Membrane transference numbers from a new emf method

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Abstract

A new method for determination of the transference numbers of two ions in ion exchange membranes has been established. The method uses emf measurements in a cell with a membrane stack, and it avoids problems of concentration-polarization, diffusion and water transport. Stack thickness is about 10 mm. The method needs less time and is more precise than a corresponding Hittorf method. The method has been developed for a cation exchange membrane, with cation sites Me\(^+\), in equilibrium with aqueous solutions of two electrolytes, first HCl and KCl, next HCl and NaCl. Transference numbers for both systems are reported with a precision of ±1%. The results imply that the ratios of the ionic mobilities, \(u_/u_{H^+}\), for \(i = K^+\) and \(Na^+\) in the membrane are constant as the mole fractions vary.

Keywords transference number, ion exchange membranes, emf measurements

Introduction

Rapid and precise methods to obtain membrane transference coefficients are important for characterization of membranes. A new theoretical description of transport in ion exchange membranes has been developed in our laboratory over the last years (for a review, see Ref [1]). We are now seeking to implement the theory, and have recently reported a new method for determination of water transference numbers and water permeabilities [2].

This work presents a new method for determination of transference numbers in ion exchange membranes when two salts are present. The method is developed for the cation exchange membrane CR61 AZL 389 (from Ionics Inc., Watertown, MA) in equilibrium with solutions of HCl and KCl. It is next applied to solutions of HCl and NaCl.

Theory

General equations

The following electrochemical cell is used

\[
\begin{align*}
H_2(g) | HCl(C_{HCl}[A]) , ACI(C_{ACl}[A]) | ^{\circ} ^{\circ} \ HCl(C_{HCl}[II]),ACI(C_{ACl}[II]) | H_2(g)
\end{align*}
\]

The symbol A is used for the alkali metal, K or Na, and \(^{\circ}\) denotes a cation exchange mem-
brane. From irreversible thermodynamics the flux equations of cell (a) may be written \[1,3\]:

\[
J_{\text{HCl}} = -L_{11} V_{\mu_1} - L_{12} V_{\mu_2} - L_{13} V_{\mu_3} - L_{14} \varphi
\]  

(1)

\[
J_{\text{ACl}} = -L_{21} V_{\mu_1} - L_{22} V_{\mu_2} - L_{23} V_{\mu_3} - L_{24} \varphi
\]  

(2)

\[
J_{\text{H}_2\text{O}} = -L_{31} V_{\mu_1} - L_{32} V_{\mu_2} - L_{33} V_{\mu_3} - L_{34} \varphi
\]  

(3)

\[
j = -L_{41} V_{\mu_1} - L_{42} V_{\mu_2} - L_{43} V_{\mu_3} - L_{44} \varphi
\]  

(4)

All transport occurs in the \(x\)-direction, and \(V\) means \(d/dx\). The gradient in electric potential is \(\varphi = \lim (\Delta \varphi/\Delta x)\) for \(\Delta x \to 0\). The \(\Delta \varphi\) is measured with \(\text{Pt} | \text{H}_2(\text{g})\) electrodes and \(j\) is the electric current density. The units of \(\Delta \varphi\) and \(j\) are \(J\)-faraday\(^{-1}\) and faraday-m\(^{-2}\).sec\(^{-1}\), respectively. The unit faraday means one mole of elementary electric charges (96487 C). The coefficients, \(L_{ij}\), are phenomenological coefficients. The units used of \(\Delta \varphi\) and \(j\) make the coefficient matrix symmetric.

The components of the solution, HCl, AC1 and \(\text{H}_2\text{O}\), are numbered 1, 2 and 3, respectively. Their chemical potential gradients are \(V_{\mu_i}\). As long as the electrolyte solutions are dilute, the components of the membrane are HM, AM and \(\text{H}_2\text{O}\), where \(M^-\) denotes the cation sites in the membrane. We assume that at any location in the membrane we can introduce an aqueous solution at 1 atm in equilibrium with the membrane composition. Integration across the membrane can thus be carried out over the aqueous solutions with known \(V_{\mu_i}\). One membrane component is chosen as the reference for the fluxes (see Ref. [3] for further details).

The principles of the transference number determination

The definition of transference coefficients of the components HCl and AC1 are:

\[
\left( \frac{J_{\text{HCl}}}{j} \right)_{\mu_\text{HCl}=0} = \frac{L_{14}}{L_{44}} = t_{\text{HCl}}
\]  

(5a)

\[
\left( \frac{J_{\text{ACl}}}{j} \right)_{\mu_\text{ACl}=0} = \frac{L_{24}}{L_{44}} = t_{\text{ACl}}
\]  

(5b)

for \(i=1,2,3\). A similar equation is valid for transfer of \(\text{H}_2\text{O}\). The frame of reference for all transference coefficients is the membrane [1]. The transference coefficient, \(t_{\text{HCl}}\), gives the number of moles HCl which are transferred from left to right in the cell, per mole electric charge. The transference coefficient is related to the transference number, the fraction of electric charge transported by \(H^+\) through the membrane. When passing one mole electric charge through cell (a), the following changes are observed:

**Left-hand half cell:**

1 mole \(H^+ - t_{H^+} \) mole \(H^+ - t_{A^+} \) mole \(A^+ = t_{A^+} \) mole HCl - \(t_{A^+} \) mole AC1

**Right-hand half cell:**

\(-1 \) mole \(H^+ + t_{H^+} \) mole \(H^+ + t_{A^+} \) mole \(A^+ = -t_{A^+} \) mole HCl + \(t_{A^+} \) mole AC1

From these mass balances the transference coefficients are equal to:

\[
t_{\text{ACl}} = t_{A^+}
\]  

(8a)

\[
t_{\text{HCl}} = - t_{A^+}
\]  

(8b)

This means that \(t_{\text{HCl}} = - t_{\text{ACl}}\). The value reflects the transport properties of the membrane.

In emf measurements we have \(j \approx 0\). Combined with eqn. (4) this gives:

\[
\varphi = \frac{L_{41}}{L_{44}} V_{\mu_{\text{HCl}}} + \frac{L_{42}}{L_{44}} V_{\mu_{\text{ACl}}} + \frac{L_{43}}{L_{44}} V_{\mu_{\text{H}_2\text{O}}}
\]  

(9)

By introducing eqn. (5) and the Onsager reciprocal relations \(L_{ij} = L_{ji}\) into eqn. (9) we get:

\[
-\varphi = t_{\text{HCl}} V_{\mu_{\text{HCl}}} + t_{\text{ACl}} V_{\mu_{\text{ACl}}} + t_{\text{H}_2\text{O}} V_{\mu_{\text{H}_2\text{O}}}
\]  

(10)

We shall use solutions with the same ionic strength on both sides of the membrane. Thus \(V_{\mu_{\text{H}_2\text{O}}} \approx 0\). Then we can neglect the contribu-
tion to emf from the water transport. This leads to the following expression:

$$d\varphi = -t_{HC}d\mu_{HCl} - t_{ACl}d\mu_{ACl}$$  \(11\)

and by using eqn. (8) we obtain:

$$d\varphi = t_{A+}d\mu_{HCl} - t_{A+}d\mu_{ACl}$$

$$= t_{A+}d(\mu_{HCl} - \mu_{ACl})$$  \(12\)

or

$$t_{A+} = \frac{d\varphi}{d(\mu_{HCl} - \mu_{ACl})}$$  \(13\)

We shall use eqn (13) to determine the transference number of $A^+$. The equation depends on the choice of electrodes through eqns. (8).

**Experimental procedure**

To find $t_{A+}$ from eqn. (13), we will use the cell in Fig. 1. The ionic strength in both half-cells is constant. The left-hand side half-cell contains the reference solution. The composition of the solution in the right-hand side half-cell shall be varied from one experiment to the next. This solution is called the test solution.

A stack of membranes constitute the junction between the cells. Half of the membranes are equilibrated with the reference solution, the other half with the test solution. This gives an initially sharp concentration gradient. The thickness of the stack shall prevent concentration changes in the half cells and disturbances by concentration-polarization.

The concentration gradient inside the stack will vary during the experiment, but this variation does not affect the emf. This is because the emf is given by the sequence of thermodynamic states, and not by their separation in the gradient (the $x$-coordinate is absent in eqn 13). The transference number is a unique function of composition. It is independent of the gradients in chemical potential.

The emf of the cell is measured with different test solutions. The change in the difference of chemical potentials between two experiments, $d(\mu_{HCl} - \mu_{ACl})$, is equal to the change in the test solution alone. The emf results are plotted versus $(\mu_{HCl} - \mu_{ACl})$. The derivative of the plot of emf as a function of $(\mu_{HCl} - \mu_{ACl})$ gives the transference number of $A^+$ in the membrane in equilibrium with the test solution.

**Materials and methods**

**Chemicals**

Chemicals were analytical grade compounds from Merck, Darmstadt. The $H_2$-gas (99.99% pure) was from AGA Norgass AS, Norway. Solutions were made with an accuracy of $\pm 0.1\%$.

**Electrode and membrane preparations**

Hydrogen electrodes were prepared according to instructions given by Ives and Janz [4]. The electrodes were stable for many weeks. Before and after each experiment, the bias potential of the electrodes was determined. If the bias was more than 0.01 mV, the electrodes were re-platinized.
The membrane sheet (CR61 AZL 389, from Ionics Inc., Watertown, MA) was cut into circles of 2 cm in diameter. All membrane pieces were cut from the same sheet, because previous experiments have shown variations in the properties of membranes from different sheets. Membrane thickness was 1.2 mm. The membrane contains sulfonated groups in a concentration of 1.6 kmol-m⁻³. The water content is about 48% of wet resin. The membranes were kept in a container of soaking solutions of HCl and KCl or of HCl and NaCl. All solutions had a total salt concentration of 0.03 kmol-m⁻³. At this concentration anions are not present in the membrane. The electrolyte fractions of HCl are given in Tables 1 and 2. The soaking solutions were replaced 10 times during a period of 8 weeks to ensure equilibrium. Then the solutions with the membranes were kept in a water bath (25.0°C), and the solutions were replaced another 3 times. This tedious procedure was necessary to establish equilibrium between the membranes and the different solutions.

**Emf measurements**

The concentration cell, illustrated in Fig. 1, is made from two glass flasks. The half-cells are connected by the membrane stack holder (for details see Fig. 2).

The stack holder was first packed with reference membranes. By reference membranes we mean membranes in equilibrium with a 1:1 solution of HCl/ACl. The left-hand side of the concentration cell was always used for this part of the membrane stack. The rest of the membranes were equilibrated with the test solution. The solutions in the cell were thermostated to 25.0°C ± 0.1°C before use. The stack was pressed together to minimize the liquid layers between the membranes.

The cell was thermostated at 25.0±0.1°C. Hydrogen electrodes were put into the half-cells. Hydrogen gas was supplied at a speed of 4–5 bubbles per second.

The emf was measured by a “617 Programmable Electrometer” from Keithley. The voltmeter was connected to an IBM Personal Computer PS/2-model 30 which recorded the emf regularly and stored the values for later analysis. Stable emf values (± 0.02 mV) were usually obtained within 2 hr.

**Method development**

The emf was first measured as a function of stack size in order to find the minimum number of membranes needed in the experiment. The time lapse before concentration-polarization of solutions is observed, varies with stack thickness. With a total of 4 membranes in the stack, polarization caused by diffusion was observed after 2–3 hr as a reduction in emf (by μV), while 8 membranes prevented such disturbances for at least 5 hr. Eight membranes were used in the following experiments. The larger the difference we have in chemical potential of the two solutions in the concentration cell, the larger is the diffusion rate. For this reason, an intermediate concentration was used for the reference solution.
Different membrane packing techniques were next investigated. Some membranes were wiped off with tissues before packing, thereby removing the liquid film between the membranes. Others were taken directly from the storing solutions. No significant difference in the results were seen. The effect of different gas velocities was then investigated. Experiments with low gas velocity (1 bubble/sec) gave an emf value of 6.59 mV. A high velocity (more than 10 bubbles/sec) gave a lower value for emf (6.50 mV), probably due to cooling of the electrode. Emf is proportional to the temperature, and a reduction of 3°C will reduce the potential by 70 μV. For this reason we used the same gas velocity in all experiments (4–5 bubbles), and a temperature control of the gas.

Altogether 11 experiments were performed to test reproducibility. In all these cases reproducibility was better than ±1%.

Results and calculations

Twenty-one different test solutions were investigated with HCl–KCl solutions. Eight solutions were examined with the system HCl–NaCl. Experimental results for the two systems are given in Tables 1 and 2.

The difference in chemical potential of HCl and AC1 where A = K, Na is:

\[ \mu_{\text{HCl}} - \mu_{\text{AC1}} = RT \ln \left( \frac{a_{\text{HCl}}}{a_{\text{AC1}}} \right) \]

\[ = RT \ln \left( \frac{y_{\text{HCl}} C_{\text{HCl}}}{y_{\text{AC1}} C_{\text{AC1}}} \right) \]  \hspace{1cm} \text{(14)}

Activity coefficients, \( y_{\text{AC1}} \), for the electrolyte solutions are given by Zemaitis et al. [5]. For HCl–KCl–water solutions, we have

\[ \ln y_{\text{HCl}} = -0.3222 + 0.3648 \ln n_{\text{HCl}} \]  \hspace{1cm} \text{(15a)}

\[ \ln y_{\text{KCl}} = -0.3342 + 0.3842 \ln n_{\text{HCl}} \]  \hspace{1cm} \text{(15b)}

For solutions of HCl–NaCl the corresponding expressions are.

<p>| TABLE 1 |
| Transference numbers, ( t_{\text{K}^+} ) and emf for the system HCl–KCl for different solution compositions, ( x_{\text{H}^+} ). Corresponding membrane compositions, ( x_{\text{HM}} ), chemical potential differences, ( \mu_{\text{HCl}} - \mu_{\text{KCl}} ), and electric potential differences, ( \Delta \phi ), are also given. |</p>
<table>
<thead>
<tr>
<th>( x_{\text{H}^+} )</th>
<th>( x_{\text{HM}} )</th>
<th>emf (mV)</th>
<th>( \Delta \phi ) (kJ-faraday(^{-1}))</th>
<th>( \mu_{\text{HCl}} - \mu_{\text{KCl}} ) (kJ-mol(^{-1}))</th>
<th>( t_{\text{K}^+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>0.019</td>
<td>-55.28</td>
<td>-5.334</td>
<td>-9.052</td>
<td>0.899</td>
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<td>0.050</td>
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<td>-3.831</td>
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<td>0.819</td>
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<td>-2.393</td>
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<td>-1.205</td>
<td>-3.407</td>
<td>0.506</td>
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<tr>
<td>0.250</td>
<td>0.204</td>
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<td>-0.881</td>
<td>-2.694</td>
<td>0.438</td>
</tr>
<tr>
<td>0.300</td>
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<td>-0.618</td>
<td>-2.071</td>
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<tr>
<td>0.350</td>
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<td>-4.28</td>
<td>-0.413</td>
<td>-1.505</td>
<td>0.331</td>
</tr>
<tr>
<td>0.400</td>
<td>0.339</td>
<td>-2.66</td>
<td>-0.257</td>
<td>-0.976</td>
<td>0.287</td>
</tr>
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<td>0.450</td>
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<td>-1.18</td>
<td>-0.114</td>
<td>-0.468</td>
<td>0.249</td>
</tr>
<tr>
<td>0.500</td>
<td>0.435</td>
<td>0.00</td>
<td>0.000</td>
<td>0.029</td>
<td>0.216</td>
</tr>
<tr>
<td>0.550</td>
<td>0.485</td>
<td>1.00</td>
<td>0.097</td>
<td>0.526</td>
<td>0.186</td>
</tr>
<tr>
<td>0.600</td>
<td>0.536</td>
<td>1.94</td>
<td>0.187</td>
<td>1.034</td>
<td>0.158</td>
</tr>
<tr>
<td>0.650</td>
<td>0.588</td>
<td>2.71</td>
<td>0.262</td>
<td>1.563</td>
<td>0.130</td>
</tr>
<tr>
<td>0.700</td>
<td>0.642</td>
<td>3.40</td>
<td>0.328</td>
<td>2.129</td>
<td>0.109</td>
</tr>
<tr>
<td>0.750</td>
<td>0.698</td>
<td>4.04</td>
<td>0.390</td>
<td>2.752</td>
<td>0.0886</td>
</tr>
<tr>
<td>0.800</td>
<td>0.755</td>
<td>4.64</td>
<td>0.448</td>
<td>3.465</td>
<td>0.0691</td>
</tr>
<tr>
<td>0.850</td>
<td>0.813</td>
<td>5.18</td>
<td>0.500</td>
<td>4.328</td>
<td>0.0502</td>
</tr>
<tr>
<td>0.900</td>
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<td>5.61</td>
<td>0.548</td>
<td>5.475</td>
<td>0.0321</td>
</tr>
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<td>0.950</td>
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<td>6.09</td>
<td>0.588</td>
<td>7.327</td>
<td>0.0158</td>
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<tr>
<td>0.975</td>
<td>0.968</td>
<td>6.30</td>
<td>0.608</td>
<td>9.110</td>
<td>0.0094</td>
</tr>
</tbody>
</table>

<p>| TABLE 2 |
| Transference numbers, ( t_{\text{Na}^+} ), and emf for the system HCl–NaCl for different solution compositions, ( x_{\text{H}^+} ). Corresponding membrane compositions, ( x_{\text{HM}} ), chemical potential differences, ( \mu_{\text{HCl}} - \mu_{\text{NaCl}} ), and electric potential differences, ( \Delta \phi ), are also given. |</p>
<table>
<thead>
<tr>
<th>( x_{\text{H}^+} )</th>
<th>( x_{\text{HM}} )</th>
<th>emf (mV)</th>
<th>( \Delta \phi ) (kJ-faraday(^{-1}))</th>
<th>( \mu_{\text{HCl}} - \mu_{\text{NaCl}} ) (kJ-mol(^{-1}))</th>
<th>( t_{\text{Na}^+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0625</td>
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<tr>
<td>0.3750</td>
<td>0.457</td>
<td>-2.39</td>
<td>-0.226</td>
<td>-1.247</td>
<td>0.220</td>
</tr>
<tr>
<td>0.5000</td>
<td>0.583</td>
<td>0.02</td>
<td>0.001</td>
<td>0.018</td>
<td>0.138</td>
</tr>
<tr>
<td>0.6250</td>
<td>0.700</td>
<td>1.48</td>
<td>0.143</td>
<td>1.283</td>
<td>0.0852</td>
</tr>
<tr>
<td>0.7500</td>
<td>0.808</td>
<td>2.45</td>
<td>0.236</td>
<td>2.739</td>
<td>0.0550</td>
</tr>
<tr>
<td>0.8750</td>
<td>0.907</td>
<td>3.39</td>
<td>0.327</td>
<td>4.838</td>
<td>0.0263</td>
</tr>
</tbody>
</table>
\[ \ln \gamma_{\text{HCl}} = -0.3164 + 0.1698 \mu_{\text{HCl}} \quad (16a) \]
\[ \ln \gamma_{\text{NaCl}} = -0.3260 + 0.3134 \mu_{\text{HCl}} \quad (16b) \]

where \( \mu_{\text{HCl}} \) is the molality of \( \text{HCl} \) in the solution. The error in \( \mu_{\text{HCl}} - \mu_{\text{NaCl}} \) is estimated to \( \pm 4 \) J. Emf is plotted (in units of kJ-faraday\(^{-1}\)) as a function of \( \mu_{\text{HCl}} - \mu_{\text{KCl}} \) (in units of kJ-mol\(^{-1}\)) in Fig. 3.

The following ion exchange equilibria have been investigated by Skrede and Ratkje [6]:

\[ \text{NaCl} \quad + \quad \text{KM} \quad \rightarrow \quad \text{KCl} \quad + \quad \text{NaM} \quad (17) \]
\[ \text{HCl} \quad + \quad \text{NaM} \quad \rightarrow \quad \text{NaCl} \quad + \quad \text{HM} \quad (18) \]

Equilibrium constants are:

\[ K_1 = \frac{a_{\text{NaM}} a_{\text{KCl}}}{a_{\text{KM}} a_{\text{NaCl}}} = 0.54 \quad (19) \]
\[ K_2 = \frac{a_{\text{HM}} a_{\text{NaCl}}}{a_{\text{NaM}} a_{\text{HCl}}} = 0.72 \quad (20) \]

We may combine these expressions to give the equilibrium constant for the KM–HM system:

\[ K_3 = K_1 K_2 = \frac{a_{\text{KCl}} a_{\text{HM}}}{a_{\text{KM}} a_{\text{HCl}}} \quad (21) \]

Membrane compositions for the system HM–KM can be derived from \( K_3 \) by assuming ideal behavior in the membrane. Results are given in Tables 1 and 2.

**Transference numbers**

The derivative of the curve in Fig. 3 gives the transference number of \( \text{K}^+ \) according to eqn. (13). In order to find the derivatives, the results in Fig. 3 were fitted to a polynomial. This was done by dividing the set of data into 3 intervals overlapping each other. Each interval was fitted to a polynomial of degree 4. The derivatives of the polynomials obtained in this matter, were used to find the transference numbers. The transference number of \( \text{Na}^+ \) was obtained in a similar manner.

Calculated results for \( t_{\text{H}^+} \) from Tables 1 and 2 are plotted against the mole fraction of \( \text{H}^+ \) in the membrane in Fig. 4. The error in the calculated transference number of \( \text{H}^+ \), \( t_{\text{H}^+} \), is less than \( \pm 0.005 \) in the presence of \( \text{K}^+ \) and slightly higher in the presence of \( \text{Na}^+ \), due to fewer experimental points.

![Fig. 3 The emf as a function of \( (\mu_{\text{HCl}} - \mu_{\text{KCl}}) \) in cell (a)](image)

![Fig. 4 The transference number of \( \text{H}^+ \) as a function of membrane composition, \( x_{\text{HM}} \), for the systems \( \text{K}^+/\text{H}^+ \) and \( \text{Na}^+/\text{H}^+ \)](image)
Discussion

Transference numbers in membranes can be obtained by two methods, the Hittorf method and the emf method [7]. Hittorf measurements were performed in cells with membrane stacks by Kontturi et al. [8,9]. Electric current was passed through the stack for 15–25 hr, and consecutive changes in composition due to electric current and diffusion were analyzed. The analysis time, which included membrane re-equilibration in HCl-solutions, was several weeks. By a suitable choice of current density and number of membranes all composition changes were kept within the stack, and polarization and diffusion were controlled also in this method. Composition analysis of the separate membranes which make up the stack were, however, time-consuming and high precision in the results were not reported [8,9].

The present emf method uses a membrane stack combined with a specific set of electrodes. Through this method problems of diffusion and polarization phenomena are avoided. The time taken to perform the experiments is shorter than for the Hittorf experiment, and results are obtained with a reproducibility of ±1%. In addition we obtain the transference number as a continuous function of composition. Previously, average values for a composition interval have been determined [7,8].

Problems with the procedure may be connected to the liquid layer between membranes. Forssell et al. [9] showed that the contribution from these layers is negligible. Our investigations confirm this different packing techniques had no significant effect on emf. The water activity can be controlled experimentally. We therefore conclude that we have improved the method for transference number determination.

The actual data obtained can be interpreted in terms of a model proposed by Ferland et al [3]. They suggested that the ionic mobility in the membrane is a function of membrane composition through:

\[ u_{H^+} = u_{H^+}^0 (1 - kx_{KM}) \]  (22a)
\[ u_{K^+} = u_{K^+}^0 (1 - kx_{HM}) \]  (22b)

where \( u_{H^+}^0 \) is the mobility of \( H^+ \) in a pure HM-membrane, and \( u_{K^+}^0 \) is the mobility of \( K^+ \) in a pure KM-membrane. The mobilities in the two-component membrane are \( u_{H^+} \) and \( u_{K^+} \) and \( x_i \) is the fraction of cationic sites held by component \( i \) in the membrane.

The physical idea behind this model is that a reduction in the mobility of an ion is proportional to the number of neighbour ions of the other kind. The parameter \( k \) is a constant chosen to give the best fit of the curve to the experimental data.

The transference numbers were fitted to this model, using a standard computer program. The calculations gave, \( k \approx 10^{-19} \) and \( u_{H^+}/u_{H^+}^0 = 4.9 \pm 0.1 \) for HM-KM, and \( k \approx 10^{-3} \) and \( u_{H^+}/u_{Na^+} = 4.2 \pm 0.2 \) for HM-NaM. We thus conclude that the interaction constant \( k \) is close to zero in both cases. For comparison the corresponding mobility ratios in infinite dilute aqueous solutions are 4.8 and 7.0, respectively.

With \( k \approx 0 \) we expect \( u_{Na^+}/u_{K^+} = 1.2 \) for the membrane. This will be checked in future experiments. The result for \( k \) is somewhat surprising, considering the fact that this membrane has a concentration of cationic sites of 1.6 kmol-m \(^{-3}\).

The values for the mobility ratios are reasonable, given some recent results on water transference numbers in the same membranes [2]. They show a linear relationship between the water transference number and the transference number of \( H^+ \). This indicates that each ion carries the same amount of water through the membrane, independent of other ions present. This is the same as saying that the interactions between the different cations moving through the membrane is very small.
Conclusions

A new method for determination of transfer-ence numbers in ion exchange membranes has been developed. Problems with diffusion causing concentration-polarization are avoided. Furthermore, the effect on the emf due to transfer of water is eliminated. The method has been established with a set of experimental results on cation exchange membranes in equilibrium with aqueous HCl/KCl and HCl/NaCl solutions. The transference numbers are given with less than 1% uncertainty.

It was found that the ratio of the ionic mobilities in the membrane did not change as the composition of the same ions in the membrane changed. The mobility ratios were $u_{H^+} / u_{K^+} = 4.9 \pm 0.1$ and $u_{11+} / u_{Na^+} = 4.2 \pm 0.2$.

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List of symbols

- $a_i$: activity of component $i$ (kmol-m$^{-3}$)
- $C_i$: concentration of component $i$ (kmol-m$^{-3}$)
- $F$: Faraday's constant (96487 C-eqv$^{-1}$)
- $j$: electric current density (faraday m$^{-2}$-sec$^{-1}$)
- $J_i$: flux of component $i$ (mol-m$^{-2}$-sec$^{-1}$)
- $k$: interaction parameter for ions in the membrane
- $K$: thermodynamic equilibrium constant
- $L_{ij}$: phenomenological coefficient related to charge and mass transfer, [mol$^2$/(J-m-sec)]$^{-1}$
- $m_i$: molality of component $i$ (mol-kg$^{-1}$)
- $R$: gas constant (8.314 J-K$^{-1}$-mol$^{-1}$)
- $t_i$: transference coefficient of component $i$
- $T$: temperature (K)
- $u_i$: mobility of component $i$ in membrane (m$^2$-sec$^{-1}$-V$^{-1}$)
- $u_{H^+}^0$: the mobility of $H^+$ in a pure HM-membrane (m$^2$-sec$^{-1}$-V$^{-1}$)
- $x$: coordinate axis (m)
- $x_{iM}$: equivalent axis of ion in the membrane
- $y_i$: activity coefficient for component $i$, concentration basis

Greek letters

- $\mu_i$: chemical potential of component $i$ (kJ-mol$^{-1}$)
- $\Delta \phi$: electric potential (kJ-faraday$^{-1}$)

References