Hydrogen-ion transport numbers in cation exchange membrane determined by emf method

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The electromotive force of the membrane cells /Hg/Hg$_2$SO$_4$/H$_2$SO$_4$, a'/ Ion exchange Nafion membrane /H$_2$SO$_4$ a''/Hg$_2$SO$_4$/Hg/ with different solution concentrations from 0.01 to 2 mol kg^{-1} H$_2$O were measured. On that basis the apparent transport number of H$^+$-ions and its dependence on external electrolyte concentration were determined. The dependence was then used for the calculation of both the transport number of H$^+$-ions and the water transference numbers. It was found that the apparent transport number of H$^+$-ions decreases with increasing external concentration while the transport number of H$^+$-ions and the transference number of water remain constant up to concentrations of 1.2 moles kg^{-1} h$_2$O

Keywords Concentration; ions; transport numbers, electromotive force; ion exchange, membrane, solutions

INTRODUCTION

Ion exchange membranes made of fluorinated and perfluorinated polymers possessing exceptional chemical, thermal and mechanical stability are used as an excellent diaphragm in dialysis as well as solid electrolyte and separator in electrochemical cells[1-4]. Transport properties of the membranes in such applications are critical for effective performance, so they are still under investigation.

The work presents part of a study of transport phenomena in the system: sulphonic acid membrane–sulphuric acid solutions aimed at determining the phenomenological equations according to nonequilibrium thermodynamic treatment of transport in the membranes. It has been the purpose of this part to determine the transport numbers of H$^+$-ions and the transference number of water.

The transport numbers of the counter-ions in the ion exchange membranes are found to be functions of the concentration of an external solution[5-7]. This property is usually well substantiated because the mobilities and relative concentrations of the co- and counter-ions in a membrane are functions of the external electrolyte concentration. The behaviour of the transference number (sometimes called mass transport number) of water $\bar{t}_w$ has been found to be quite similar[5-7]. Moreover its values are particularly dependent on water content in the membrane[8-10]. However, in the homogeneous membranes with small water content the $\bar{t}_w$ tends to small values being independent on the external solution concentration[9].

The aforementioned properties of the counter-ion transport number and water transference number are to some extent contradicted by the results of the other works[9,11-13]. The results of Arnold and Swift[12], and Leszko and Koblańska[13] show that $\bar{t}_+$ and $\bar{t}_w$ may, within the limits of experimental error, be independent of concentration, or their change is very small.

There are two methods normally used to determine the transport numbers: (i) direct measure of $\bar{t}_+$ and $\bar{t}_w$ which is some form of the Hittorf procedure; (ii) indirect emf method consisting of the measurements of the membrane concentration potential, i.e. the electromotive force (emf) of a membrane cell:

Electrode 1	Electrolyte a'	Membrane	Electrolyte a''	Electrode 2

In the present work the second method was chosen.

EXPERIMENTAL

Perfluorinated NAFION-120 membrane (DuPont, USA) was used. Its chemical composition, ionic capacity, conductivity and other parameters were described elsewhere[14].

The membranes were conditioned in boiling water and transformed into the H$^+$-form. Before emf measurements they were equilibrated in the solution of higher concentration for at least 12 h.

The emf measurements were performed by means of two reversible mercury–mercurous sulphate electrodes inserted in the cell solutions (without liquid junction); so the investigated membrane cells were as follows:

$$/\mathrm{Hg}/\mathrm{Hg_2SO_4}/\mathrm{H_2SO_4},a'|\mathrm{Membrane}|\mathrm{H_2SO_4},a''/\mathrm{Hg_2SO_4}/\mathrm{Hg}/$$

A two-compartment cell made of Plexiglass was used. Each compartment, with /Hg/Hg$_2$SO$_4$/SO$_4^{--}$ electrode separated from the other by a membrane 1.5 cm in diameter, was filled with H$_2$SO$_4$ solution and left to stand for ~30 min. The solutions in the compartments were then renewed and the potential (marked as E_M) was measured using voltmeter V-531 (Unitra, Poland) with an internal resistance of 1000 MΩ. The measurements were repeated with successively renewed solutions until further renewal caused no change in the potential obtained. The final potential E_M remained unchanged within ±0.02 mV over a period of 0.5–2.0 h.

The solutions in the membrane cell were stirred

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vigorously so that a further increase did not modify the potential. The cell and magnetic stirrer were placed in an air bath at 303 K.

The concentration ratio of the solutions in both compartments was varied from 1.16 to 2.01.

The mercury–mercurous sulphate electrodes prepared according to Ives and Janz[15] were equilibrated in the individual H_2SO_4 solutions for at least 24 h.

The potential of the cell with the same solutions but, instead of a membrane, separated by a plexiglass plate with a small channel, 0.2 mm in diameter, was measured prior to E_M.

CALCULATION OF TRANSPORT NUMBERS

Two main approaches are commonly used for calculation of membrane potential. The first based on the idealized concept of Teorell, Meyer and Sievers (TMS) with various refinements[5] represents the membrane potential φ_M by an equation in which mean activities in the membrane phase must be used, and which neglect the effect of solvent transfer on the potential. Consequently the transport numbers derived from that equation have been called the apparent transport numbers.

The second, more realistic approach based on thermodynamics and non-equilibrium thermodynamics[5] takes into account the effect of electro-osmotic water transport and describes the membrane potential φ_M in terms of Scatchard's equation[16]:

$$\varphi_M = -\frac{RT}{F}\int_{I}^{II}\sum_{1}^{n}\bar{t}_k \, \mathrm{d}\ln a_k \tag{1}$$

where:

$\bar{t}_k$ = the transference number of the 'k' component
a_k = the activity of the 'k' component
n = the number of components in a solution
R, T and F have their usual meaning.

In our cells with H_2SO_4 solutions and 'internal' electrodes, and with the application of the appropriate TMS equation for φ_M, the emf value E_M may be expressed with the following equation:

$$E_M = -1.5\frac{RT}{F}\bar{t}_{H^+(app)}\ln\frac{m'f'_\pm}{m''f''_\pm} \tag{2}$$

where:

$\bar{t}_{H^+(app)}$ is the apparent transport number, which is assumed to be constant in the concentration range from m' to m'',
m' and m'' = the molalities of the two external solutions,
$f'_\pm$ and $f''_\pm$ = the mean ionic activity coefficients of the two solutions.

While deriving that equation, the necessary assumptions concerning the activities in the membrane phase and about the right boundary conditions on the membrane/solution interface were made.

Quite similar is the formula for the emf value E_0 of the concentration cell without membrane, but instead of $\bar{t}_{H^+}$ the appropriate transport numbers of H^+-ions t_{H^+} in the free solution with a mean concentration $(m'+m'')/2$ must be used.

The difference $E_M - E_0$ is then expressed in the following formula:

$$E_M - E_0 = 1.5\frac{RT}{F}(t_{H^+} - \bar{t}_{H^+(app)})\ln\frac{m'f'_\pm}{m''f''_\pm} \tag{3}$$

Equation (3) was used for $\bar{t}_{H^+}$(app) calculations as it eliminates the non-ideal values of the mercury-mercurous electrode potentials exhibited in any particular measurement.

For the calculation, the t_{H^+} values given by Hamer[17] and the $f_\pm$ values given by Dobos[18] were used.

As has been already mentioned the true transference numbers occur only in the Scatchard's equation. The electro-osmotic water transport term of that equation:

$$\varphi_{os} = -\frac{RT}{F}\int_{I}^{II}\bar{t}_W \, \mathrm{d}\ln a_W \tag{4}$$

where: $\bar{t}_W$ and a_W are the water transference number and water activity, respectively. This equation may be reformulated on the base of the Gibbs–Duhem equation (for H_2SO_4 solution):

$$\mathrm{d}\ln a_W = -m\frac{3M_W}{1000}\mathrm{d}\ln a_\pm \tag{5}$$

where:

$a_\pm$—the mean ionic activity of H_2SO_4 solution,
M_W—the water molecular weight,
m—the molar concentration of the H_2SO_4 solution.

After introducing that formula to the Scratchard's equation (1) and then to the expression for the EMF of the membrane cell studied, the following equation may be obtained:

$$E_M = -1.5\frac{RT}{F}\left(\bar{t}_{H^+} - 2M_W\frac{m}{1000}\bar{t}_W\right)\ln\frac{m'f'_\pm}{m''f''_\pm} \tag{6}$$

where: m is the mean molar concentration $(m'+m'')/2$.

The comparison of equations (6) and (2) results in the relation between $\bar{t}_{H^+(app)}$, $\bar{t}_{H^+}$ and $\bar{t}_W$:

$$\bar{t}_{H^+(app)} = \bar{t}_{H^+} - 0.036\, m\, \bar{t}_W \tag{7}$$

A similar relation for 1:1 electrolytes was given by Lakshminarayanaiah[10]. Moreover his evaluation has shown that the relation is able to give values for $\bar{t}_+$ agreeing well with those measured directly. The results of some other works[6,7,10,19] proved that independently determined $\bar{t}_+$ and $\bar{t}_W$ taken for the calculation of the EMF gave the cell emf's which agree satisfactorily with the observed potentials of membrane cell even in high concentration ranges.

Based on these conclusions, equation (7) was used to calculate the $\bar{t}_{H^+}$ and $\bar{t}_W$ values from the experimentally determined dependence of the apparent transport number $\bar{t}_{H^+(app)}$ on the external concentration. For this purpose the constancy of $\bar{t}_{H^+}$ and $\bar{t}_W$ in successive narrow concentration ranges must be assumed. Consequently the $\bar{t}_{H^+}$ and $\bar{t}_W$ values like the $\bar{t}_{H^+(app)}$ values ought to be considered as corresponding to the mean concentration of the solutions adjacent to membrane surfaces.

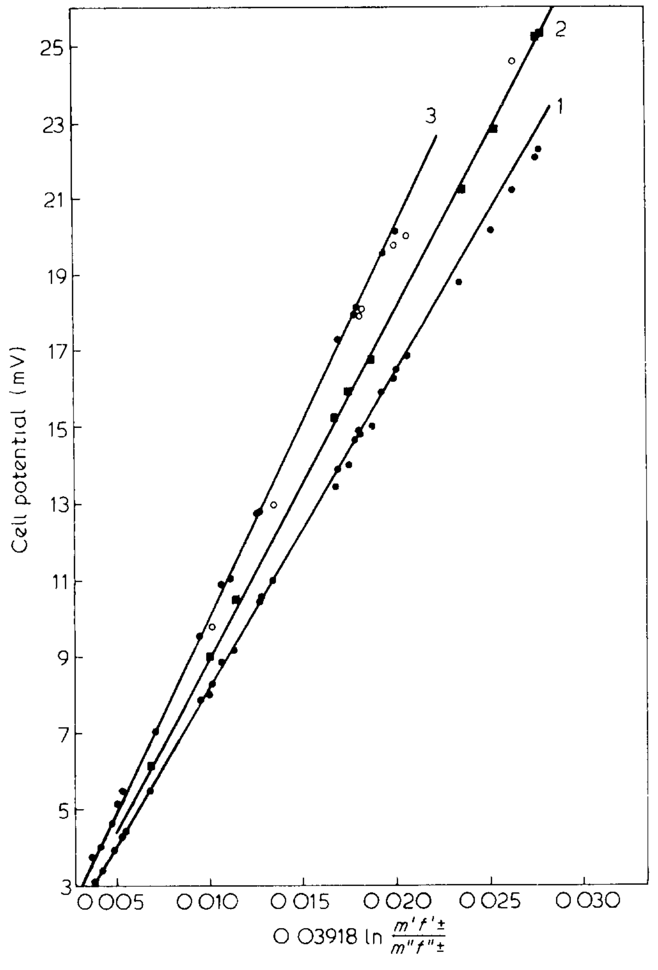

Figure 1 Plots of the cell potentials E_0 and E_M *versus* $-0.03918 \ln (m'f')/(m''f'')$. 1, E_0 of the cells ($Hg/Hg_2SO_4/H_2SO_4, m'/H_2SO_4, m''/Hg_2SO_4/Hg$); 2 and 3 E_M of the cells ($Hg/Hg_2SO_4/H_2SO_4, m'$/NAFION membrane/$H_2SO_4, m''/Hg_2SO_4/Hg$) with mean concentration <0.5 and >1.5, respectively

RESULTS AND DISCUSSION

The experimental values for the emf: E_0 and E_M, the apparent transport number of H^+-ions and the permselectivity are given in *Figures 1* and *3*. The permselectivity was calculated according to relation[5]:

$$P_S = \frac{\bar t_{H^+(app)} - \bar t_{H^+}}{1 - \bar t_{H^+}}$$

According to equation (2) E_M as well as E_0 ought to be a strictly linear function of $\ln a'_\pm/a''_\pm$, so that the E_M and E_0 values are shown on one plot *versus*:

$$-1.5RT/F(\ln m'f'_\pm)/(m''f''_\pm) \quad (Figure\ 1)$$

The accordance of experimentally determined E_0 with the calculated straight line is visible. However, at higher values of the abscissa the divergences are noticeable. It is an indication that in cells with large differences in solution concentration the assumption concerning the constancy of $\bar t_H$ in the concentration range from m' to m'' is no more valid.

The experimental E_M values are placed on two lines, 2 and 3, one of which (3) represents the E_M of the cells with low mean external concentration, up to ~0.5 mol kg^{-1} H_2O, the second (2), the cells at mean concentrations higher than ~1.5 mol kg^{-1} H_2O. The E_M of the cells with moderate mean external concentration (0.77–1.26 mol kg^{-1} H_2O) are placed between the two lines. Most probably, such a distribution of the E_M values is caused by a characteristic feature of H_2SO_4 sorption in the membrane with changes in the external solution concentration. This can be seen in *Figure 2* where the sorption of H_2SO_4 in Nafion R-120 membrane is shown. (The data obtained in our laboratory will be subsequently published[20].) The initial and final parts of the sorption curve may be assumed to represent the straight line dependence on external concentration, which correspond well with the two straight line dependences of E_M given in *Figure 1*.

The curves 1, 2 and 3 in *Figure 3* show the dependence of the apparent and 'true' transport numbers of H^+-ions as well as the water transference numbers calculated according to the presented method on the external concentration. Numerical values of the numbers are given in *Table 1*.

The course of curve 1 does not require any comments. It resembles the data one can find in the literature for other cation exchange membranes in: H, K, Na, Cs, Rb chlorides[6,7,10] and KOH[21] solutions in the case of an anion exchange membrane. Curves 2 and 3 show rather unusual results; both the $\bar t_H$ and $\bar t_w$ values are

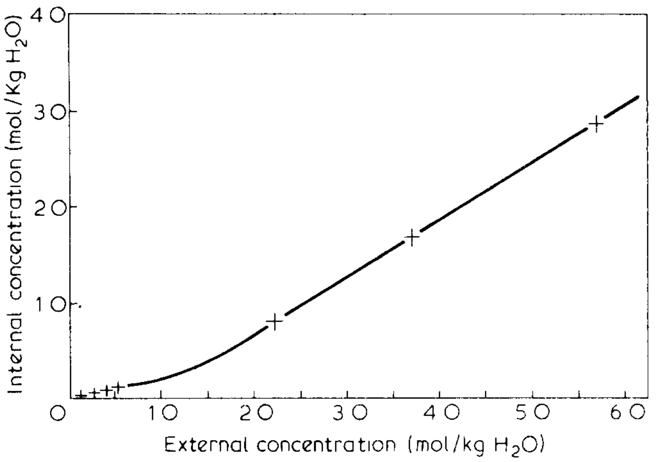

Figure 2 Dependence of the internal solution concentration in NAFION membrane on concentration of the external H_2SO_4 solution

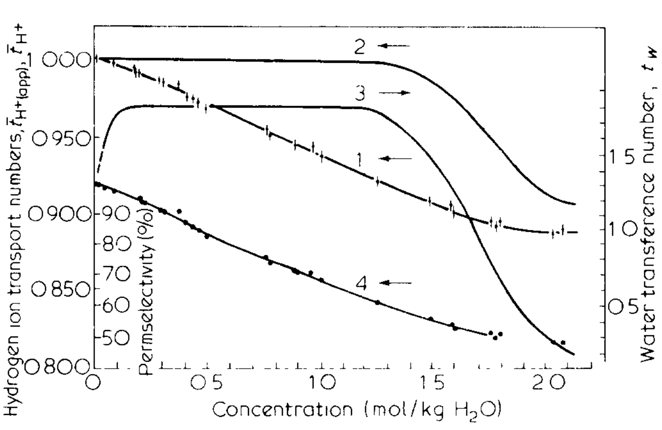

Figure 3 Variation of NAFION membrane transport numbers and permselectivity with external solution concentration: 1, hydrogen ion apparent transport number $\bar t_{H^+(app)}$ ± 0.002 (experimental), 2, hydrogen ion transport number $\bar t_{H^+}$ ± 0.004; 3, water transference number $\bar t_w$ ±0.1; 4, permselectivity P_S ± 0.5

Table 1 Transport numbers of H^+-ion and water transference number of NAFION membrane in H_2SO_4 solutions

External concentration (mol/kg H_2O)	Apparent transport number, ±0.002	Transport number ±0.004	Water transference number, ±0.1
0.100	0.995	1.000	1.3
0.200	0.999	1.000	1.5
0.300	0.983	1.000	1.8
0.400	0.977	1.000	1.8
0.500	0.969	1.000	1.8
0.600	0.963	1.000	1.8
0.700	0.956	1.000	1.8
0.800	0.950	1.000	1.8
0.900	0.944	1.000	1.8
1.000	0.937	1.000	1.8
1.100	0.931	1.000	1.8
1.200	0.924	1.000	1.8
1.300	0.918	0.998	1.7
1.400	0.912	0.996	1.6
1.500	0.906	0.990	1.5
1.600	0.901	0.975	1.3
1.700	0.898	0.960	1.0
1.800	0.895	0.945	0.8
1.900	0.892	0.938	0.7
2.00	0.890	0.914	0.3
2.10	0.890	0.902	0.2
2.20	0.889	0.902	0.2

independent of external concentration in the range up to ~ 1.2 mol kg^{-1} H_2O. The maximum value of $\bar{t}_{H^+}$ equal to 1 confirms the results of Arnold and Swift[12] which have been obtained in similar membrane cells with H_2SO_4 solutions. However, according to those authors $\bar{t}_{H^+} \approx 1$ even in 5 N H_2SO_4 solution. This may result from the specificity of the electro-osmotic method used by the cited authors. However, it may be concluded that the maximum values of $\bar{t}_{H^+}$ exhibited to such high concentration as ~ 1.2 mol kg^{-1} H_2O is due to a specific immobilization of sulphate ions in the system.

It is difficult to explain the initial part of curve 3 representing $\bar{t}_{H^+}$. Attempts will be made in subsequent studies.

Some limitations exist concerning the values of $\bar{t}_{H^+} < 1$. In the investigated system (emf measured with the aid of the electrodes reversible to sulphate ions) only the stoichiometric transport numbers could be obtained[22]. They are sums of really existing transport numbers of H^+-ions and the transport number of HSO_4-ions. So, the true transport numbers of H^+ ions in a membrane in contact with more concentrated solutions (molarities > 1.2 mol kg^{-1} H_2O) may be lower.

The reliability of the presented results will be proved by further data based on sorption and electro-osmotic methods.

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