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A Method for Determination of Transport Numbers in Ion Exchange Membranes

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A method for the simultaneous determination of transport numbers of several ions in ion exchange membranes is presented. In the present method a stack of closely packed cation exchange membranes is used. The transport numbers were calculated from the changes of the amounts of the ions in each membrane caused by the electric current analogously to the Hittorf's method. The method was applied to determine the transport numbers of sodium and potassium ions at different ratios in cation exchange membrane (Ionics 61 AZL 389).

The transport numbers of ions in ion exchange membranes are usually measured in systems consisting of a membrane between two binary electrolyte solutions. The two methods normally used are the Hittorf's method and the emf method.[1] The essential feature of the Hittorf's method as applied to electrolyte solutions is that the ionic flow through the homogeneous zone is measured simultaneously with the electric current. In binary systems where we have only one kind of counterion the membrane can be considered to be homogeneous and thus the Hittorf's method is applicable. Strictly speaking this is true only for the ideal membrane where the transport number of the counterion is equal to one. Therefore this transport number actually measures the ideality of the ion exchange membrane. The same is also true for the emf method.

However, if more than one ion can move in the membrane there will be concentration changes on the boundaries causing diffusion effects in the membrane in addition to the pure electric migration. Thus the Hittorf condition is not valid any more. Even though the "transport number" obtained is of practical importance since it describes the electric permeability under these specific conditions, it cannot be identified with the Hittorf's transport number as understood in an electrolyte solution, because it depends on current density.[2]

In the present method a stack of closely packed cation exchange membranes was used. One half of the membranes in the stack was equilibrated in a solution containing the cations, the transport numbers of which were to be determined. The other half was in the hydrogen form. A suitable quantity of electricity was passed through the stack so that the cations moved toward the membranes in hydrogen form. In the stack we have both diffusion and electric migration. Nevertheless, if the electric current and the time are properly chosen a part of the stack will remain unchanged and the diffusion processes do not take place in this zone. The transport of ions through this homogeneous zone* is only due to electric

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* One must take into account that when we are speaking of the homogeneity in ion exchange membrane, we disregard inhomogeneities due to the microstructure.

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migration, and the quantity transported and as a result of this the transport numbers can be obtained by analyzing the ion content of the membranes.

This method is analogous to the Hittorf's method in electrolyte solutions provided that the boundary effects between the membranes in the stack can be neglected.

THEORY

Transport of ions in ion exchange membranes is controlled by diffusion and electric migration. These two transport phenomena can be taken to be independent and superimposed. Thus the total flux of ion i (J_i) consists of two parts

$$J_i = J_i^{\mathrm{D}} + J_i^{\mathrm{Migr}} \tag{1}$$

where J_i^{D} is the diffusion flux and J_i^{Migr} is the migration flux.

$$J_i^{\mathrm{D}} = -\sum_{l=1}^{n} v_{il} \sum_{j=1}^{n} D_{ij} \frac{\mathrm{d}c_j}{\mathrm{d}x} \tag{2}$$

$$J_i^{\mathrm{Migr}} = t_i I / z_i F \tag{3}$$

In eqns. (2) and (3), c_j is the concentration of and D_{ij} are the diffusion coefficients of component j, v_{il} is the stoichiometric coefficient of ion i, t_i is the transport number of ion i, z_i is the charge number of ion i, F is the Faraday constant, and I is the electric current density.

The fluxes J_i, J_i^{D}, and J_i^{Migr} are to be related to some reference frame. A reasonable and practical choice for reference frame is the membrane itself. The immobility of the membrane sets constraints to the diffusion fluxes (J_i^{D}) as the membrane itself is one of the components. If no co-ions are present in the membrane only interdiffusion takes place and bulk diffusion vanishes. This in fact means that in eqn. (2) only crossdiffusion coefficients D_{ij} ($i \neq j$) exist.

The over-all flux is given usually by the so-called extended Nernst-Planck equation which according to Helfferich[2] is

$$J_i = (J_i)_{\mathrm{diff}} + (J_i)_{\mathrm{el}} + (J_i)_{\mathrm{con}} =$$

$$-D_i\left(\frac{\mathrm{d}c_i}{\mathrm{d}x} + z_i c_i \frac{F}{RT}\frac{\mathrm{d}\phi}{\mathrm{d}x} + c_i \frac{\mathrm{d}\ln f_i}{\mathrm{d}x}\right) + c_i \mathrm{v} \tag{4}$$

$(J_i)_{\mathrm{diff}}$ is the diffusion flux, $(J_i)_{\mathrm{el}}$ the flux of electric transfer, and $(J_i)_{\mathrm{con}}$ the convection part of transfer. D_i is the ionic diffusion coefficient, c_i the concentration of ion i, f_i the molar activity coefficient of ion i, ϕ the electric potential, and v the rate of motion of the center of gravity.

Obviously, eqns. (1), (2) and (3) correspond to eqn. (4). However, when we compare these equations the following facts have to be taken into account: Firstly, eqn. (4) is not exact, because the Nernst-Planck equations include the coupling between the components in a simplified form.[3-6] Secondly, in eqns. (1), (2) and (3) all transport quantities including diffusion coefficients are referred to the membrane and therefore, the convective terms vanish. The fluxes of electroneutral components such as water are to be presented by equations analogous to (1, 2, 3) where t_i/z_i is the so-called reduced transport number. Thirdly, the terms $(J_i)_{\mathrm{diff}}$ and $(J_i)_{\mathrm{el}}$ in eqn. (4) do not correspond to the terms J_i^{D} and J_i^{Migr} in eqns. (2) and (3), since $(J_i)_{\mathrm{el}}$ further includes that part of J_i^{D} coming from the coupling to the other gradients and from the electric migration term.

The transport number of ion i (t_i) is according to eqn. (3):

$$t_i = z_i F J_i^{\mathrm{Migr}}/I$$

In experiments the electric current and the total flux J_i are readily obtainable, but in practice the division of J_i into J_i^{D} and J_i^{Migr} is virtually impossible. Therefore the experiments have to be arranged so that the diffusion flux J_i^{D} is neglible which in fact means that concentration gradients must vanish. That is why we have to have a homogeneous zone in the membrane through which the fluxes are measured. Actually, this is the so-called Hittorf method of transport number determination as used in electrolyte solutions, where the reference frame is the solvent instead of the membrane.

When using only one membrane between two solutions it is difficult to simultaneously keep the membrane homogeneous and to measure the flux, because the flux must be calculated from the concentration changes. When there is only one counterion these difficulties can be overcome by using the so-called concentrations clamp-method.[7] However, when there are two or more counterions this kind of arrangement cannot be achieved in practice.

In systems containing two or more counterions we have to be able to control and determine the concentration profiles in the membrane. This can be achieved by using a stack of membranes as was used by Hellferich[2] in interdiffusion measurements. However, in a stack of ion exchange membranes the liquid films between the membranes are the source of inhomogeneity. In our next paper we have shown that the effect of these liquid films becomes negligible when the thicknesses of the films are small compared with the thicknesses of the membranes.

EXPERIMENTAL

The transport numbers of sodium and potassium in cation exchange membrane (Ionics 61 AZL 389) were determined. Nine different mixtures of NaCl and KCl in water, the total concentrations of which were 0.1 mol/dm^3, were investigated, namely those having $\mathrm{Na}^+/\mathrm{K}^+$ ionic fractions of $\frac{8}{1}$, $\frac{6}{1}$, $\frac{4}{1}$, $\frac{2}{1}$, $\frac{1}{1}$, $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{6}$, and $\frac{1}{8}$. Prior to each measurement, the membranes were equilibrated with the appropriate solution for several weeks. The membranes in hydrogen form were equilibrated in 0.1 mol/dm^3 HCl-solution for the same length of time.

Apparatus

The apparatus used in transport number measurements is presented in Fig. 1. Between two electrode compartments we have a stack of ion exchange membranes tightly fitted in the tube (T). The anode compartment, which is well-stirred, is filled with the solution used to equilibrate the membranes into the sodium and potassium form. Silver plate was the anode used ($\mathrm{Ag}+\mathrm{Cl}^- \overset{-e}{\rightleftarrows} \mathrm{AgCl}$). The cathode compartment is filled with HCl solution whose concentration is the same as the total concentration in the anode compartment. In the stack we have eleven similarly equilibrated cation exchange membranes on the left side of the stack and twelve membranes in hydrogen form on the right side. A potentiostat (PAR 173) was used to control the constant electric current through the stack.

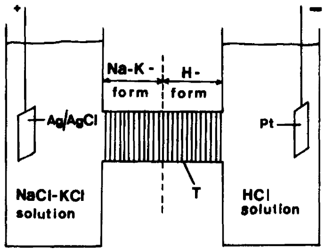

Fig. 1. The apparatus used to measure transport numbers.

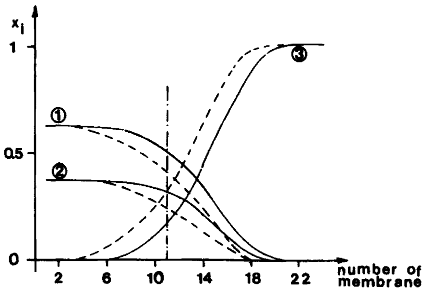

Fig. 2. Measured concentration distributions of potassium (1), sodium (2) and hydrogen ion (3) in the stack with (–) and without (---) electric current. x_i is the mole fraction of the ion i and the ion exchange capacity was 0.45±0.01 mmol. The concentrations in equilibrating solution were $C_{K^+}=C_{Na^+}=0.05$ mol/dm^3.

Measurements

The transport number measurements were performed in the cell described in Fig. 1. The measuring time from one experiment to another varied from 15 to 25 h and the electric current used in most of the measurements was 1.5 mA, when the membrane area was about 3.1 cm.^{2} Also experiments using electric currents of 3.0 mA and zero were done. The cell lay in a thermostat the temperature of which was (25±0.05) °C. After the measurements the membranes from the stack were put one by one into separate bottles containing hydrochloric acid of the concentration 0.1 mol/dm^3. After equilibrating for several weeks the concentrations of sodium and potassium in the bottles were analyzed by flame photometry to obtain the amounts of these ions in each membrane. With the aid of these results we were able to find the homogeneous region in the stack and also to calculate the amounts of sodium and potassium transported through this homogeneous region. With this information we

Table 1. Measured transport numbers of sodium and potassium ions in cation exchange membrane (Ionics 61 AZL 389).[a]

Ratio C_{Na^+}/C_{K^+} in		Transport numbers		Ratio of mobilities
equilibrating solution	"homogeneous" membrane	t_{Na^+}	t_{K^+}	u_{Na^+}/u_{K^+}
8.00	4,27	0,814	0,186	1,02
6.00	3,50	0,765	0,235	0,93
4.00	2,07	0,678	0,322	0,98
2.00	1,19	0,545	0,464	0,99
1.00	0,610	0,386	0,614	1,02
0.506	0,290	0,200	0,800	0,85
0.167	0,138	0,094	0,906	0,76
0.125	0,084	0,050	0,950	0,63

[a] The total concentration $C_{Na^+}+C_{K^+}=0.1$ mol/cm^3 in every equilibrating solution and their pH values were adjusted to be approximately nine. In each measurements the ion exchange capacity of used membranes is (0.45±0.01) mmol when the diameter of the membrane is 2.0 cm and its thickness is about 0.1 cm. The magnitude of electric current was 1.5 mA and the current efficiency varied from 0.95–1.05. It is reasonable to assume that deviations from 1.0 were due to the errors in analysis of Na$^+$ and K$^+$.

could calculate the transport numbers analogously to the Hittorf's method for determination of transport numbers in electrolyte solutions.

It must be pointed out that the method of analysis of the membrane content used in this work – namely analyzing each membrane separately and not several membranes equilibrated in the same solution and then analyzing it as a whole – is not a very accurate one due to the cumulative errors resulting from many separate determinations. Therefore we can conclude that the error limits in transport numbers are about 5 %. This, of course, can be easily avoided but in these preliminary investigations we wanted to be sure that the homogeneous zone is formed and also to obtain information regarding the exchange diffusion inside the stack (see Fig. 2).

RESULTS AND DISCUSSION

The results are presented in Table 1. As can be seen the ratio of mobilities is near to unity except in the cases where the amount of sodium is small compared with the amount of potassium the ratio then approaching the value in aqueous solutions. This result clearly shows that the assumption of constant mobilities as assumed in Nernst-Planck equation is not valid within the whole concentration ratio range. The sum of transport numbers (t_K+, $t_{Na}+$) is in all cases near unity indicating the small role of other ions.

The effect of electric current density was tested in some experiments but no significant differences in transport numbers were observed while varying electric current density.

An experiment was performed without electric current to obtain estimates for the interdiffusion coefficients of sodium and hydrogen as well as potassium and hydrogen in the membrane. The values of the interdiffusion coefficients were in agreement with the values given in Helfferich's book.[2] In every case these interdiffusion coefficients were smaller than the diffusion coefficients in water.

In the experiments thicknesses of the water layers on the membranes were estimated to be much less than one per cent of the membrane thickness. The transport number of the counterion in the membrane is different from that in water.

The flux through the water layer is, however, determined by the transport numbers in the membrane, because the diffusion in the thin water layer compensates for this difference in transport numbers. This means that the water layer adapts itself to the transport determined by the ion exchange membrane. This is treated in more detail in our subsequent paper.

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