The Transport Numbers and Mobilities of Ions in the Sodium/Lithium and Sodium/Rubidium Systems in a Cation-Exchange Membrane

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The transport numbers of cations and the conductivites in two systems – sodium/lithium and sodium/rubidium – were determined at different concentration ratios of these ions in a cation-exchange membrane. The mobilities of individual ions in the ion-exchange membrane were calculated from these data. The transport numbers are almost linearly dependent on the ionic fraction inside the membrane, which is much different from the ionic fraction in the equilibrating solution. In the case of alkali metal ion mixtures, a good estimate of transport numbers is obtained when the ion content of the membrane is analyzed.

Ion-exchange membranes are used in many branches of chemical industry and in a variety of power sources. One of the reasons why more extensive use of ion-exchange membranes has not been made is the lack of knowledge of their permeability properties in the multicomponent case. This is especially the case in many applications of electrodialysis and also in the recently studied method for the separation of electrolytes using countercurrent electrolysis.[1,2] The ordinary methods for determination of transport numbers in ion-exchange membranes are such that they actually measure the electrical permeability, which includes the additional effect of polarization layers at the membrane/solution interface.[3,4] This kind of procedure may be pertinent for practical purposes, but leaves the question of the influence of the membrane itself (or of the concentration polarization layers themselves) unanswered. Therefore it is important to be able to study ion transport in ion-exchange membranes without the contribution of polarization phenomena. When combining these results with the results obtained from the measurements of electrical permeability, valuable information on the polarization phenomenon can be obtained.

In two previous papers,[5,6] a method for the simultaneous determination of transport numbers of a mixture of ions in an ion-exchange membrane has been presented. In Ref.5, the transport numbers of sodium and potassium ions present in different ratios in a cation-exchange membrane (Ionics 61AZL389) were determined. In the present paper the results of measurements of the transport numbers of two systems – sodium/lithium and sodium/rubidium – in the same membrane but at different concentration ratios of these ions are presented. To complete the data for these systems, the conductivity of the membranes was also measured. This, together with the measured transport numbers, allows us to determine the molar conductivity (mobility) of individual ions in ion-exchange membranes. The conductivity measurements were carried out using two separate methods as described by Ojala and Forssell.[7]

Theory

The method[5] used to determine the transport numbers is based directly on the definition of the transport number t_i:

$$t_i = z_i F J_i^{migr}/j \tag{1}$$

where z_i is the charge number of ion i, F is Faraday's constant, J_i^{migr} is the migration flux of ion i, and j is the electric current density. The migration flux is measured by a method analogous to Hittorf's method for electrolyte solutions. Thus, the transport number is referred to the membrane just as Hittorf's transport number is referred to the solvent. When the conductivity of the membrane, $\varkappa$, is known for each particular electrolyte mixture we can calculate the mobility of an ion, λ_i, using the equation

$$\lambda_i = t_i \varkappa/(|z|_i c_i^m) \tag{2}$$

where c_i^m is the concentration of ion i in a membrane. It should be noted that the mobility obtained from eqn. (2) cannot be used as the mobility in the Nernst-Einstein relationship,[8] at least without strong experimental support. This is due to the fact that the membrane phase behaves as a very concentrated solution. However, Forsell[9] recently published results which show that in the case of cations, the ionic diffusional mobility is approximately equal to the ionic electrical mobility, indicating that the mechanism of ion transport for diffusion is similar to that for electrical conduction. This result becomes evident when it is born in mind that diffusion in ion-exchange membranes in the ideal case is mainly exchange diffusion, not bulk diffusion.

Experimental

Circular membranes with a diameter of 2.00 cm and a thickness of 0.12 cm were used. Two series of measurements were made. In the first series, eight different mixtures of NaCl and LiCl in water, as well as pure NaCl and pure LiCl in water were investigated. In the mixtures, the molar Li^+/Na^+ ratios used were $\frac{8}{1}$, $\frac{4}{1}$, $\frac{2}{1}$, $\frac{1}{1}$, $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{6}$ and $\frac{1}{8}$. In the second series, six different mixtures of NaCl and RbCl in water, as well as pure NaCl and pure RbCl in water were investigated. In the Na^+/Rb^+ mixtures the molar ratios were $\frac{8}{1}$, $\frac{4}{1}$, $\frac{1}{1}$, $\frac{1}{4}$, $\frac{1}{6}$ and $\frac{1}{8}$.

Prior to each measurement, the membranes were equilibrated in the appropriate solution for several weeks. The hydrogen-ion form of the membrane required by the measuring method[5] was produced by equilibrating the membranes in

HCl solution for the same length of time. All electrolyte solutions used had a total concentration of 0.1 mol dm^{-3}. The apparatus and methods of measurement have been described in detail: the method of determination of transport numbers in Ref. 5 and the method of determination of conductivity in Ref. 7. The concentrations of ions inside the membranes were determined by atomic absorption spectrophotometry (Varian AA-975). The galvanostat was a PAR model 173 D. All the chemicals used were Merck *p.a.* products.

Results and discussion

The selectivity coefficient K_b^a for the univalent counter ion-exchange reaction

$$a + \bar{b} = \bar{a} + b \tag{3}$$

(where the bar refers to the inside of the ion-exchange membrane) is determined by the equation:

$$K_b^a = \bar{x}_a x_b/(\bar{x}_b x_a) \tag{4}$$

where $\bar{x}_i$ is the ionic fraction of ion i in the membrane and x_i is the mole fraction of ion i in the solution.[4] The values of K_{Li}^{Na} and K_{Rb}^{Na} were 1.31 ± 0.025 and 0.486 ± 0.025, respectively, obtained from eqn. (4) using linear regression.

The measured transport numbers and mobilities calculated according to eqn. (2) (after the measurement of the conductivity) are reported in Table 1 for the Li^+/Rb^+ counter ion system and in Table 2 for the Na^+/Rb^+ counter ion system. In Figs. 1 and 2 the transport numbers are presented as a function of ionic fraction of ion inside the cation-exchange membrane. Clearly, for both systems studied the transport numbers are to a good degree of accuracy linearly dependent on ionic fraction inside the membrane. However, when the concentration of the slower-moving ion decreases, deviations from the linear dependence begin to occur. To understand this phenomenon more experimental work has to be done, but one cause seems to be relatively clear: part of the counter ions are practically unable to move because of strong interaction with the ion-exchange resin. This interaction is due to the structure of the resin matrix which allows the formation of gaps where ions are hidden.

Table 1. Measured conductivities, transport numbers and mobilities of sodium and lithium ions in a cation-exchange membrane (Ionics 61AZL389) at 25 °C.

c_{Li}/c_{Na}[a]	x_{Li}^{m}[b]	x^{m}/Scm^{-1}	t_{Li}^{m}	t_{Na}^{m}	λ_{Li}^{m}[c]	λ_{Na}^{m}[c]
∞	1.00	0.0020	1.00	0.00	2.0	–
8.00	0.79	0.0021	0.78	0.22	2.0	2.1
4.00	0.71	0.0022	0.72	0.28	2.2	2.2
2.00	0.58	0.0023	0.56	0.44	2.4	2.6
1.00	0.41	0.0024	0.41	0.59	2.4	2.4
0.500	0.24	0.0025	0.23	0.77	2.3	2.5
0.250	0.15	0.0029	0.13	0.87	2.5	3.0
0.167	0.12	0.0029	0.08	0.92	2.0	3.2
0.125	0.091	0.0029	0.04	0.96	1.4	3.2
0.00	0.000	0.0031	0.00	1.00	–	3.1

[a] Concentration ratio in the equilibrating solution. [b] Ionic fraction in the membrane. [c] in $Scm^{2}mol^{-1}$.

Table 2. Measured conductivities, transport numbers and mobilities of sodium and rubidium ions in a cation-exchange membrane (Ionics 61AZL389) at 25 °C.

c_{Na}/c_{Rb}[a]	x_{Na}^{m}[b]	x^{m}/Scm^{-1}	t_{Na}^{m}	t_{Rb}^{m}	λ_{Na}^{m}[c]	λ_{Rb}^{m}[c]
∞	1.00	0.0030	1.00	0.00	3.1	–
8.00	0.80	0.0029	0.77	0.23	3.2	3.7
4.00	0.68	0.0032	0.69	0.31	3.6	3.4
1.00	0.36	0.0038	0.35	0.65	3.8	4.0
0.250	0.15	0.0043	0.13	0.87	4.1	4.7
0.167	0.10	0.0043	0.08	0.92	4.2	4.8
0.125	0.085	0.0046	0.07	0.93	4.1	5.0
0.00	0.000	0.0048	0.00	1.00	–	5.0

[a] Concentration ratio in the equilibrating solution. [b] Ionic fraction in the membrane. [c] In $Scm^{2}mol^{-1}$.

The greatest problem when determining the transport numbers and conductivities is the variation in the properties of the cation-exchange membranes used. To save time, the measurements described were made using a large number of membranes, instead of equilibrating the same membranes repeatedly. The capacity of the separate membranes varied from one membrane to another. This behaviour was pronounced when the membranes were cut from different sheets. According to our experience, this variation in properties did not so much effect the transport numbers (less than 5%) but had a more severe effect on conductivites. Another source of error is the amount of free salt inside the membrane. We measured the percentage of free salt to be ca. 5%. This amount is so small that we were not able to distinguish its effect, and within experimental error the current efficiency was unity.

From Figs. 1 and 2 it can be deduced that in the case of alkali metal ion mixtures, a good estimate for transport numbers is obtained when the ion content of the membrane is analyzed. It must be noted that the mole fraction inside the membrane is very different from the mole fraction in the equilibrating solution. Furthermore, this kind of procedure can be applied only in the case of alkali metal ions; preliminary experiments with alkaline earth cations indicate that these cations behave differently.
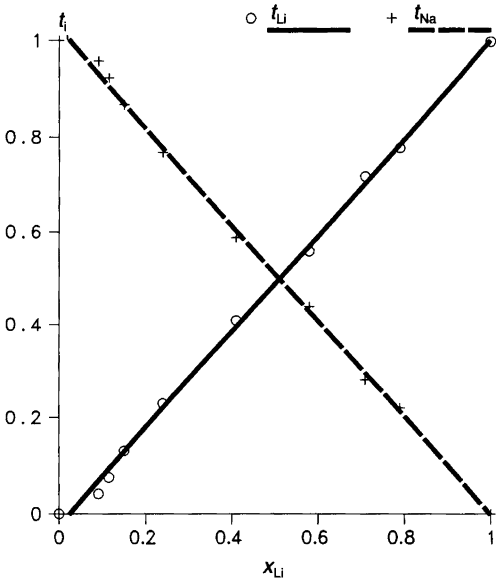
Fig. 1. The transport numbers of sodium and lithium ions in Ionics 61AZL389 cation-exchange membrane as a function of the ionic fraction of lithium ion inside the membrane.
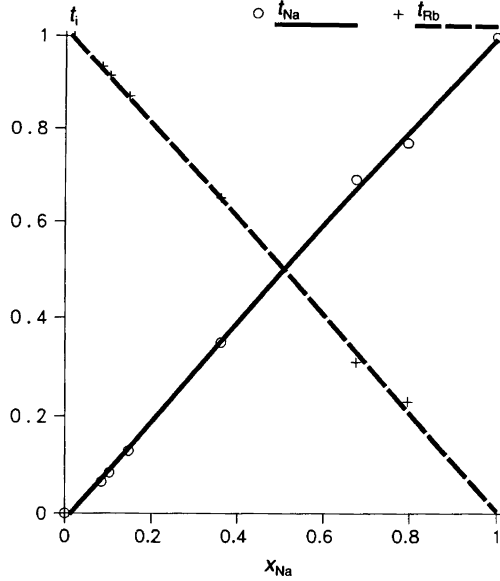
Fig. 2. The transport numbers of sodium and rubidium ions in Ionics 61AZL389 cation-exchange membranes as a function of the ionic fraction of sodium ion inside the membrane.

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