

# Transport Properties of a Cation Exchange Membrane with Sodium and Potassium as Counterions

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The measured transport properties for the cation exchange membrane Ionics 61AZL389 in the  $\text{Na}^+ + \text{K}^+$  mixed counterion states are presented. The transport numbers of counterions and of water as well as the specific conductivity of the membrane showed approximately linear behaviour as a function of ionic fraction in the membrane. It is therefore concluded that it is possible to estimate the transport numbers of counterions from known selectivity coefficients and concentrations in the external solution. The transport number of water and the specific conductivity of the membrane can also be evaluated reasonably accurately using data for membranes in pure homoionic states. The separation ratio was found to be constant over a wide range of concentration ratios under the hydrodynamic conditions used experimentally.

Ion exchange resins have traditionally been used in different kinds of electrolytic separation processes.<sup>1</sup> It therefore seems quite strange that ion exchange membranes have not been utilized for the same purpose, despite the fact that ion exchange membranes can be continuously regenerated by an electric current. One cause may be a lack of knowledge of transport properties in ion exchange membrane systems in the case of electrolyte mixtures. To be able to characterize the transport process across the ion exchange membrane in the multi-ion case and under the influence of an electric field one must know the following quantities: the transport numbers of each ion and of water, the specific conductivity of the membrane and the separation ratio, which describes the permeability of individual ions in the membrane system including the boundary layers just adjacent to the membrane surface. Because this information has to be known at different total concentrations of the counterions of the bulk solution and for different ratios of the counterions, it is a tedious task to produce such data. This is due to the fact that the methods of measurement of the transport numbers and the separation ratio require a long measuring time and entail laborious preliminary preparations as well as a lot of analytical work. Furthermore, the separation ratio is dependent on the hydrodynamic conditions, and its numerical value therefore does not have the same kind of generality as, e.g., the transport numbers.

Recently, data have been published for transport numbers in a membrane for the systems  $\text{Na}^+/\text{K}^+$ ,  $\text{Li}^+/\text{Na}^+$  and  $\text{Na}^+/\text{Rb}^+$ <sup>2,3</sup> when the total concentration of equilibrating solution was  $0.1 \text{ mol dm}^{-3}$  while the concentration ratios of ions varied from 8/1 to 1/8. From these data certain simple relationships could be obtained, such as the approximate linear dependence of the transport numbers on the mole fraction inside the ion exchange membrane. We now com-

plete the data on the above-mentioned transport properties in a membrane for the case of the  $\text{Na}^+/\text{K}^+$ -system; i.e. the data presented earlier for the transport numbers is complemented by data on conductivities, the transport number of water and the separation ratio. Furthermore, the selectivity coefficient<sup>4</sup> for the ion exchange reaction occurring is presented because of its essential role in determining the transport process inside the membrane.

## Experimental

The cation exchange membrane used, Ionics 61AZL389, has a polystyrene base and sulfonate exchange groups, and is cross-linked with vinyl compounds and reinforced with modacrylic. The thickness of the membrane sheet was 1.2 mm and the diameter of the circular membrane used for the experiments was 2.0 cm. The selectivity coefficient ( $K_K^{\text{Na}}$ ) for the ion exchange reaction



where M is the fixed ion group ( $-\text{SO}_3^-$ ) in the membrane, was determined conventionally by analyzing the ion content of the membrane after equilibration.<sup>4</sup> The transport numbers of sodium and potassium ions in the membrane were taken from Ref. 2, and the conductivities were measured as described in Ref. 5. The dependence of membrane conductivity on temperature was also studied when the membrane was in a pure sodium state.

The transport number of water, i.e. the electroosmotic water transfer, was measured in a cell similar to the one described in Refs. 6 and 7. The volume of solution in each half-cell was about  $30 \text{ cm}^3$ . The diameter of the exposed membrane was 0.81 cm and the diameters of the two capil-

Table 1. Measured transport quantities in Ionics 61AZL389 cation exchange membrane in Na<sup>+</sup> + K<sup>+</sup> mixed counterion states in 25 °C.

$c_{\text{NaCl}}/c_{\text{KCl}}^a$	$\bar{c}_{\text{Na}^+}/\bar{c}_{\text{K}^+}^b$	$\bar{t}_{\text{Na}^+}^c$	$\bar{t}_{\text{Na}^+}^d$	$\bar{t}_w^e$	$\bar{x}/\text{Scm}^{-1}$	$\bar{\lambda}_{\text{Na}^+}^f$	$\bar{\lambda}_{\text{K}^+}^f$	$S$
$\infty$	$\infty$	1.0	1.0	15.2	0.0032	2.7	—	—
8/1	4.27	0.81	0.81	14.6	0.0035	2.8	2.7	2.02
6/1	3.50	0.76	0.77	14.4	0.0036	3.0	3.2	—
4/1	2.07	0.68	0.68	13.9	0.0037	3.3	3.2	1.39
2/1	1.19	0.52	0.55	13.5	0.0041	3.4	3.4	—
1/1	0.61	0.35	0.39	12.6	0.0042	3.7	3.6	1.34
1/2	0.29	0.21	0.20	11.8	0.0046	3.5	4.1	—
1/4	0.21	0.12	0.15	11.7	0.0048	3.5	4.2	1.39
1/6	0.14	0.083	0.094	11.6	0.0048	3.1	4.1	—
1/8	0.084	0.063	0.050	11.4	0.0049	2.5	4.0	1.39
0	0	0.0	0.0	10.8	0.0049	—	4.1	—

<sup>a</sup>Concentration ratio in the equilibrating solution. <sup>b</sup>Concentration ratio in the membrane. <sup>c</sup>Calculated values. <sup>d</sup>Observed values. <sup>e</sup> $l = 19.42 \text{ mA cm}^{-2}$ . <sup>f</sup> $\text{Scm}^2 \text{ mol}^{-1}$ .

larities were ca. 0.36 mm. The electric current density was varied from 2.9 mA cm<sup>-2</sup> to 38.8 mA cm<sup>-2</sup>. The experiments were always performed in two directions by changing the polarity of the electrodes. The accuracy of the measurements was about 5%.

The separation ratios for the sodium and potassium ions were measured as described earlier,<sup>8</sup> and in these measurements the thickness of the diffusion layer at the membrane was found to be about 0.25 mm.

Unless otherwise stated, all of these measurements were carried out when the total concentration of electrolyte in the external solution was 0.1 mol dm<sup>-3</sup>. The sodium/potassium ratios in equilibrating solutions and in the membrane are given in Table 1. The temperature in all experiments was 25 °C. The chemicals used were of analytical reagent grade. The determination of sodium and potassium ions was done by AAS (Varian AA-975). The potentiostat used for the electroosmosis experiments was a PAR model 173 D.

## Results and discussion

The capacity of the membranes was about 0.8 mequiv g<sup>-1</sup> or 1.2 mequiv g<sup>-1</sup> of wet membrane, depending on which sheet the membranes were cut from. These values are much smaller than those of George and Courant,<sup>9</sup> but agree with the results of D'Alessandro<sup>10</sup> for the same type of membranes. Capacities in various alkali metal ionic states differed by less than 5%. The water content, expressed as weight percent of water in the wet membrane, was: Li<sup>+</sup>, 32.0; Na<sup>+</sup>, 33.0; K<sup>+</sup>, 31.0; Rb<sup>+</sup>, 29.1; Cs<sup>+</sup>, 27.8; H<sup>+</sup>, 32.7. The selectivity coefficient  $K_K^{\text{Na}}$  for the ion exchange reaction (1) is

$$K_K^{\text{Na}} = (\bar{c}_{\text{Na}^+}/c_{\text{Na}^+})/(\bar{c}_{\text{K}^+}/c_{\text{K}^+}) = (\bar{m}_{\text{Na}^+}/m_{\text{Na}^+})/(\bar{m}_{\text{K}^+}/m_{\text{K}^+}) \quad (2)$$

$$= (\bar{x}_{\text{Na}^+}/x_{\text{Na}^+})/(\bar{x}_{\text{K}^+}/x_{\text{Na}^+})$$

where the bar refers to the membrane phase,  $c$  is the molar concentration,  $m$  is the molality and  $x$  is the mole fraction or ionic fraction of cations. If the selectivity coefficient is

constant it can be determined from the slope of the relationship  $\bar{c}_{\text{Na}^+}/\bar{c}_{\text{K}^+} = f(c_{\text{NaCl}}/c_{\text{KCl}})$ . From Fig. 1 it can be seen that this relationship is linear to a good degree of accuracy, and from the slope one obtains:  $K_K^{\text{Na}} = 0.540 \pm 0.013$ . It has to be realized that the selectivity coefficient does not necessarily have to have a constant value, and that constancy of its value means that  $(\bar{f}_{\text{Na}^+}/y_{\text{Na}^+})/(\bar{f}_{\text{K}^+}/y_{\text{K}^+})$  is approximately constant, where  $\bar{f}_{\text{Na}^+}$  and  $\bar{f}_{\text{K}^+}$  are the rational activity coefficients in the membrane and  $y_{\text{Na}^+}$  and  $y_{\text{K}^+}$  are molal activity coefficients in the external solution.<sup>11</sup> Our result is in slight discrepancy with that of Ref. 11.

When the measured transport numbers given in Ref. 2 are plotted against the ionic fraction of sodium ion inside the membrane, a plot which is linear to a good degree of accuracy is obtained (Fig. 2 and Table 1). This means that the transport numbers can be estimated using the selec-

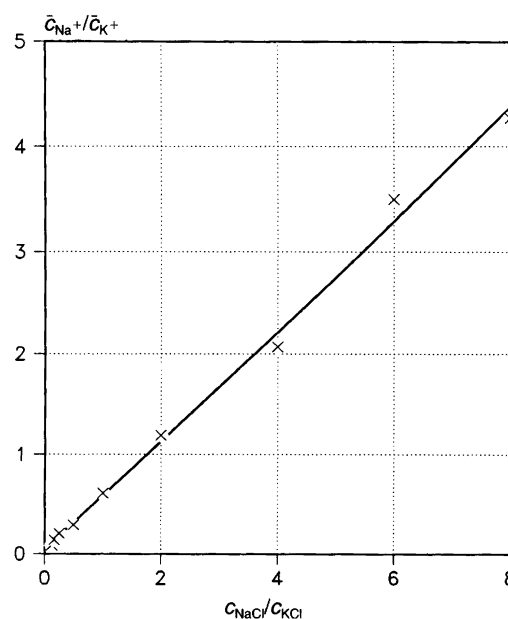


Fig. 1. The ratio of sodium ions to potassium ions in the membrane as a function of the ratio in the equilibrating solution.

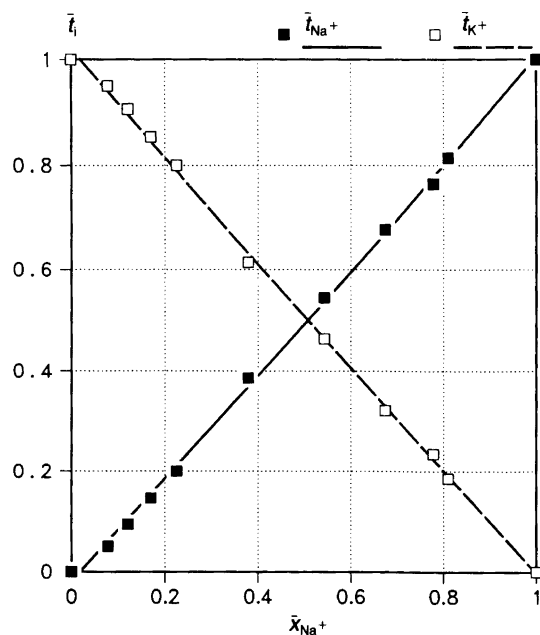


Fig. 2. The transport numbers of sodium and potassium ions in the membrane as a function of the ionic fraction of sodium ion in the membrane.

tivity coefficient and the concentrations in bulk solutions,  $c_{\text{NaCl}}$  and  $c_{\text{KCl}}$ , as follows:

$$\bar{t}_{\text{Na}^+} \approx K_{\text{K}}^{\text{Na}} c_{\text{NaCl}} / (c_{\text{KCl}} + K_{\text{K}}^{\text{Na}} c_{\text{NaCl}}) \quad (3a)$$

$$\bar{t}_{\text{K}^+} \approx 1 - \bar{t}_{\text{Na}^+} \quad (3b)$$

Calculations show that using eqns. (3a) and (3b), relatively accurate values for  $\bar{t}_{\text{Na}^+}$  and  $\bar{t}_{\text{K}^+}$  are obtained. Significant deviations occur when the ionic fraction of the non-preferred ion,  $\bar{x}_{\text{Na}^+}$ , is small (Table 1). The same behaviour was observed in the  $\text{Li}^+\text{-Na}^+$  and  $\text{Na}^+\text{-Rb}^+$  systems.<sup>3</sup> The opposite results were obtained by Meares and Sutton;<sup>12</sup> in their measurements the transport number of the thermodynamically preferred ion was especially low when it occurred in small amounts.

The specific conductivity of the membrane ( $\bar{\kappa}$ ) and the calculated molar conductivities (mobilities) of sodium and potassium ions ( $\bar{\lambda}_{\text{Na}^+}$ ,  $\bar{\lambda}_{\text{K}^+}$ ) are presented in Table 1. To obtain some idea of the influence of temperature, the specific conductivities were measured in the temperature range 15–85°C when the membrane was in a pure sodium state. These results are presented in Fig. 3, and one can conclude that careful thermostating is essential. When the specific conductivity is plotted against the ionic fraction of sodium ion a linear relationship is again obtained when  $\bar{x}_{\text{Na}^+} > 0.2$  (Fig. 4). Below this value the linearity fails. The shape of the curve resembles that in Ref. 6 for the  $\text{Na}^+\text{-H}^+$  system and that in Ref. 7 for the  $\text{Na}^+\text{-Sr}^{2+}$  system, but is quite different from that in Ref. 7 for the  $\text{Na}^+\text{-Cs}^+$  system, in which the specific conductivity is almost constant when  $\bar{x}_{\text{Na}^+} > 0.3$ . The specific conductivities and the mobilities in

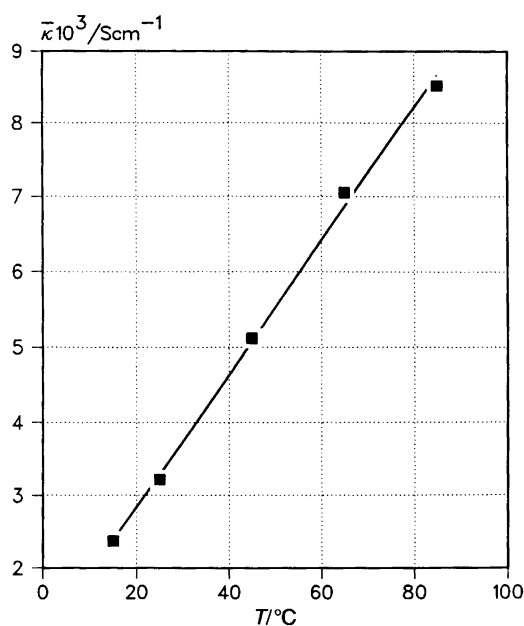


Fig. 3. The dependence of specific conductivity of the membrane on temperature.

the membrane when it is in a pure sodium or potassium state are somewhat different from those presented earlier,<sup>3,5</sup> because membranes were cut from different sheets; the molar conductivities of these ions in the membrane are almost the same as given in Refs. 9 and 10. The transport number of water  $\bar{\tau}_w$  defined as in Refs. 4–7, 13 and 14 is presented in Table 1. The correction due to the influence of electrode reactions and partial molar volumes of the salts on  $\bar{\tau}_w$  was found to have a maximum value of 0.67 (in 0.1 M

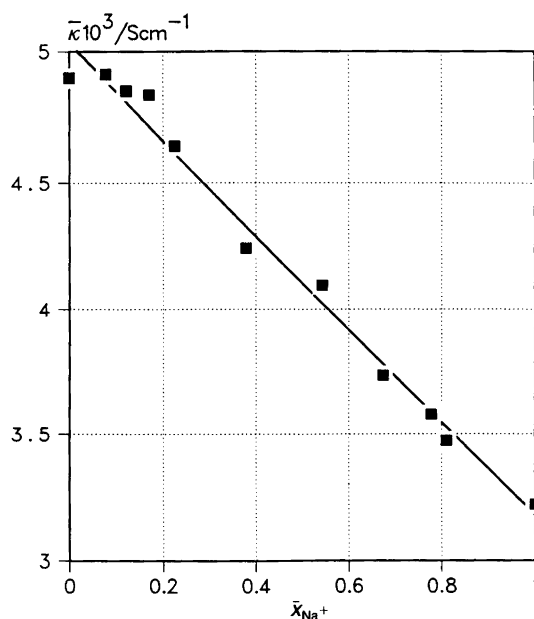


Fig. 4. The specific conductivity of the membrane as a function of ionic fraction of sodium ion in the membrane.

KCl). The concentration changes in the half-cells of the electroosmosis cell during a run were less than 2.5%; thus the osmotic water flow should be negligible. In Fig. 5 we have plotted  $\bar{\tau}_w$  as a function of ionic fraction inside the membrane. These curves resemble that in Ref. 6 but are different from those in Ref. 7, in which the curves have maxima. Thus, in our case the estimation of  $\bar{\tau}_w$  can be done simply using the data from electroosmotic measurements when the membrane is in a pure sodium or potassium state. From the water content and capacity data we can calculate that there are ca. 15 molecules of water for one sodium ion, i.e. all the water inside the membrane is "moving"; in the pure lithium ion case some additional water must probably penetrate into the membrane. Many investigators<sup>9,15-18</sup> have reported that  $\bar{\tau}_w$  increases considerably when the electric current density is small enough but remains constant at high current densities. This behaviour might be connected with the existence of a plateau or limiting current region in the polarization curve,<sup>19</sup> a fundamental characteristic of an ion exchange membrane.<sup>20</sup> The main explanation for this anomalous electroosmotic flow is the heterogeneity of membranes.<sup>9,15-18</sup> In many practical applications the electric current densities used are so high that  $\bar{\tau}_w$  remains constant.

To clarify the influence of ion type and concentration on electroosmotic flow, we measured  $\bar{\tau}_w$  in the pure sodium and lithium state in 0.1 and 1.0 M external solutions and in the potassium state in 0.1 M external solution as a function of current density (Fig. 6). The results agree with those previously reported:<sup>15</sup> water transport decreases as the external concentration is increased, and  $\bar{\tau}_w$  also decreases in the order  $\text{Li} > \text{Na} > \text{K}$ . One reason for the decrease of  $\bar{\tau}_w$  when increasing the concentration of the external solution

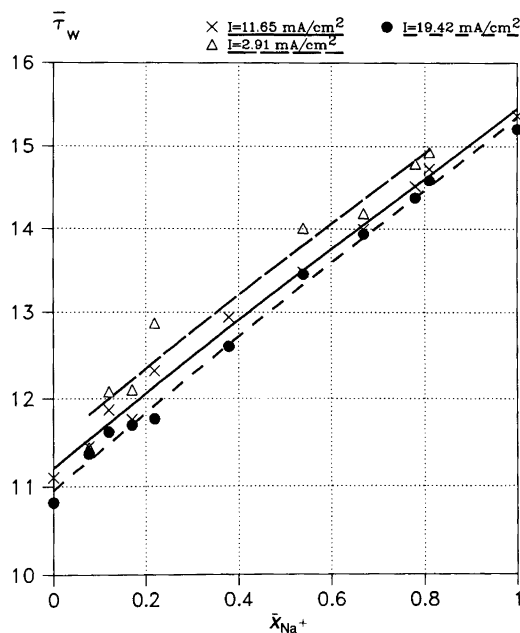


Fig. 5. The transport number of water in the membrane at different current densities as a function of ionic fraction of sodium ion in the membrane.

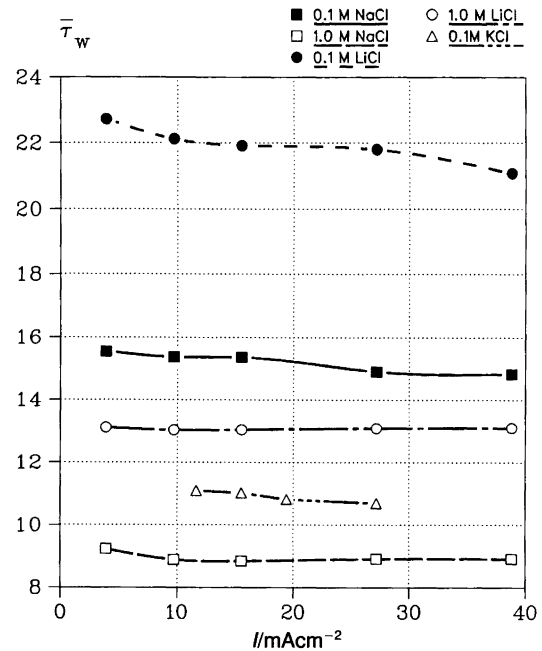


Fig. 6. The transport number of water in membrane in different pure homoionic states as a function of current density.

can be the lowering of current efficiency as the result of co-ion leak. This means that if the water transport number  $\bar{\tau}_w$  is reported as mol water per mol transferred cation, the decrease will not be as drastic as shown in Fig. 6. Indusekhar and Krishnaswamy<sup>18</sup> have calculated  $\bar{\tau}_w$  in both ways, and they did not observe a decrease of water transport with increasing concentration, regardless of how they performed the calculations. Another explanation might be the decrease in the water content of the membrane.<sup>15</sup> From Figs. 5 and 6 it can be seen that  $\bar{\tau}_w$  depends slightly on current density in 0.1 M external solutions but is constant in more concentrated solutions. Water transport numbers measured in pure, homoionic states of the membrane are very near those reported in Refs. 9 and 21.

The separation ratio,  $S$ ,<sup>22</sup> which includes the effect of concentration polarization, is defined in the following way:

$$S = (J_{k^+}/c_{k^+})/(J_{Na^+}/c_{Na^+}) \quad (4)$$

where  $J_{k^+}$  and  $J_{Na^+}$  are the ionic fluxes through the ion exchange membrane, and  $c_{Na^+}$  and  $c_{k^+}$  are the concentrations of ions on that side of the cation exchange membrane from which cations are transferred through the membrane by electric current. From Table 1, where the measured values for  $S$  are presented, it can be seen that  $S$  remains constant from a concentration ratio of 4/1 to 1/8. This is a surprising result; it cannot be explained using the transport numbers and selectivity coefficients even if we take account of the transport processes occurring in stagnant polarization layers. To understand this phenomenon the influence of hydrodynamics on the polarization layer have to be considered. These studies are in progress.

## Conclusions

The approximate model for calculating the transport numbers of cations in binary mixtures in the type of membrane studied by using selectivity coefficients and concentration ratios of external solutions seems to work quite well. By using the "triangle rule".<sup>4,23</sup>

$$K_b^a = K_c^a K_b^c \quad (5)$$

one can easily estimate a new selectivity coefficient, which makes it possible to obtain estimates for transport numbers in systems for which measurements have not yet been made.

From these measurements, as well as those presented earlier,<sup>3</sup> it can be seen that the ratio of the mobilities is almost unity one, i.e. the faster ion accelerates the slower one and the slower one retards the faster one to a certain extent as a function of ionic fraction of the slower ion. If the ionic fraction of the slower ion is below this limit the ratio of the mobility of the slower ion to that of the faster one drops below one. One reason for this behaviour might be the heterogeneity of this type of membrane. In the mixed counterion states our results differ from those of Meares and Sutton<sup>12</sup> and of McHardy *et al.*<sup>7</sup> obtained for the Na<sup>+</sup>-Cs<sup>+</sup> system.

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