of $0-15$ %. The theoretical radial distribution curve corresponding to 15 % *anti* conformer was also found to be in poorer agreement with the experimental one than the curve for a model based on only the *syn* conformer. We concluded that there is no evidence for the presence of a second conformer.

The results from our present study compared very well with the earlier electron diffraction [1] and microwave [2] works (see Table 3). Comparison with the recent electron diffraction work on dimethyl carbonate $(CH_3OCOOCH_3)$[9] showed no substantial difference between values of comparable parameters. In both the formate and carbonate only comparable conformers *syn* and *syn-syn* were found.

It is of interest to compare two structurally related molecules like methyl formate and methylvinyl ether.[10] The $C(sp^2)-O$ bond is longer by 0.02 Å in the ether than in the formate and the $C-O-C$ value is 4° greater in the ether. Also, in contrast to methyl formate, two conformers (73 % *syn* and 27 % *anti*) are observed for methylvinyl ether at 210 °C. Assuming that the entropy differences of conformers are similar, these results are in agreement with the *ab initio* molecular orbital calculations [11] showing the *anti* form to be $4-8$ kcal mol⁻¹ above the *syn* form in methyl formate while the *anti* form is only $1-2$ kcal mol⁻¹ above the *syn* form in methylvinyl ether (1 kcal = 4.184 kJ).

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The Coefficients for Isothermal Transport. II. Cation Exchange Membrane and Electrodes Reversible to One of the Cations

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A rigorous thermodynamic description of electrolyte transport across a membrane has been given in a previous publication by Førland, Førland and Ratkje.[1] Specific for their presentation is that the number and kind of components used to describe the system, conform with the phase rule. The presentation deals only with measurable quantities. This ensures an independent choice of forces in the flux equations.

When restrictions such as selectivity of the membrane and of the electrodes are imposed on the mass and charge transfer, relations between the phenomenological coefficients of the flux-force system may be developed.[1,2] Relations were obtained for anion electrodes and a cation selective membrane.[1] This communication is a supplement to the previous work. The effect of substituting anion electrodes by cation electrodes is investigated. Information of the relative size of the phenomenological coefficients is developed.

Transports in an ion exchange membrane placed between electrodes reversible to a cation. The number of mass fluxes in a transport system of n components is $(n-1)$, the flux of the n'th component being chosen as the zero reference.[1] With an electric current passing through the system there are independent forces. In the Førland-Ratkje formalism these are the $(n-1)$ gradients in chemical potential and the gradient in electric potential.[1] The fluxes J_i are linear combinations of the forces X_j:

$$J_i = \sum_{j=1}^{n} L_{ij} X_j \tag{1}$$

When the fluxes are linearly dependent

$$\sum_{i=1}^{n} \alpha_i J_i = 0 \tag{2}$$

general relations between the phenomenological coefficients have been developed.[1,2]

$$\sum_{i=1}^{n} \alpha_i L_{ij} = 0 \quad j = 1,...,n \tag{3}$$

α_i, $i = 1,...,n$, are coefficients giving the interdependency.

Consider as an example the transport of the components HCl, NaCl and H_2O with reference to the membrane component HM. The membrane is conducting cations only. The system which includes electrodes reversible to the H^+-ion, is illustrated in Fig. 1.

When anion reversible electrodes are chosen, an electrolyte flux is defined by the flux of the cation of a component. In the present case, with a common anion Cl^- and cation reversible electrodes, the total flux of electrolytes, $J_{HCl} + J_{NaCl}$, is defined by the flux of Cl^-. As no current is carried by Cl^- the linear dependency among the fluxes is

$$J_{HCl} + J_{NaCl} = 0 \qquad (4)$$

Eqn. (4) corresponds to (2) with $\alpha_1 = \alpha_2 = 1$ and $\alpha_3 = \alpha_4 = 0$. The relations between the phenomenological coefficients are thus

$$L_{11}' + L_{2i}' = 0 \quad i = 1,...,4 \qquad (5)$$

The coefficients are primed to indicate that cation reversible electrodes are used. The physical meaning of eqn. (4) or (5) is that the transport of charge in one direction across the membrane is balanced by a charge transport in the opposite direction. This is obviously so when no net current is passing (simple interdiffusion) but due to the specific choice of electrodes the statement is also true for $I \neq 0$ in this macroscopic description where J_{HCl} includes the transfer of H^+ via the electrodes.

For comparison, the relations (3) are for the same system with chloride reversible electrodes [1] (indicated by unprimed coefficients)

$$L_{1i} + L_{2i} = L_{4i} \quad i = 1,...,4 \qquad (6)$$

While $L_{12}' \leq 0$, from eqn. (5) and the requirement $L_{ii} \geq 0$, L_{12} need not be negative from eqn. (6). The transport of HCl and NaCl do not balance when current is passed. The excess transfer of say H^+ relative to Na^+ in one direction is compensated by the electrode yield of Cl^- to achieve electroneutrality in each compartment.
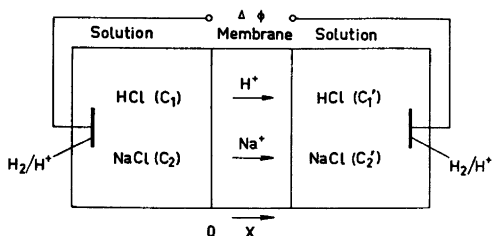

Fig. 1. A cation exchange membrane separating two solutions of HCl and NaCl. The electrodes are reversible to the H^+-ion.

The description given above for selective cation transport across membranes is redundant, due to eqn. (2). But as the cation restricted transport is a limiting case of the general case allowing passage also of anions, it may be useful to keep the redundant equation system (1). This is because the redundant coefficient sets of L_{ij} and L_{ij}' are subject to the restrictions (3) which will give a limit behaviour of nonredundant coefficient sets, as shown below:

We have previously [1] defined the electrode independent diffusion coefficients l_{ij} which are related to L_{ij} by

$$l_{ij} = L_{ij} - (L_{nj}L_{in})/L_{nn} \qquad (7)$$

In our case of cation selective membrane transport the diffusion coefficients obey

$$l_{1i} + l_{2i} = 0 \quad i = 1,... \qquad (8)$$

From eqns. (7–8) and the general restriction $l_{ii} \geq 0$ we have

$$l_{12} = L_{12} - \frac{L_{14}L_{24}}{L_{44}} = L_{12} - t_1 t_2 L_{44} \leq 0 \qquad (9)$$

t_1 and t_2 are electric transference numbers of the component 1 and 2, respectively. t_i is defined by (see Ref. 1 for details)

$$t_i = L_{i4}/L_{44} \quad i = 1,2 \qquad (10)$$

As $t_1 + t_2 = 1$ or $t_i \leq 1$ we have from eqn. (9)

$$L_{12} \leq 0.25 \, L_{44} \qquad (11)$$

$$L_{i4} \leq L_{44} \quad i = 1,2 \qquad (12)$$

By inserting eqns. (11) and (12) into (6) one obtains

$$L_{ii} \leq 0.75 \, L_{44} \quad i = 1,2 \qquad (13)$$

Conclusion. The relations which can be developed between the phenomenological coefficients for ion-selective membrane transport from a rigorous thermodynamic description, are electrode dependent, but permit a detailed analysis of the system on the macroscopic phenomenological level. They furthermore provide experimental testing criteria for the single phenomenological coefficients, as limits for their behaviour can be developed.

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