Determination of the electrolyte and osmotic permeability coefficients by the conductometric and emf methods

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Abstract

The emf method has been compared with the conductometric one in determining the apparent electrolyte permeability of membrane ($P_s^{(v)}$). It has been found that this method is limited to the membranes of low permeability ($P_s^{(v)}/l_m$ of the order 10^{-7} m/s). In order to obtain the real permeability coefficient (P_s) the conductometric method of determining the osmotic flow has been proposed. The influence of concentration polarisation on P_s has been estimated. The extended expression for the polarisation correction factor has been derived. The thickness of polarisation layer has been calculated from the limiting current density, determined using the membrane Nafion 117.

Introduction

The electrolyte permeability belongs to the basic characteristics of membranes dedicated for the dialysis techniques. Usually the diffusion flux of electrolyte through a membrane is determined by measuring the concentration changes of the more dilute solution (*c''*, initially water) e.g. conductometrically. The changes of concentrations can also be detected by measuring the emf of concentration membrane cell, which depends on the concentration ratio (*c''/c'*). That method is rather rarely used.

In this work we compare the results obtained by the conductometric and emf methods. As both methods are based on the measurement of single quantity (*c''* (cond) or *c''/c'* (emf)), it is possible to determine only the apparent permeability coefficient of electrolyte , $P_s^{(v)} \propto (c'-c'')^{-1} dc''/dt$, not the real one, $P_s \propto (c'-c'')^{-1} dn''/dt$. In order to determine the last one determine the osmotic permeability coefficient, $P_v \propto (c''-c')^{-1} dV''/dt$, has to be known. This can be measured directly, e.g. by tracing the movement of liquid meniscus in a calibrated capillary attached to the membrane

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cell. As such method is rather bothersome and difficult for automatization, here we propose to determine P_v by measuring c'(cond), c''(cond), and applying the mass conservation law.

The influence of the concentration polarisation on P_s and P_v will also be discussed. The polarisation correction factor (eq.(13)) will be derived from the transport equation consisting of the diffusive and convective components. The thickness of polarisation layer will be determined from the limiting current density measurements using a highly selective ion-exchange membrane and the same cell/electrolyte system as in the diffusion experiments.

Some remarks

The flux of a solute through a membrane, J_s is given by:

$$J_s = \frac{1}{S_m}\frac{dn''_s}{dt} = P_s\left(\frac{c'-c''}{l_m}\right) \tag{1}$$

where S_m, l_m is the area, thickness of membrane, respectively. To determine P_s one should measure dn''/dt ($c''<c'$). Usually dc''/dt, not dn''/dt, is determined. In that case, using $n''_s = c''V''$ we get not P_s, as defined by eq.(1), but:

$$P_s^{(v)} = \frac{V''}{S_m}\frac{dc''}{dt}\left(\frac{l_m}{c'-c''}\right) = P_s + c''P_v \tag{2}$$

where

$$P_v = -\frac{1}{S_m}\frac{dV''}{dt}\left(\frac{l_m}{c'-c''}\right) \tag{3}$$

For $c'' \to 0$ $P_s^{(v)} \to P_s$. Thus, measuring the concentration changes of only enough dilute solutions we get $P_s^{(v)}$ close to P_s. Substituting c', obtained from eq.(5) assuming that V', V''=const ($V'=V'^0$, $V''=V''^0$), into eq.(2) one gets after integration:

$$Y = \frac{l_m}{S_m(1/V'^0 + 1/V''^0)}\ln\left(\frac{c'^0 - c''^0}{c'^0 - c'' + (c''^0 - c'')V''^0/V'^0}\right) = P_s^{(v)}t \tag{4}$$

The above equation is usually used for the determination of $P_s^{(v)}$ by the least squares method.

If the concentration of solute is measured on both sides of membrane (c', c''), then from:

$$c'V' + c''V'' = c'^0V'^0 + c''^0V''^0 = n_s \tag{5}$$

and assuming that

$$V' + V'' = V'^0 + V''^0 \tag{6}$$

we get:

$$V'' = \frac{c'(V'^0 + V''^0) - n_s}{c'-c''} \tag{7}$$

which can be used for the determination of P_v (eq.(3)) and P_s from eq.(2) (having previously determined P_v and $P_s^{(v)}$).

The emf method

Contrary to the conductometric method the measurement of the emf of concentration membrane cell gives only information on the ratio of concentrations, whereas for the estimation of permeability coefficient *c'* and *c''* have to be known. This can be only done assuming that there is no volume transfer between the solutions bathing a membrane. In that case it is possible to calculate the calibration curves $c' = f(E)$ and $c'' = f(E)$. The procedure is as follows. Starting from the solutions of concentrations *c'*, *c''* and the volumes of *V'*, *V''*, *E* is calculated for different amounts of salt transferred from the solution (') to (''), Δn_s, using the formulae:

$$c' = c' - \Delta n_s / V' , \ c'' = c'' + \Delta n_s / V'' , \ m = \frac{c}{\rho - c M_s} , \ E = f\left(\bar{t}_{1,app}, m'' \gamma_\pm'' / m' \gamma_\pm'\right)$$ (8a-d),

where the data on the density of solution, ρ, and the mean activity coefficient, $\gamma_\pm$, are taken from literature. The formula for *E* depends on a given membrane concentration cell. For our system with NaCl and the silver-silver chloride electrodes it takes the form:

$$E = -2 \frac{RT}{F} \bar{t}_{1,app} \ln\left(\frac{m'' \gamma_\pm''}{m' \gamma_\pm'}\right)$$ (9)

$\bar{t}_{1,app}$ can be determined from the same diffusion experiment. Having calculated *c'*, *c''* and *E* for 4-5 values of Δn_s, the calibration curves $c' = f(E)$ and $c'' = f(E)$ can be expressed as a quadratic equation of *E* with a very good accuracy.

Concentration polarisation

As the stirring of solutions near the membrane surface is not enough effective to eliminate concentration polarisation effect (Fig. 1a), it should be taken into account if the real permeability coefficient should be determined. In the polarisation layers the flux of electrolyte is a sum of diffusive and convective parts, the latter caused by the osmotic flow through the membrane:

$$J_s = -D_s \frac{dc}{dx} + c J_v$$ (10)

Assuming the stationary state and D_s=const, the solution of the above equation in the appropriate boundary conditions yields:

$$c'^{(m)} = J_s / J_v + \exp(J_v l_p / D_s)(c' - J_s / J_v)$$ (11a)

$$c''^{(m)} = J_s / J_v + \exp(-J_v l_p / D_s)(c'' - J_s / J_v)$$ (11b)

Eq.(12), defining observed ($P_{s,exp}$, $P_{v,exp}$) and real permeabilities (P_s, P_v):

$$J_\alpha = -P_{\alpha,exp}(c'' - c')/l_m = -P_\alpha(c''^{(m)} - c'^{(m)})/l_m \quad \alpha = s, v \tag{12}$$

yields the following relationship for the calculation of P_s and P_v:

$$\frac{P_s}{P_{s,exp}} = \frac{P_v}{P_{v,exp}} = \frac{c'' - c'}{c''^{(m)} - c'^{(m)}} \tag{13}$$

where $c'^{(m)}$, $c''^{(m)}$ are given by eqs.(11a,b). If J_v is going to zero, then eq.(13) takes the well known form:

$$\frac{P_s}{P_{s,exp}} = \frac{P_v}{P_{v,exp}} = \frac{1}{1 - 2P_{s,exp}l_p/(D_s l_m)} \tag{14}$$

To determine the thickness of polarisation layer one can used the limiting current method (Fig.1b). When using a highly selective ion-exchange membrane, the limiting current density, is related to the thickness of polarisation layer, l_p, by the following expression [i,ii] ($z_1 = -z_2 = 1$):

$$I_{lim} = \frac{FD_s}{(\bar{t}_1 - t_1)} \frac{c}{l_p} \tag{15}$$

where $\bar{t}_1$, t_1 are transport numbers of ion "1" in the membrane, electrolyte solution, respectively. The above equation is derived under assumption that there is no volume transfer through the membrane, i.e. the flux of ion "1" in the polarisation layer is given by ($z_1 = -z_2 = 1$):

$$J_s = -D_s \frac{dc}{dx} + t_1 I/F \tag{16}$$

During the measurement with an ion-exchange membrane, which is not ideal one, there is a volume flow, J_v, consisting of the electroosmotic, $J_{v,el}$, and the osmotic contribution, $J_{v,osm}$. The last component from the concentration difference building up across the membrane. Thus, eq.(16) should be extended to:

$$J_1 = -D_s \frac{dc}{dx} + t_1 I/F + cJ_v \tag{17}$$

where:

$$J_v = J_{v,el} + J_{v,osm} \tag{18}$$

Comparing eq.(17) with the expression for flux of ion „1" through the membrane:

$$J_1 = \bar{t}_1 I/F - P_s\left(c''^{(m)} - c'^{(m)}\right)/l_m \tag{19}$$

and solving with respect to c in the appropriate boundary conditions:

    side (') of membrane: $c(x=0)=c$, $c(x=l_p)=c'^{(m)}=0$,

    side ('') of membrane: $c(x=0)=c''^{(m)}$, $c(x=l_p)=c$,

we get:

$$I_{lim} = \frac{Fc\left(J_v + \left(1 - \exp(-J_v l_p / D_s)\right)P_s / l_m\right)}{\left(1 - \exp(-J_v l_p / D_s)\right)\left(\bar{t}_1 - t_1\right)} \tag{20}$$

and

$$c''^{(m)} = c\left(1 + \exp\left(-J_v l_p / D_s\right)\right) \tag{21}$$

As the osmotic component of J_v depends on $c''^{(m)}$:

$$J_{v,osm} = P_v\left(c''^{(m)} - c'^{(m)}\right) / l_m \xrightarrow{\;c'^{(m)} \to 0\;} P_v c''^{(m)} / l_m \tag{22}$$

it is not possible to find analytical solution for $c''^{(m)}$ and, consequently for $J_{v,osm}$. Therefore we take the highest possible value of $c''^{(m)}$ resulting from eq.(21): $c''^{(m)} \to 2c$ for $J_v \to 0$ (J_v is positive). The electroosmotic contribution of J_v is given by:

$$J_{v,el} = \left(\frac{FJ_v}{I}\right)_{\Delta c, \Delta p = 0} \frac{I}{F} \tag{23}$$

Thus, knowing P_v and $(FJ_v/I)_{\Delta c, \Delta p = 0}$ one can calculate J_v needed for the calculation of l_p from eq.(20). If $J_v \ll D_s / l_p$ and $P_s / l_m \ll D_s / l_p$, then eq.(20) simplifies to (15).
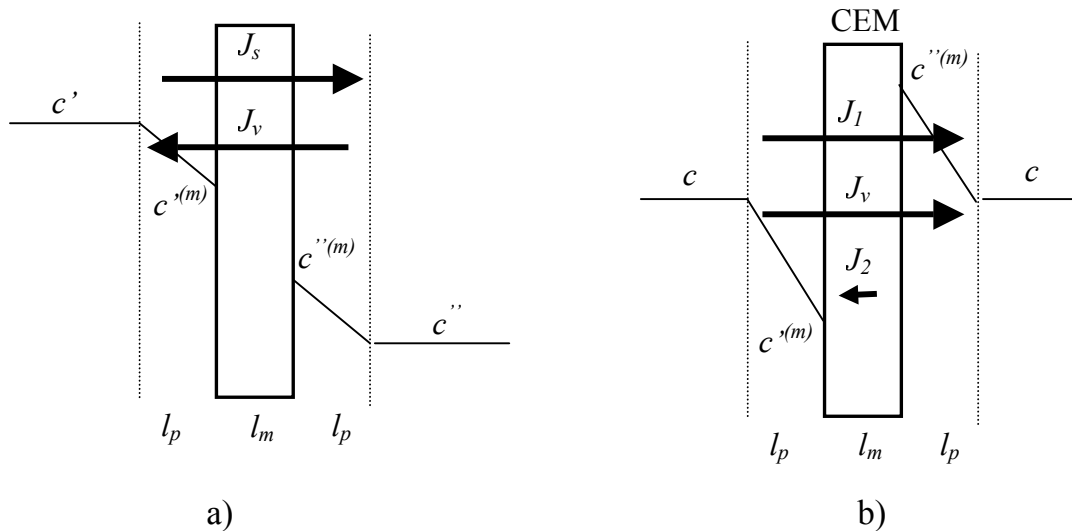

Fig. 1. Concentration polarisation layers during a) the diffusion of a solute through a membrane, b) passage of electric current, $I = F(J_1 - J_2)$, through a cation-exchange membrane.

Experimental

Two membranes of totally different permeabilities have been chosen. The first one is a cation-exchange membrane with sulfonate groups (KESD, Galena, Poland), the second one is a porous polysulfone membrane obtained in our laboratory by the phase-inversion method.

The system for measurement the permeability coefficient consists of the membrane cell equipped with two silver/silver chloride electrodes, connected to the multimeter Unigor 380, and two conductometric probes connected to the multifunction computer meter CX-731 (Elmetron, Poland) (Fig.2). The exposed membrane area was 15.4 cm^2, the volume of each half-cell – ca. 170 cm^3. The

signals have been collected every 1 min. The conductance of solutions and the emf have been approximated as first or higher order polynomial function of time. The calibration curves $c'=f(E)$ and $c''=f(E)$ have been determined as described above.
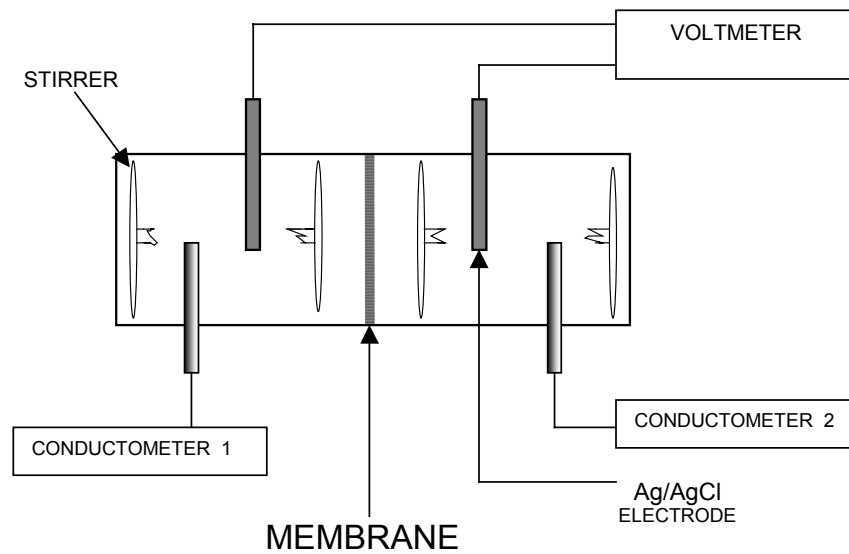

Fig. 2. Diffusion measurement system the cell is equipped with two conductometric probes and the silver/silver chloride electrodes.

The system for measuring the limiting current consists of the diffusion cell equipped with two pairs of the silver/silver chloride electrodes electrodes (Fig.3). The first one supplies the electric current from the potentiostat ($I=U_g/R$, U_g is given by the generator, $R=20\Omega$), the second one, located closer to the membrane, measures the potential drop on the membrane, U_m. The cation-exchange membrane Nafion 117 and 0.02 M NaCl solution have been used. The measurements have been done for the same stirring rate as in the diffusion experiments.
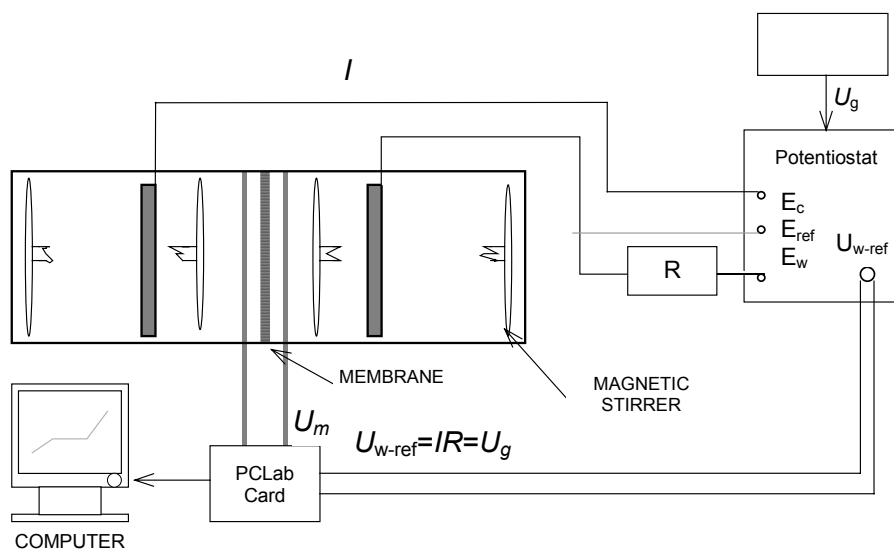

Fig. 3. Polarisation measurement system.

Results

The changes of concentration of dilute solution, c'', determined by the conductivity and emf methods are shown in Fig.4. It is seen that only for the dense membrane KESD the slopes of $c''(t)$ are similar for both methods. Consequently, $P_s^{(v)}/l_m$ estimated from c''(cond.) and from c''(emf) are similar for KESD, whereas for the porous membrane PS1 $P_s^{(v)}/l_m$ (emf) is much higher than $P_s^{(v)}/l_m$ (cond) (Fig.5, Table 1). One of the reasons of that overestimation may be the lack of equilibrium between silver/silver chloride electrodes and the solutions because of high diffusion through PS1.
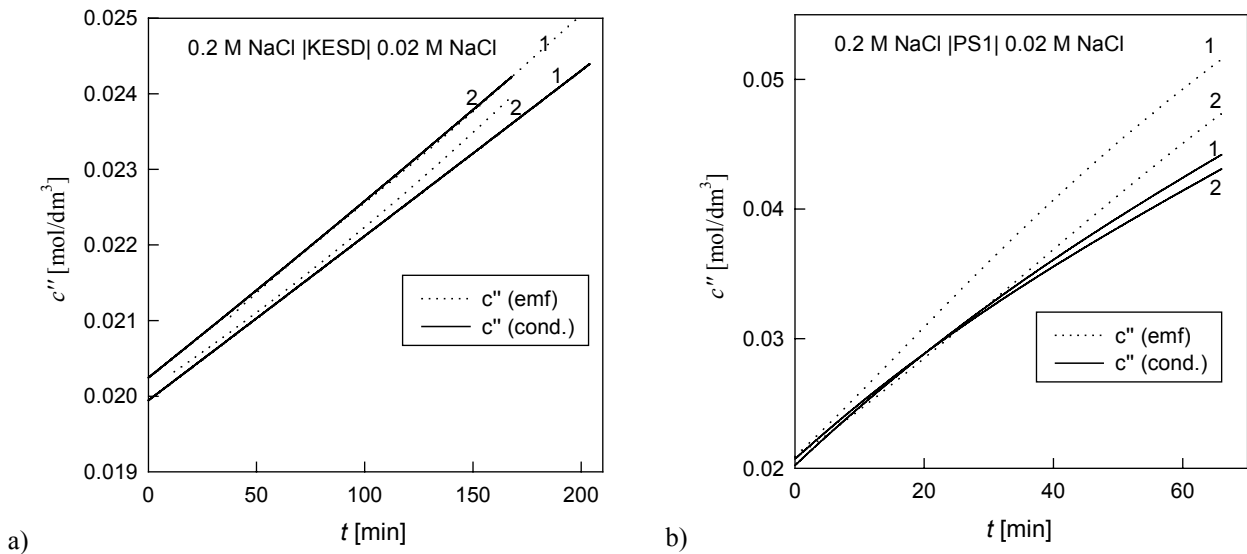

Fig. 4. Concentration of dilute solution, c'', vs. time estimated from the conductivity (solid line) and emf (dotted line) measurements; 1, 2 denotes the no. of measurement; a) the cation-exchange membrane KESD, b) porous polysulfone membrane PS1.

Fig. 5. $P_s^{(v)}/l_m$ (eq.(2)) vs. time estimated from the conductivity (solid line) and emf (dotted line) measurements; 1, 2 denote the no. of measurement; a) the cation-exchange membrane KESD, b) porous polysulfone membrane PS1.
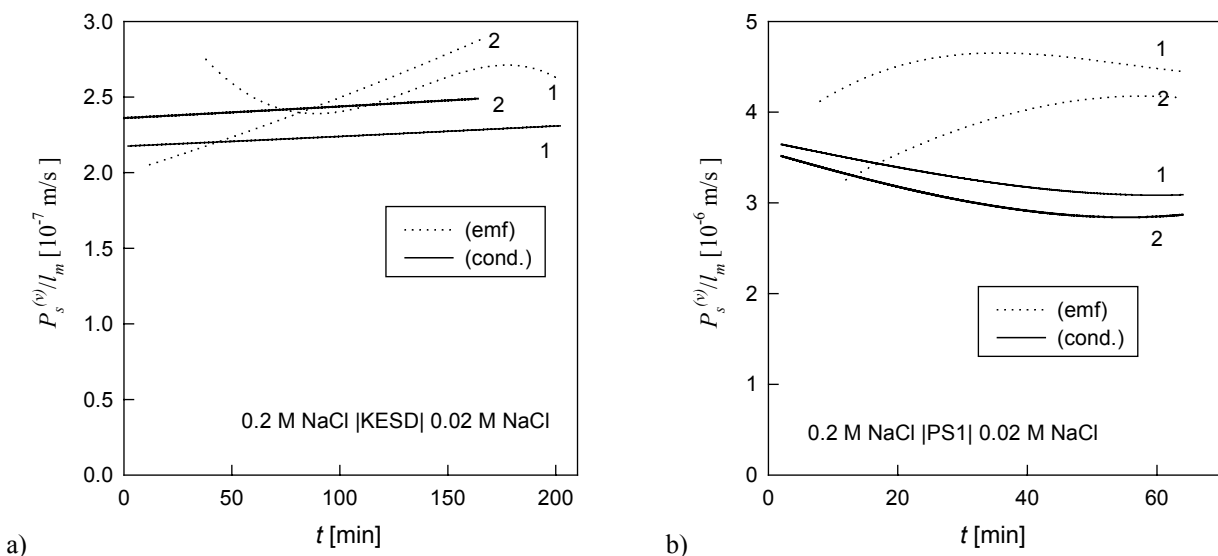
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In the case of dense KESD the value of $P_s^{(v)}/l_m$ during the experiment should be rather constant, because the changes of concentration are very small. Indeed, $P_s^{(v)}/l_m$ (cond.) does not change with time substantially, contrary to $P_s^{(v)}/l_m$ (emf). The greater changes of the latter may result from the calibration curve $c'=f(E)$ based on the assumption $V''=$const, whereas the concentration-conductance calibration curves have been determined without any assumption. The mean $\hat{P}_s^{(v)}/l_m$ calculated from eq.(4) using the least squares method are shown in Table 1.

Table 1. $\hat{P}_s^{(v)}/l_m$ from eq.(4) (the least squares method).

run	$\hat{P}_s^{(v)}/l_m$ [10^{-7} m/s]	R^2
	KESD	
1) cond.	2.438	0.9999
1) emf	2.569	0.9992
2) cond.	2.381	0.9999
2) emf	2.418	0.9977
	PS1	
1) cond.	30.96	0.9992
1) emf	45.24	0.9997
2) cond.	28.68	0.9988
2) emf	41.15	0.9986

In Fig.6 $P_s^{(v)}$, P_s, and P_v for KESD, calculated from eqs.(2), (3) and (7), are shown. Always a small increase of permeability coefficients with time is seen. Their mean values and standard errors, calculated according to eqs.(24), (25), are gathered in Table 2.

$$\hat{P}_i = \int_0^{t_{run}} P_i dt / t_{run} \quad P_i = P_s^{(v)}/l_m, P_s/l_m, P_v/l_m \tag{24}$$

$$\Delta\hat{P}_i = \frac{1}{t_{run}} \int_0^{t_{run}} \left(\sum_k \left(\frac{\partial P_i}{\partial x_k} \Delta x_k \right)^2 \right)^{1/2} dt \tag{25}$$

In eqs.(24), (25) x_i denotes experimentally determined quantities: $V'^{,0}$, $V''^{,0}$, coeffcients of polynomials approximating the time dependence of conductances of solutions; Δx_i is a standard error of x_i.
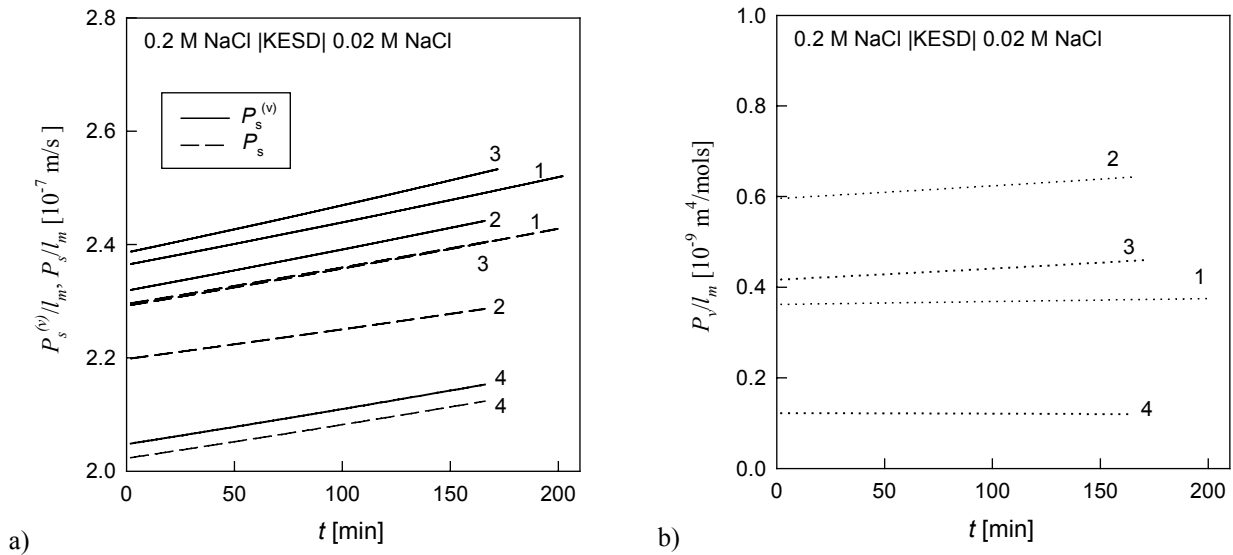
Fig. 6. a) $P_s^{(v)}/l_m$ (solid line, eq.(2)) and P_s/l_m (dashed line, eq.(2)), b) P_v/l_m (dotted line, eqs.(3) and (7)), vs. time; 1-4 denote the no. of measurement; 0.2 M NaCl | KESD | 0.02 M NaCl, 25°C.

Table 2. The mean values of $P_s^{(v)}/l_m$, P_s/l_m, P_v/l_m, and their standard errors, calculated according to eqs.(24), (25); 0.2 M NaCl|KESD|0.02 M NaCl, 25°C.

run	$\hat{P}_s^{(v)}/l_m$ [10^{-7} m/s]	$\hat{P}_s/l_m$ [10^{-7} m/s]	$\hat{P}_v/l_m$ [10^{-10} m^4/s·mol]
1	2.44 ± 0.15	2.36 ± 0.15	3.73 ± 0.24
2	2.38 ± 0.20	2.24 ± 0.19	6.19 ± 0.51
3	2.47 ± 0.10	2.37 ± 0.10	4.40 ± 0.18
4	2.13 ± 0.35	2.11 ± 0.35	1.20 ± 0.20
mean (1-4)	2.36	2.27	3.9
std.dev.	±0.15	±0.12	±2.1

It is seen that repeatability of $P_s^{(v)}$ and P_s is relatively good, whereas that of P_v is poor. However, the calculated from 4 runs mean value of P_v ($3.9 \cdot 10^{-10}$ m^4/s·mol) does not deviate substantially from that obtained by the direct measurement of volume flow ($4.2 \cdot 10^{-10}$ m^4/s·mol). In order to show which of the experimentally determined variable has the greatest influence on a permeability coefficient, the absolute values of partial derivatives $\left|\partial \ln P_i / \partial \ln x_k\right|$ have been calculated (Fig.7, a_i' and a_i'' denote coefficients approximating the conductance of solutions: $G' = a_0' + a_1't$, $G'' = a_0'' + a_1''t$). It is seen that indeed the osmotic permeability coefficient is the most sensible to errors quantity. All of the measured variables, except a_0'' corresponding to the initial concentration of dilute solution, influence P_v very strongly. a_0'' is of minor importance also in the case of $P_s^{(v)}$ and P_s, together with a_1' and V'^0 characterising the concentrated solution.
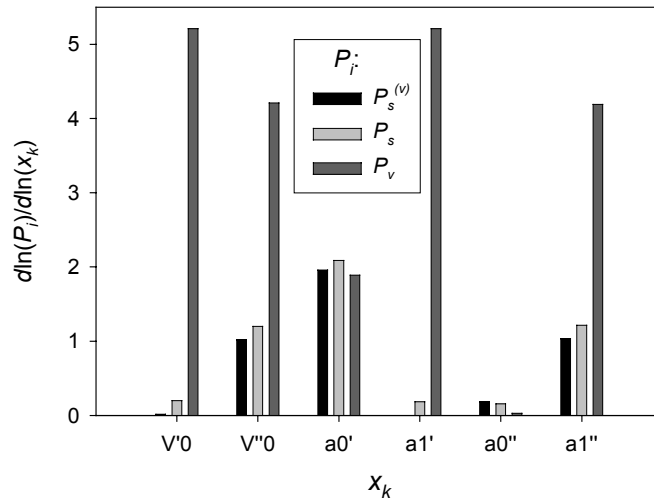
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Fig. 7. $\left| \partial \ln P_i / \partial \ln x_k \right|$ averaged over the time of run 1, 0.2 M NaCl|KESD|0.02 M NaCl.

Influence of polarisation layers

From the current-voltage curves for the system Nafion 117|0.02 M NaCl with and without stirring (Fig.8) we have determined I_{lim} to be 28.6 and 12.1 A/m^2, respectively. This membrane system is characterised by the following transport coefficients: P_s=0.41·10^{-11} m^2/s, P_v=5·10^{-14} m^5/mol·s [iii], $(FJ_v/I)_{\Delta c, \Delta p=0}$ =1.75·10^{-4} m^3/mol [iv]; the diffusion coefficient of NaCl in polarisation layer D_s=1.535·10^{-9} m^2/s. For the above values of I_{lim} eq.(20) yields l_p=0.168 mm with stirring, and l_p=0.401 mm without stirring. The estimated value of volume flow consisting of electroosmotic and osmotic contribution is of the order 10^{-7} m/s and is ca. 100 smaller than D_s/l_p. Thus, eq.(15) gives similar values of l_p (0.167 and 0.395 mm, respectively) as the more exact eq.(20).
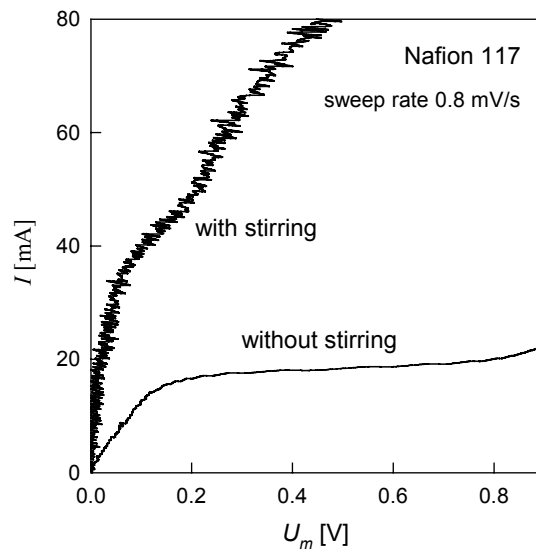

Fig. 8. Current-voltage curves for Nafion 117|0.02 M NaCl placed in the diffusion cell.

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With l_p=0.168 mm eq.(13) yields for the system 0.2 M NaCl|KESD|0.02 M NaCl 4.2% higher value of P_s/l_m, then that listed in Table 2 (mean(1-4)). The simplified eq.(14) only slightly overestimates P_s/l_m (5.2%) comparing to eq.(13) with $c'^{(m)}$, $c''^{(m)}$ given by eqs.(11a,b). However, for higher values of J_v or c' the discrepancy between correction factors calculated from both equations will increase. E.g. for c'=1 M from eq.(13) it results that $P_s \approx P_{s,exp}$ ($P_s/P_{s,exp}$=1.005), whereas eq.(14), not containing c', yields the same value $P_s/P_{s,exp}$=1.052 as previously (taking $P_{s,exp}$ and $P_{v,exp}$ values as for c'=0.2 M).

Conclusions

1. Regarding the electrolyte permeability coefficient, $P_s^{(v)}$ the emf method yields similar results as the conductometric one only in the case of dense membranes of low permeability. It is not appropriate method for membranes of high permeability.

2. The determination of volume permeability coefficient from the changes of concentrations of solutions on both sides of a membrane is possible, however the high accuracy of measurements is required.

3. When calculating the correction for polarisation layers eq.(13), not (14), should be rather used.

4. When determining the thickness of polarisation layer, l_p, from the limiting current density using the Nafion 117 membrane the corrections for the diffusion of electrolyte and volume osmotic flux through that membrane can be omitted; both eqs.(15) and (20) yield practically the similar values of l_p.

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