A New Method for Measuring Transference Numbers

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The transference numbers of cations through a cation exchange membrane are fixed by the composition of the surrounding electrolyte. During electrolysis cations are conducted through the membrane out of the anode side container. Fixed cation fluxes into this container are regulated to compensate for the loss of the same cations through the membrane. Then transference number ratios are found to be equal to the measured cation current ratios.

The validity of the Onsager reciprocal relations is of cardinal importance in the field of irreversible thermodynamics. For the case of isothermal electrical and matter transport this is tested by the numerical equality of the transference numbers determined directly by the Hittorf method and indirectly by the e.m.f.'s of the cells with transference.

For electrolytic conduction processes we define the transference number of an ion as the fraction of current carried by that ion. In order to measure meaningful and accurate transference numbers of ions in membranes, various modifications of the Hittorf method have been tried.¹ This work is concerned with investigating a new method that hopefully will improve transference measurements.

The principle of the Hittorf method is shown in Fig. 1a. The electrolytes on both sides of the membrane should be nearly the same during the electrolysis. The membrane matrix is chosen as frame of reference. From measurements with certain cation exchange membranes it has been found¹ that the anode side electrolyte determines the transference numbers for sufficient high electrical current densities. It is then possible to modify the Hittorf method by omitting one cation species from the cathode side solution. The total gain of this cation to

the cathode side after the electrolysis is completed is determined by the usual analytical methods. In this way the analytical difficulties are reduced, but the diffusion problem is larger than for the unmodified Hittorf method.

The new method applied to a cation exchange membrane M is shown in Fig. 1b. During the electrolysis the electrical current from the two anode chambers passes through a small middle chamber before the cathode chamber. The electrolytes on both sides of the membrane

Fig. 1. Methods for measuring transference numbers. a. The Hittorf method; b. The new method. M, membrane for investigation; m, ion exchange membranes; C, constant current source; A, ammeters; R, variable resistors; S, stirrer; I_1 , I_2 , separate ion currents.

M are the same mixture with components having two different cation species. Thus the transference of ions through the membrane M is fixed by the composition of the electrolyte. The two anode chambers contain electrolytes with each of the two cations from the mixture, respectively. The separate ion currents from the anode chambers into the middle chamber are conducted through the two cation exchange membranes m. The ratio of these ion currents is regulated to compensate for the loss of the same ions through M to keep the composition of the middle chamber unchanged. We have the simple relation (1) between cation transference numbers t_1 and separate cation currents I_1 .

$$t_1/t_2 = I_1/I_2 \quad (1)$$

Using the relationship (2) we can calculate the transference numbers (3):

$$t_1 + t_2 = 1 \quad (2)$$

$$t_1 = I_1/(I_1 + I_2); t_2 = I_2/(I_1 + I_2) \quad (3)$$

The experiments are carried out by selecting several electrical current ratios close to the

expected transference number ratio. After each electrolysis the change in composition in the middle chamber is determined by analyzing a sample. The actual transference number is found by interpolating to the point of balance, where the composition is not changed (Fig. 2).

The cross section areas of the membranes m are much smaller than for the membrane M. This reduces the problem of interdiffusion between the anode chambers and the middle chamber, although the electrical current density through M might still be low. Also to some extent the diffusions into the two anode chambers will counter-balance.

When electrical current is passed the concentration of the solution near the anode side of M will be lowered because both cations and anions are transported away. The diffusion from the bulk of the solution will tend to restore its concentration. Because the anode side solution determines the transference number, the apparent value will be changed, now given by the concentrations at the interface between membrane and solution. The concentration difference between bulk and interface is reduced by fast stirring in the middle chamber.

Fig. 2. Interpolation to the point of balance for the transference number t_1 . Current ratios $I_1/(I_1 + I_2)$ versus ionic fraction x_1 and t_1 versus x_1 . $\square$, composition before electrolysis; $\circ$, after electrolysis; ∇ , point of balance. Line A connecting points of selected current ratios with the initial composition; line B connecting the points after electrolysis. Line C: t_1 versus x_1 .

EXPERIMENTAL

The method was used to determine the transference numbers t_H and t_K for H^+ - and K^+ -ions through the cation exchange membrane Permaplex C-20 (from Permutit Co. Ltd.) in equilibrium with a solution of 0.2 M HCl and 0.3 M KCl in mixture. It has been found² that $1 \geq t_H + t_K > 0.995$.

The middle chamber contained only 2 ml, while the cathode chamber held 550 ml of this solution. The two anode chambers had 300 ml of 0.5 M HCl and 0.5 M KCl, respectively. The cross section areas of the membranes M and m were 1.15 cm² and 0.13 cm², respectively. The electrodes were Ag/AgCl.

The electrical current densities I over M were varied from 10 to 40 mA/cm². For each value of I three experiments were carried out with the cation current ratio fixed at different levels around the expected point of balance. The apparent transference number t_H' connected to the specific value of I was found by interpolation.

The electrolysis lasted for 15 to 20 min. The resulting change of the HCl concentration in a sample from the middle chamber was determined by titration against a solution of NaOH, which was standardized against the original store solution of HCl and KCl mixture.

Fig. 3. The apparent transference number t'_H versus electrical current density I . O, with vertical bar, experimental; A, apparent transference numbers with diffusion; B, linear regression line; C, 70 % confidence limits.

It has been found³ that the transference number of water is a linear function of the transference number of protons in this system. Thus the water content in the middle chamber will not change, and it is sufficient to analyze for change in one component only.

RESULTS AND DISCUSSION

The apparent transference numbers t'_H are given in Fig. 3.

The low value for t'_H when having a small value for I was caused by interdiffusion over the two membranes m . The concentration gradient between the middle chamber and the HCl container was larger than over the KCl container. Thus diffusion alone tended to increase the HCl concentration in the middle chamber. Therefore less electrical current through the HCl container was needed to acquire the point of balance. The apparent transference number t'_H as calculated from the measured electrical current ratio would then be too small.

Acta Chem. Scand. A 30 (1976) No. 10

The concentration profiles through the two membranes m depend upon the electrical current densities I_H and I_K , respectively. Assuming the total cation concentration to be constant through the membrane, the concentration gradient is proportional to the gradient of the ionic fraction.

The excess proton transference caused by diffusion is compensated by potassium ion flux in the opposite direction. The total potassium ion flux density J_K over the membrane m between the middle chamber and the HCl container can be estimated as a combination of electrical transference and diffusion by the following equation.

$$J_K = I_H t_K - D_{HK} \frac{dx_K}{dy} \quad (4)$$

The potassium ion flux J_K , the electrical current density I_H , and the interdiffusion coefficient D_{HK} have equivalent units. The ionic fractions for K^+ - and H^+ -ions inside the membrane are x_K and x_H , respectively, with $x_K + x_H = 1$. The distance through the membrane is given in relative units y , from 0 (HCl side) to 1 (mixture side). On the membrane surfaces $y=0$ and $y=1$ we have $x_K = x_{K1}$ (very low) and $x_K = x_{K2}$, respectively. The very small contamination of KCl in the HCl container is caused by interdiffusion in between the electrolysis experiments.

The transference number t_K is expressed by the ion mobilities u_K and u_H or by the ratio $m = u_K/u_H$ and by x_K .

$$t_K(x_K) = \frac{x_K u_K}{x_K u_K + (1 - x_K) u_H} \quad (5)$$

$$t_K(x_K) = \frac{m x_K}{(m - 1) x_K + 1} \quad (6)$$

With no current and assuming a constant gradient $dx_K/dy = (x_{K2} - x_{K1})/(1 - 0) = x_{K2}$ we find the lower limit for J_K . The upper limit for J_K/I_H is determined by the supply for K^+ -ions from the contamination of KCl in HCl solution. We have $t_K(x_{K1}) \approx m x_{K1} \ll 1$. This gives us (7):

$$-D_{HK} x_{K2} < J_K < +I_H t_K(x_{K1}) \quad (7)$$

Introducing eqn. (6) into eqn. (4), assuming D_{HK} to be constant, and integrating between $y=0$ and $y=1$ we find an implicit relation between J_K and I_H .

$$\frac{mI_H D_{HK}}{(mI_H - (m-1)J_K)^2} \ln \left(\frac{mI_H x_{K2} - (1 + (m-1)x_{K2})J_K}{mI_H x_{K1} - (1 + (m-1)x_{K1})J_K} \right) + \frac{(m-1)D_{HK}}{mI_H - (m-1)J_K} (x_{K2} - x_{K1}) = 1 \quad (8)$$

We are interested in the asymptotic behaviour when $I_H \gg D_{HK}$ and therefore $|J_K| \ll I_H$. This gives us the explicit relation (9) with (10).

$$J_K(I_H) \approx I_H t_K(x_{K1}) [1 - \exp(-m \frac{I_H}{D_{HK}}) f(x_{K1}, x_{K2})] \quad (9)$$

$$f(x_{K1}, x_{K2}) = \frac{x_{K2}}{x_{K1}} \exp [+ (m-1)(x_{K2} - x_{K1})] \quad (10)$$

When I_H is very large the exponential function $\exp(-mI_H/D_{HK})$ will dominate the factor $1/x_{K1}$. Then eqn. (9) gives us eqn. (11) in agreement with eqn. (7).

$$J_K(I_H) \approx I_H t_K(x_{K1}) \quad (11)$$

Then H^+ -ions will carry nearly the entire electrical current from the HCl container without significant diffusion. Similarly K^+ -ions will carry all but a negligible amount of the electrical current from the KCl container.

It can be shown⁴ that the liquid diffusion layer at membrane M will cause a deviation between the apparent transference number t_H' and the true transference number t_H^0 , this deviation being proportional to the electrical current density I .

$$t_H' - t_H^0 = \text{constant} \times I \quad (12)$$

The true transference number t_H^0 should be valid for transference through a membrane in equilibrium with the bulk solution having concentrations C_{HCl}^0 and C_{KCl}^0 .

The true transference number t_H^0 is estimated by linear extrapolation to zero electrical current density. The linear regression is based on points where diffusion is assumed to be negligible (Fig. 3).

The final result (with standard deviations) is

$$t_H^0 = 0.6520 \pm 0.0035 \text{ for}$$

$$C_{HCl}^0 + C_{KCl}^0 = 0.500 \pm 0.001 \text{ mol/l with}$$

$$x_{HCl}^0 = 0.400 \pm 0.001$$

The true transference number t_H^0 for the same type of membrane and the same mixture has been estimated from results with the modified Hittorf method^{5,6}

$$t_H^0 = 0.665 \pm 0.025 \text{ (Okeyo } ^5)$$

$$t_H^0 = 0.6417 \pm 0.0048 \text{ (Pongsakorn } ^6)$$

Pongsakorn used electrical current densities from 40 to 140 mA/cm².

FINAL REMARKS

This method can be generalized by having any convenient combination of electrodes or membranes as ion sources or ion sinks for cations and anions in order to measure transference numbers. Also a modification of this method can be used to determine concentration profiles over the membrane M when the composition of the electrolyte on the two sides are different.

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