

ON THE DETERMINATION OF TRANSPORT COEFFICIENTS OF ION EXCHANGE MEMBRANES

by S. KOTER

Institute of Chemistry, N. Copernicus University, Toruń

The limitation of application of additivity rule to the measurement of diffusion is shown. The exact expressions for practical flows and forces for the system with concentration and pressure differences as driving forces for different definitions of mean concentration are derived.

Some of the transport coefficients of ion-exchange membranes, like
– permeability coefficients of diffusion and osmosis,
– apparent transport number of ions,
are usually determined for the finite concentration difference of electrolyte solutions separated by a membrane in zero-current, isobaric-isothermal conditions. Because the state of the membrane is a function of the concentration of the external solution, the coefficients determined are the mean values for that concentration range. In order to obtain the coefficients corresponding to a given concentration (so called differential coefficients) one of the two methods can be applied:

- 1) described by Pusch [1],
- 2) proposed and used by McAres *et al.* [2–4].

The first one consists in the measurement of a given quantity y ($y \equiv$ diffusional flow, osmotic flow, electromotive force of concentration membrane cell) with increasing concentration difference, Δc_s , keeping as constant the mean concentration. The gradient of the curve $y = f(\Delta x)$, where x is a function of the concentration ($x \equiv c_s, \ln(a_{\pm}), \mu_s^c, \Pi$, etc.), at $\Delta c_s \rightarrow 0$

$$y' = (\partial y / \partial \Delta x)_{\Delta c_s = 0} \quad (1)$$

is the differential coefficient for a given concentration c_s ($y' \equiv$ permeability coefficient, apparent transport number of ions).

The above method is, however, tedious and at higher concentrations the determination of small concentration changes in the case of the measurement of diffusion is not very accurate and time consuming.

The second method consists in the measurement of quantity y in narrow concentration intervals ($c_{S,i-1} \div c_{S,i}$) and the calculation of y for ($c_{S,0} \div c_{S,n}$) according to the additivity rule

$$y = y_0(c_{S,0} \div c_S = c_{S,0}) = 0 \quad (2)$$

$$y = y_n(c_{S,0} \div c_S = c_{S,n}) = \sum_{i=1}^n y(c_{S,i-1} \div c_{S,i}) \quad n=1,2,\dots,l_p$$

where l_p is the number of measurements.

Next y is approximated as a function of x . The differential transport coefficient is equal to the derivative

$$y' = \partial y / \partial x \quad (3)$$

In the case of diffusional and osmotic flows ($y \equiv J$) the additivity rule, the base for Meares' method, is fulfilled for stationary states. The proof given in [5] should be supplemented by two remarks.

i/ The additivity rule is fulfilled, if the transport coefficients do not depend on the pressure.

Deriving once more the flow equation under the assumption that the flow is constant in each layer of a membrane, perpendicular to the direction of the flow, we get

$$d_m J = \int_{c_{S,0}}^{c_{S,n}} P_x dx + \int_{P_0}^{P_n=P_0} L_p = \int_{c_{S,0}}^{c_{S,n}} P_x dx \quad (4)$$

Here the pressure part, although equal to zero, is taken into account to stress the fact that the pressures of hypothetical solutions between layers can be different [6], even if the pressures on both sides of the membrane are equal. Thus, if P_x depends not only on the concentration, but also on the pressure, then the equality (5) (additivity rule) need not to be fulfilled

$$\int_{c_{S,0}}^{c_{S,n}} P_x(c_{S,p}) dx = \int_{c_{S,0}}^{c_{S,1}} P_x(c_{S,p}) dx + \dots + \int_{c_{S,n-1}}^{c_{S,n}} P_x(c_{S,p}) dx \quad (5)$$

because in the concentration intervals $c_{S,0} \div c_{S,1}, \dots, c_{S,n-1} \div c_{S,n}$ the pressure profiles are different from that in $c_{S,0} \div c_{S,n}$

ii/ With a negligible pressure effect, but a not negligible influence of concentration on the thickness of the membrane, the additivity rule should be written according to equations (4,5) as

$$(d_m J)(c_{S,0} \pm c_{S,n}) = \sum_{i=1}^n (d_m J)(c_{S,i-1} \pm c_{S,i}) \quad (6)$$

and transport coefficient should be calculated from the formula

$$P_x = \partial(d_m J)/\partial x \quad (7)$$

In the case of diffusional flows determined only from the concentration changes of a diluted solution it is not possible to apply the additivity rule, unless the measurements of volume osmotic flow are made.

From the definitions of flow of a solute, J_s , and of volume osmotic flow, J_v , across the membrane of area A

$$J_s = \frac{1}{A} \frac{dn_{s,0}}{dt} \quad J_v = \frac{1}{A} \frac{dV_0}{dt} = \bar{v}_s J_s + \bar{v}_w J_w \quad (8,9)$$

and from the equation (10)

$$n_{s,0} = c_{s,0} V_0 \quad (10)$$

we get

$$J_s^{V,0} = J_s - c_{s,0} J_v = \frac{V_0}{A} \frac{dc_{s,0}}{dt} \quad (11)$$

In equations (8–11) $c_{s,0}$ is the concentration of a diluted solution, $n_{s,0}$ - the number of a moles of solute in volume V_0 of a diluted solution, J_w - flux of the solvent in respect to the membrane, and \bar{v}_s , \bar{v}_w are their partial molar volumes of the solute and solvent, respectively.

It results from equation (11) that only measurements of the diffusion always to the same solution $c_{s,0}$, *i.e.* $c_{s,0} \pm c_{s,1}$, $c_{s,0} \pm c_{s,2}$, ..., etc., allows the calculation of a well defined flow $J_s^{V,0}$, which can be differentiated. In the case of measurements in interval, $c_{s,i-1} \pm c_{s,i}$, according to schema (2) or (6), it is not possible to calculate $J_s^{V,0}(c_{s,0} \pm c_{s,k})$, because in each interval $c_{s,0}$ in equation (11) changes to $c_{s,i-1}$, *i.e.* is not constant. Only additional measurements of J_v allow the application of the additivity rule in this case, making possible the calculation of the flux $J_s = J_s^{V,0} + c_{s,0} J_v$ from equation (11).

The expression (12), resulting by differentiating $d_m J_s^{V,0}$ (equation (11)) by x ,

$$\partial(d_m J_s^{V,0})/\partial x = \partial(d_m J_s)/\partial x - c_{s,0} \partial(d_m J_v)/\partial x \quad (12)$$

tends towards $\partial(d_m J_s)/\partial x$, if $c_{s,0}$ is small enough.

Otherwise, again the measurements of volume osmotic flow J_v should be carried out in order to calculate both $\partial(d_m J_s)/\partial x$ and $\partial(d_m J_w)/\partial x$.

Equation (11) resolves additionally ambiguity related to the kind of diffusional flux determined from the changes of the solution concentration [7].

Choice of the practical transport equations

In literature different expressions for diffusional flux ($J_D = J_s/\tilde{c}_s - \bar{v}_w J_w$ [8] $J_D = J_s/\tilde{c}_s - J_w/\tilde{c}_w$ [1,9] – (sufficient approximations for diluted solutions) and different definitions of the mean concentration \tilde{c}_s (arithmetic, logarithmic, defined by equation (16)) [7–10] can be met. Therefore it would be useful to derive the correct equations, necessary for the exact calculation of transport coefficients.

The starting transport equations are

$$J_s = L_{ss}\Delta\mu_s + L_{sw}\Delta\mu_w \quad J_w = L_{ws}\Delta\mu_s + L_{ww}\Delta\mu_w \quad (13a,b)$$

The transformations of fluxes and forces, with invariant entropy production and Onsager reciprocity relation (under the condition that equations (13) fulfil it) are given by equations (14) [11]

$$J' = A J \quad F' = A^{-1T} F \quad L' = A L A^T \quad (14a,b,c)$$

where J, F are vectors of fluxes and forces to be transformed, J', F' – vectors of new fluxes and forces, A – transformation matrix, L, L' – matrices of the old and new transport coefficients.

Transforming fluxes and forces from equations (13) with the help of (14) one gets the following practical fluxes and forces listed in Table 1, for two definitions of mean concentration \tilde{c}_s^a and \tilde{c}_s^b .

The notation in Table 1 is as follows:

$$\Delta\Pi = -\Delta\mu_w^c/\bar{v}_w \quad (15)$$

\tilde{c}_s^a is defined by formula [7,8]

$$\tilde{c}_s^a = \Delta\Pi/\Delta\mu_s^c \quad (16)$$

whereas \tilde{c}_s^b – by formula (17)

$$\tilde{c}_s^b = \frac{\Delta\Pi/\Delta\mu_s^c}{1 + \bar{v}_s\Delta\Pi/\Delta\mu_s^c} \quad (17)$$

resulting from equations (18,19)

$$\tilde{c}_s\Delta\mu_s^c + \tilde{c}_w\Delta\mu_w^c = 0 \quad \bar{v}_s\tilde{c}_s + \bar{v}_w\tilde{c}_w = 1 \quad (18,19)$$

\tilde{c}_w is determined by \tilde{c}_s and equation (19).

The examination of expressions listed in Table 1 shows that the simplest and the most comfortable (from the experimental point of view) transport equations are obtained for the mean concentration defined by equation (17). The transport equations with new fluxes and forces are valid as long as linear equations (13) are, whereas the mean concentration is a transformation parameter, which determines the form of the transformed flows and forces.

Table 1
List of chosen transformations of fluxes and forces for two mean concentrations,
 \tilde{c}_s^a and \tilde{c}_s^b , (formulae (16,17)).

J'_1	J'_2	F'_1	F'_2
J_s	J_w	$\Delta\mu_s$	$\Delta\mu_w$
J_s	J_v	$(1 + \bar{v}_s \tilde{c}_s^a) \Delta\Pi / \tilde{c}_s^a$	$\Delta p - \Delta\Pi$
J_s	J_v	$\Delta\Pi / \tilde{c}_s^b$	$\Delta p - \Delta\Pi$
$J_s - \tilde{c}_s^a J_v$	J_v	$(1 + \bar{v}_s \tilde{c}_s^a) \Delta\Pi / \tilde{c}_s^a$	Δp
$J_s - \tilde{c}_s^a \bar{v}_w J_w$	J_v	$\Delta\Pi / \tilde{c}_s^a$	Δp
$J_s - \tilde{c}_s^b J_v$	J_v	$\Delta\Pi / \tilde{c}_s^b$	Δp
$J_s / \tilde{c}_s^a - J_v$	J_v	$(1 + \bar{v}_s \tilde{c}_s^a) \Delta\Pi$	Δp
$J_s / \tilde{c}_s^a - \bar{v}_w J_w$	J_v	$\Delta\Pi$	Δp
$J_s / \tilde{c}_s^b - J_v$	J_v	$\Delta\Pi$	Δp
$J_s / \tilde{c}_s^a - J_w / \tilde{c}_w$	J_v	$(1 - (\bar{v}_s \tilde{c}_s^a)^2) \Delta\Pi$	$\Delta p + \bar{v}_s \tilde{c}_s^a \Delta\Pi$
$J_s / \tilde{c}_s^b - J_w / \tilde{c}_w$	J_v	$(1 - \bar{v}_s \tilde{c}_s^b) \Delta\Pi$	Δp

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