. To be able to understand the meaning of this relationship we have studied the mass balances of the cell.

**Mass balances and solution procedure**

From the point of view of the mass balances compartments 1 and \(n\) must be treated separately while compartments 2 to \(n-1\) have the same functional form. In all the previous as well as the subsequent derivations we assume a ternary mixture with two cations and a common anion to be separated, and ideal behaviour in ion-exchange membranes. Before going on to consider the concentrations of individual ions in separate compartments we present the total concentrations in the compartments:

\[
C_i^1 + C_i^2 = IA / (\dot{V}^o F) = C_i^*; \quad i = 1, 2, \ldots, n-1 \quad (8)
\]

and

\[
C_i^1 + C_i^2 = [(\dot{V}^i / \dot{V}^0 - 1)IA / F + (C_i^1 + C_i^2) \dot{V}^0] / (\dot{V}^i + \dot{V}^0) \quad (9)
\]

where \(C_i^1\), \(C_i^2\) are the concentrations in the feed solution and \(C_i^*\) is the total concentration in compartments \(1, 2, \ldots, n-1\). Eqn. (8) shows that the total concentrations are equal in the compartments \(1, 2, \ldots, n-1\), which is important to realize when estimating the total IR-drop across the cell. Using the usual procedure the individual ion concentrations in each compartment could be obtained, but the algebra involved is so tedious that it is more reasonable.
to resort to an iterative solution. For this iteration the following equations in addition to the previous ones were derived:

\[ J_i^2 = C_i^i \hat{V}^i / A; \quad i = 1, 2 \]  
(10)

\[ C_i^{i+2} = \frac{(C_i^{i+1} - C_i^{i}) \hat{V}^i + IAC_i^{i+1}[F(SC_i^{i+1} + C_i^{i+1})]}{((C_i^{i+1} - C_i^{i}) \hat{V}^i + IAC_i^{i+1}[F(SC_i^{i+1} + C_i^{i+1})])S_i^{i+1}} \]  
(11)

\[ i = 1, 2, \ldots, n-2 \]

and

\[ C_i^{i} / C_i^{i+2} = \frac{(\hat{V}^{i+1} + \hat{V}^{i})C_i^{i+1} - \hat{V}^{i+1}C_i^{i+1} + IASC_i^{i+1}[F(SC_i^{i+1} + C_i^{i+1})]}{(\hat{V}^{i+1} + \hat{V}^{i})C_i^{i+1} - \hat{V}^{i+1}C_i^{i+1} + IASC_i^{i+1}[F(SC_i^{i+1} + C_i^{i+1})]} \]  
(12)

The mass balances are presented in the form of concentration ratios, since the total concentrations can be easily calculated with the aid of eqns. (8) and (9) and thus the evaluation of ionic concentration is easy.

The solution is carried out using the following algorithm:

1. Values of the following quantities are given: \( \hat{V}^0, \hat{V}^i, \hat{V}^+, I, C_i^i, S_i^i, A \) and the number of cation exchange membranes.

2. Assume a value for the total separation factor \( S' \) or use the value obtained in step 8.

3. Calculate \( C_1^i \) and \( C_2^i \) using eqns. (2) and (8).

4. Calculate \( C_3^i \) and \( C_4^i \) using eqns. (4), (10) and (8).

5. Calculate \( C_5^{i+2} / C_i^{i+2}; \quad i = 1, 2, \ldots, n-3 \) using eqns. (11), (12), and (9).

6. \( C_i^i \) and \( C_i^+ \) are obtained from eqns. (11) and (9).

7. Using eqn. (12) calculate the ratio of the feed solution concentrations which is determined by the values \( C_i^i \) and \( C_i^+ \) in step 3.

8. Calculate a new estimate for \( S' \) using the values obtained in steps 3 and 7.

9. (a) If \( \left| \frac{S_i^{i+1} - S_i^i}{S_i^i} \right| < 0.001 \) go to step 10.

10. The problem is solved and the concentration ratios as well as the total concentrations in each compartment are known.

The iteration converges rapidly and as a starting point we successfully used eqn. (13)

\[ S' = S^n \]  
(13)

where \( m \) is the number of cation-exchange membranes. Eqn. (13) is strictly valid when the current efficiency \( \eta_i \) is zero, i.e. there is no product stream out of the cell and the separation efficiency is at its maximum.

**Measurements**

The experiments were carried out in the ternary system NaCl–KCl–H₂O. The total concentration of the feeding solution \( \hat{V}^i \) was 0.03 mol dm⁻³ and the concentration ratio was unity, i.e. \( C_{k-1}/C_{k+1} = 1 \). This total concentration was used because at this concentration only a vanishingly small amount of free salt is inside the cation exchange membrane.

In every measurement presented here the electric current, the rate of the water feed, \( \hat{V}^+ \), and the feed rate of the feeding solution, \( \hat{V}_i \), were kept constant. In the first set of experiments the number of cation-exchange membranes was varied one by one from one to five, keeping the product stream \( \hat{V}_i \) constant. In the second set of experiments the product stream \( \hat{V}_i \) was varied in the case of five cation-exchange membranes. Since \( \hat{V}^0 \) was kept constant the overflow \( \hat{V}^0 \) is changed as well as the current efficiency [cf. eqn. (7)].

The system was deduced to have reached the steady state when the concentrations in the product stream remained unchanged. Depending on the number of membranes, the time required to reach steady state varied from several hours to several days.

The cations were analyzed by AAS and the result was checked using eqn. (6), with \( \hat{V}_i^0 \) and \( IA \) being known.

**Table 1.** Experimental results for the separation of Na⁺ and K⁺ ions using cation-exchange membrane Ioniics 61AZL389.*

<table>
<thead>
<tr>
<th>Number of membranes</th>
<th>( \hat{V}^0 ) / ml h⁻¹</th>
<th>( \hat{V}^+ ) / ml h⁻¹</th>
<th>( S' ) meas.</th>
<th>( S ) calc.</th>
<th>( \varepsilon )</th>
<th>( \eta_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.344</td>
<td>8.00</td>
<td>1.39</td>
<td>1.40</td>
<td>1.00</td>
<td>0.041</td>
</tr>
<tr>
<td>2</td>
<td>0.361</td>
<td>7.84</td>
<td>1.94</td>
<td>1.41</td>
<td>0.95</td>
<td>0.044</td>
</tr>
<tr>
<td>3</td>
<td>0.365</td>
<td>7.87</td>
<td>2.74</td>
<td>1.43</td>
<td>0.98</td>
<td>0.044</td>
</tr>
<tr>
<td>4</td>
<td>0.375</td>
<td>7.87</td>
<td>3.61</td>
<td>1.41</td>
<td>0.96</td>
<td>0.045</td>
</tr>
<tr>
<td>5</td>
<td>0.375</td>
<td>7.87</td>
<td>4.57</td>
<td>1.39</td>
<td>0.97</td>
<td>0.045</td>
</tr>
<tr>
<td>6</td>
<td>2.72</td>
<td>6.07</td>
<td>2.90</td>
<td>1.39</td>
<td>0.94</td>
<td>0.310</td>
</tr>
<tr>
<td>7</td>
<td>5.33</td>
<td>3.46</td>
<td>1.63</td>
<td>1.35</td>
<td>0.92</td>
<td>0.610</td>
</tr>
<tr>
<td>8</td>
<td>7.90</td>
<td>0.895</td>
<td>1.38</td>
<td>1.40</td>
<td>0.94</td>
<td>0.900</td>
</tr>
</tbody>
</table>

*The rate of water feed \( \hat{V}^0 = \hat{V}^0 + \hat{V}^+ \); electric current \( i = IA \) = 6.75 mA; \( \varepsilon = C_i \hat{V}_i^0 F / I \) (parameter indicating the co-ion leak); \( C_i \) is a measured value; surface area of the membrane \( A = 2.0 \) cm².
Results and discussion

Table 1 lists the results obtained. In Fig. 2 the logarithm of the total separation factor $S'$ is plotted against the number of membranes when $V^*$ is constant ($\eta = 0.04$). Fig. 2 also shows the theoretically computed relationship, which agrees very well with the measured data. In Fig. 3 the logarithm of the total separation factor $S'$ is plotted against the current efficiency $\eta$. Again, relatively good agreement between theoretical and experimental values can be seen. The results clearly show that when the current efficiency is allowed to fall a good separation is achieved. The degree of lowering is, of course, a question of optimum conditions for each particular case.

The results verify the theoretical model used. Therefore it is justified to say that on increasing the number of cation-exchange membranes we can increase the separation efficiency in an exponential manner, as predicted by the theoretical computations. The separation efficiency is, however, an order of magnitude lower than in counter-current electrolysis,$^{1,13}$ but the advantage of the present method is the easier practical realization. Further advantages are the possibility of ion-exchange of the common anion simultaneously with the separation,$^{14}$ and the fact that co-ion leak cannot have cumulative effect when increasing the number of membranes. Naturally, tailor-made ion-exchange membranes open up new prospects for this kind of separation process. In the case of ions with different charges the present method is a promising one because the separation ratio is usually very high and the current efficiency can therefore have a high value. Because of the simplicity, but reliability of the theoretical model, optimization of the process is relatively easy to achieve.

References


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