COMMUNICATION

Determination of Transport Numbers of Ions in Ion Exchange Membranes from EMF Measurements

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The transport number of ions in ion-exchange membranes is one of the most important properties which describes their utility in electro-processes (electrodialysis, electrolysis). The standard procedure of determining the transport number consists in the measurement of the emf of concentration membrane cell using either the indicator electrodes (*e.g.* the Ag/AgCl electrodes – cell 1a) or the reference electrodes (*e.g.* the saturated calomel electrodes – cell 2).

cell 1a Ag|AgCl(s)| MCl_{z_1} m′|MEMBRANE| MCl_{z_1} m″ |AgCl(s)|Ag   [1,2,3]

1b Hg|Hg$_2$SO$_4$(s)| H$_2$SO$_4$ m′ |MEMBRANE| H$_2$SO$_4$ m″ |Hg$_2$SO$_4$(s)|Hg   [4]

1c Pt,H$_2$| KOH m′ |MEMBRANE| KOH m″ |H$_2$,Pt   [5]

1d Hg|HgO(s)| NaOH m′ |MEMBRANE| NaOH m″ |HgO(s)|Hg   [6]

cell 2

Hg|Hg$_2$Cl$_2$(s)| KCl sat.|| $M_{v_1}A_{v_2}$ m′|MEMBRANE| $M_{v_1}A_{v_2}$ m″|| KCl sat.|Hg$_2$Cl$_2$(s)|Hg [7–10]

In both cases (cells 1 and 2) the dependence of activity of electrolyte on the concentration and temperature has to be known. However, the application of ion-exchange membranes covers also such electrolytes, for which the thermodynamic data are not always available. The aim of this paper is to show how to avoid this problem and to what extent can we rely on the emf measured with the reference saturated calomel electrodes. At first let us remind the meaning of the emf of the concentration membrane cell.

The emf of the cell 1, *E(ind)*, is the sum of the membrane potential, E_m, and the difference of potentials of two electrodes, ΔE_{el}

$$E(ind) = E_m + \Delta E_{el} \qquad \text{where} \quad \Delta E_{el} = \frac{RT}{z_i F} \ln \frac{a_i''}{a_i'} \tag{1,2}$$

In (2) *i* denotes ion in respect to which the electrodes are reversible; *i*=1 – cation, *i*=2 – anion. The emf of the cell 2, *E(ref)*, is given by

$$E(ref) = E_m + \Delta E_{dif} \tag{3}$$

where ΔE_{dif} is the difference of the liquid junction potential on the boundaries – saturated calomel electrode| $M_{v_1}A_{v_2}$ solution. From the transport equations of irreversible thermodynamics (thermodynamic treatment is also possible [11]) and Gibbs-Duhem equation the following expression for E_m results [2,12]:

$$E_m = -\frac{RT}{F} \frac{(v_1 + v_2)}{v_1 z_1} \int_{m'}^{m''} \bar{t}_{1,app} d\ln a_{\pm} - \frac{RT}{z_2 F} \ln \frac{a_2''}{a_2'} = -\frac{RT}{F} \frac{(v_1 + v_2)}{v_1 z_1} \bar{\tilde{t}}_{1,app} \ln \frac{a_{\pm}''}{a_{\pm}'} - \frac{RT}{z_2 F} \ln \frac{a_2''}{a_2'} \tag{4}$$

The meaning of $\bar{t}_{1,app}$ in (4) is:

$$\bar{t}_{1,app} = \bar{t}_1 - z_1 \frac{c_1}{c_0} \bar{t}_0 = \bar{t}_1 - z_1 v_1 m M_0 \bar{t}_0 \tag{5}$$

where $\bar{t}_1, \bar{t}_0$ are the transport numbers of cation and water, respectively, m is the molality of solution, M_0 is the molar mass of water. $\tilde{\bar{t}}_{1,app}$ is the mean of $\bar{t}_{1,app}$ in the concentration range m', m''. From the definition of $\bar{t}_{1,app}$ the following relation holds:

$$\bar{t}_{1,app} + \bar{t}_{2,app} = 1 \tag{6}$$

Substitution of (2) and (4) into (1) yields the exact relation between $E(ind)$ and $\tilde{\bar{t}}_{1,app}$
a) when indicator electrodes are reversible in respect to cations ($i=1$ in (2))

$$E(ind,1) = \frac{RT}{F} \frac{(v_1 + v_2)}{v_1 z_1}(1 - \tilde{\bar{t}}_{1,app})\ln\frac{a''_\pm}{a'_\pm} = -\frac{RT}{F} \frac{(v_1 + v_2)}{v_1 z_2}\tilde{\bar{t}}_{2,app} \ln\frac{a''_\pm}{a'_\pm} \tag{7}$$

b) when indicator electrodes are reversible in respect to anions ($i=2$ in (2))

$$E(ind,2) = \frac{RT}{F} \frac{(v_1 + v_2)}{v_1 z_1}\tilde{\bar{t}}_{1,app})\ln\frac{a''_\pm}{a'_\pm} = -\frac{RT}{F} \frac{(v_1 + v_2)}{v_1 z_2}(1 - \tilde{\bar{t}}_{2,app}) \ln\frac{a''_\pm}{a'_\pm} \tag{8}$$

In the derivation of (7) and (8) the relation $a_1^{v_1} a_2^{v_2} = a_\pm^{v_1 + v_2}$ has been used. In the case of the cell 2 ((3)) two assumptions have to be made

$$a''_2/a'_2 = a''_\pm/a'_\pm \qquad \text{and} \qquad \Delta E_{dif} = 0 \tag{9a,b}$$

to obtain the useful equation:

$$E(ref) = \frac{RT}{F}\left(\frac{(v_1 + v_2)}{v_1 z_1}\tilde{\bar{t}}_{1,app}) + \frac{1}{z_2}\right)\ln\frac{a''_\pm}{a'_\pm} = -\frac{RT}{F}\left(\frac{(v_1 + v_2)}{v_2 z_2}\tilde{\bar{t}}_{2,app} + \frac{1}{z_1}\right)\ln\frac{a''_\pm}{a'_\pm} \tag{10}$$

With (7,8) and (10) three combinations can be obtained in which $RT/F \ln a''_\pm/a'_\pm$ is eliminated thus giving $\tilde{\bar{t}}_{1,app}$ as a function of simultaneously measured electromotive forces only. (7) and (8) yield the exact apparent transport number:

$$\tilde{\bar{t}}_{1,app} = \frac{1}{1 - E(ind,1)/E(ind,2)} \tag{11}$$

Because not always the electrodes reversible in respect to the cations and anions of the electrolyte can be found, the two remaining combinations ((7)+(10)->(12), (8)+(10)->(13)) should be also taken into account.

$$\tilde{\bar{t}}_{1,app} = \frac{E(ref)/E(ind,1) - v_2/(v_2 + v_2)}{E(ref)/E(ind,1) - 1} \quad \text{or} \quad \tilde{\bar{t}}_{2,app} = \frac{v_1/(v_1 + v_2)}{1 - E(ref)/E(ind,1)} \tag{12}$$

$$\tilde{\bar{t}}_{1,app} = \frac{v_2/(v_1 + v_2)}{1 - E(ref)/E(ind,2)} \quad \text{or} \quad \tilde{\bar{t}}_{2,app} = \frac{E(ref)/E(ind,2) - v_1/(v_1 + v_2)}{E(ref)/E(ind,2) - 1} \tag{13}$$

(12) and (13) are based on the assumptions (9a and b), therefore it would be interesting to show, at least for one electrolyte, how much they can affect the calculated $\tilde{\bar{t}}_{1,app}$. It should be noticed that for symmetrical electrolytes, because of symmetry of (12) and (13), it is sufficient to check it only for one pair of electrodes, *e.g.* electrodes reversible to anions, but in the full range of $\tilde{\bar{t}}_{1,app}$, *i.e.* from 0 (anion-exchange membrane) to 1 (cation-exchange

membrane). Then the results for a cation-exchange membrane and electrodes reversible to anions will correspond to an anion-exchange membrane and electrodes reversible to cations (and vice versa). The validity of (12) and (13) as well as of (10) has been checked for the cation (MRF, Russia) and anion (AESD, TU Wrocław, Poland) exchange membranes in the solutions of NaCl at 20°C. The measurements of $E(ind,2)$ and $E(ref)$ have been performed for 0.1–0.2–0.5–1.0–2.0–4.0 m NaCl, using the silver/silver chloride electrodes and the saturated calomel electrodes. The apparent transport numbers of Na^+ calculated from (8,10) and (13), denoted as $\tilde{\tilde{t}}_{1,app}(i)$, $\tilde{\tilde{t}}_{1,app}(r)$, $\tilde{\tilde{t}}_{1,app}(i,r)$, respectively, are shown in Fig. 1. Unfortunately, it is seen that the discrepancies between these transport numbers are significant for both types of membranes. In the case of the cation-exchange membrane (MRF) $\tilde{\tilde{t}}_{1,app}(i,r)$ exceeds 1 to a higher degree than the standard deviation of $\tilde{\tilde{t}}_{1,app}(i,r)$, (=0.013) calculated from (13) assuming the standard deviations of $E(ind,2)$ and $E(ref)$ equal 0.2 mV. Using $\tilde{\tilde{t}}_{1,app}(i)$, calculated from the thermodynamically exact formula (8), it can be estimated that the difference between (10) (assumptions (9)) and (3) for both membranes ranges from 1 to 4 mV in concentrated solutions of NaCl. Certainly, the contribution of ΔE_{dif} could be diminished by choosing salts with ions of similar mobilities, *e.g.* KCl instead of NaCl. Contrary to the cation-exchange membrane the discrepancy between $\tilde{\tilde{t}}_{1,app}(i)$ and $\tilde{\tilde{t}}_{1,app}(i,r)$ for AESD is small even for 1 m NaCl. This is because $\tilde{\tilde{t}}_{1,app}$ is small and $E(ref)$ is of opposite sign to $E(ind,2)$. Consequently, (13) is not so sensitive to the systematic error of $E(ref)$ ((10)) introduced by the assumptions (9).

Another problem is to what extent the concentration polarization (to some extent reduced by the stirring of solution) influences the discrepancies between $\tilde{\tilde{t}}_{1,app}(i)$, $\tilde{\tilde{t}}_{1,app}(r)$, $\tilde{\tilde{t}}_{1,app}(i,r)$. Taking into account the polarization, the equation for E_m (4) should be substituted by (14) comprising both the membrane potential, E_m, and the drop of potentials in the polarization layers, $E_{dif}'^{(pol)}, E_{dif}''^{(pol)}$, adjacent to the membrane:

$$E_m^{(pol)} = E_{dif}'^{(pol)} + E_m + E_{dif}''^{(pol)} = -\frac{RT}{F}\left(2\tilde{\tilde{t}}_{1,app}\ln\frac{a_\pm''}{a_\pm'} + 2(\tilde{\tilde{t}}_{1,app} - \tilde{t}_{1,app})\ln\frac{a_\pm''^{(m)}a_\pm'}{a_\pm''a_\pm'^{(m)}} - \ln\frac{a_2''}{a_2'}\right) \qquad (14)$$

In (14), written for 1:1 electrolyte, $a_\pm', a_\pm''$ denote the bulk activities, $a_\pm'^{(m)}, a_\pm''^{(m)}$ – activities of electrolyte at the surface of membrane. Analyzing (14) (see Table 1) it is found that the polarization does not influence the difference between $\tilde{\tilde{t}}_{1,app}(r)$ and $\tilde{\tilde{t}}_{1,app}(i)$, even if the assumptions (9) do not hold, and the discrepancy between $\tilde{\tilde{t}}_{1,app}(i,r)$ and $\tilde{\tilde{t}}_{1,app}(i)$ is only slightly dependent on the polarization. The role of good stirring of solutions in the determining $\tilde{\tilde{t}}_{1,app}$ is also evident.

Although the weakness of the reference electrodes has been demonstrated, they would be useful in the case when the dissolved material of the indicator electrode should not be in contact with the investigated membrane, Then, from the emf of membrane cell measured with reference electrodes ((3)) and from the emf of cell without transference, reference el.|| solution m' | indicator el. indicator el.| solution m'' || reference el., the latter given by

$$E = \Delta E_{dif} - \frac{RT}{z_i F}\ln\frac{a_i''}{a_i'} \qquad (15)$$

one gets (7) or (8), depending on the indicator electrodes used ($i=1$ or 2). To complete the above discussion the method based on the knowledge of transport properties of the solution should be mentioned [3]. From the measurement of the emf of concentration cell with and without membrane the transport number can be calculated from:

$$\tilde{\tilde{t}}_{1,app} = \tilde{t}_{1,app}\frac{E(with\ membrane)}{E(without\ membrane)} \qquad (16)$$

Table 1. Influence of concentration polarization on $\bar{\bar{t}}_{1,app}(i)$, the differences $\bar{\bar{t}}_{1,app}(r) - \bar{\bar{t}}_{1,app}(i)$ and $\bar{\bar{t}}_{1,app}(i,r) - \bar{\bar{t}}_{1,app}(i)$, calculated for 0.5–1.0 m NaCl, $\tilde{t}_{1,app} = 0.37$, the difference between $E(ref)$ measured and E calculated from eq.(10) taking $t_{1,app}(i)$ is 2.5 mV.

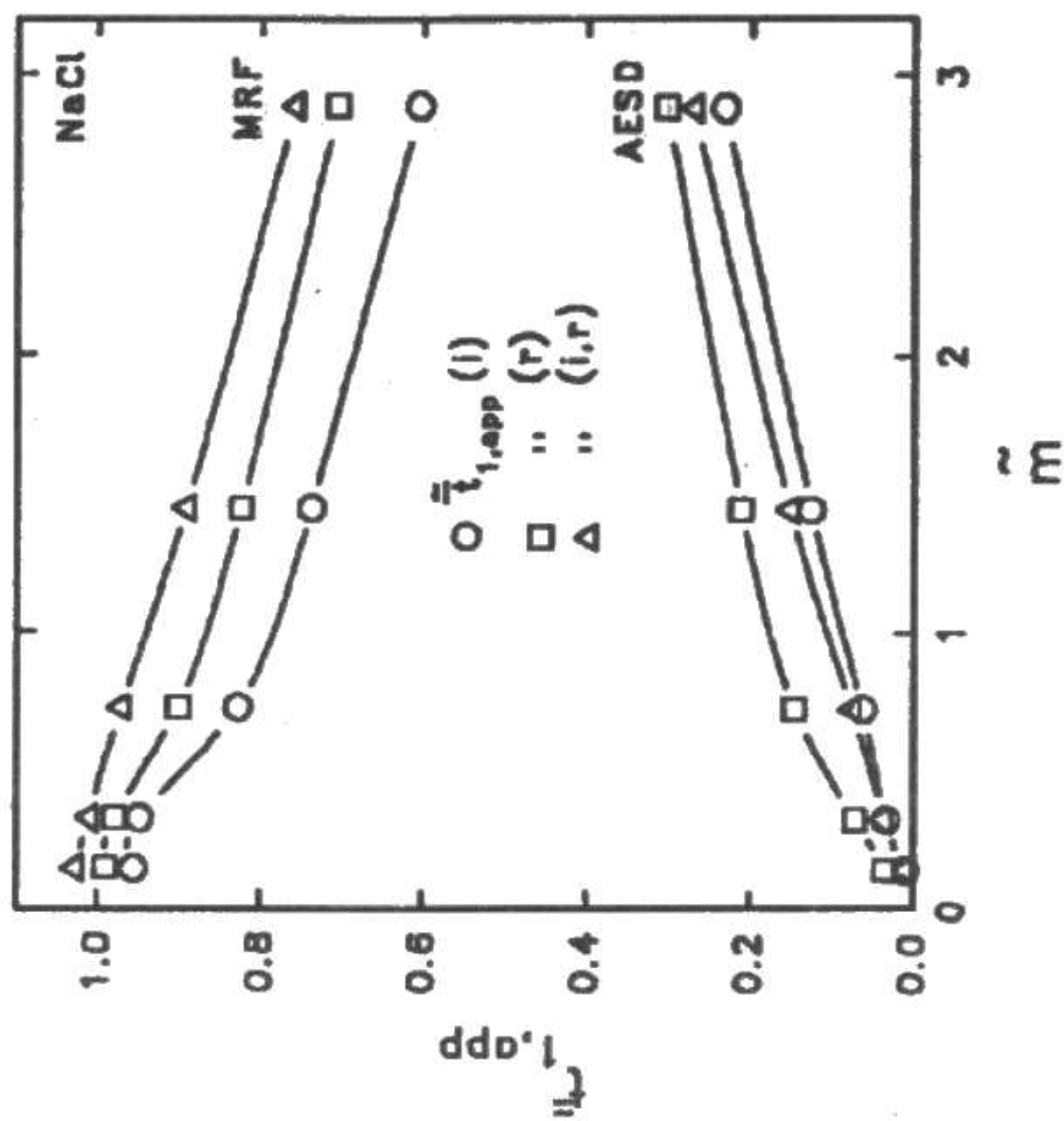| $\frac{a'_\pm(m)}{a''_\pm(m)}$	cation-exchange membrane (MRF)			anion-exchange membrane (AESD)		
	$\bar{\bar{t}}_{1,app}(i)$	$\bar{\bar{t}}_{1,app}(r) - \bar{\bar{t}}_{1,app}(i)$	$\bar{\bar{t}}_{1,app}(i,r) - \bar{\bar{t}}_{1,app}(i)$	$\bar{\bar{t}}_{1,app}(i)$	$\bar{\bar{t}}_{1,app}(r) - \bar{\bar{t}}_{1,app}(i)$	$\bar{\bar{t}}_{1,app}(i,r) - \bar{\bar{t}}_{1,app}(i)$
1.00	0.830	0.075	0.147	0.062	0.075	0.011
1.05	0.760	0.075	0.133	0.109	0.075	0.019
1.10	0.690	0.075	0.124	0.156	0.075	0.028

Figure 1. Dependence of $\bar{\bar{t}}_{1,app}(i)$, $\bar{\bar{t}}_{1,app}(r)$, $\bar{\bar{t}}_{1,app}(i,r)$, for cation (MRF) and anion (AESD) membranes on the mean molality of NaCl, T=20°C.

CONCLUSIONS

The exact measurement of apparent transport number without knowledge of thermodynamic data is possible only with the electrodes reversible in respect to ions of the electrolyte.

The transport numbers from the electromotive forces measured with reference and indicator electrodes differ too much from those obtained from the exact equations to be useful for precise works. However, for the routine measurements to control the quality of membranes they could be sufficient, especially in the cases:

(i) anion-exchange membrane and reference electrodes + indicator electrodes reversible in respect to anions,

(ii) cation-exchange membrane and reference electrodes + indicator electrodes reversible in respect to cations.

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