Transport of Nonelectrolyte-Water Mixtures through Cellulose Membranes

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Measurements of the transport properties of cellulose membranes for the mixtures methanol-water and formamide-water are reported. The measured approach of the mole fractions of the nonelectrolyte to its equilibrium value are interpreted in the framework of linear irreversible thermodynamics in a novel way. The permeabilities of the membranes of the different substances are discussed in terms of phenomenological coefficients. It is shown that these depend on the equilibrium mole fraction in an essential way. A discussion of this effect is given.

1. Introduction

Although the transport properties of membranes for nonelectrolyte-water mixtures have received some attention in the past1–3, no really accurate measurements have as yet been reported and, furthermore, the interpretation of the data in terms of irreversible thermodynamics has not been on the necessary level of sophistication. In this article, a method of measuring the transport properties with very high accuracy is described (Section 2). In Section 3, a theoretical description of the transport phenomenon is undertaken and it is shown how this description allows for a simple method to obtain the permeabilities of the membrane. Here we understand the word permeability in the sense of Krämer and Sauer2, i.e., it is defined as the ratio of a particle flux and a mole fraction difference. The usefulness of these quantities lies in their definition in terms of measurable quantities, a property that the phenomenological coefficients for this problem do not share. The permeabilities so obtained for the systems methanol-water and formamide-water are presented in Section 4. These are then discussed in terms of the phenomenological coefficients describing the transport phenomenon. Some technical theoretical details are given as an appendix.

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2. Materials and Methods

The membranes used in the experiments reported here consist of regenerated cellulose (type SM 11536 supplied by Sartorius Membranfilter GmbH, Göttingen, Germany). The moist membrane filters are kept refrigerated and immersed in a 30% ethanol solution in closed glass dishes when in storage. Under these storage conditions the transport properties of the membranes do not change measurably for periods of a year and longer. The pores of the membranes measure between 50 and 100 Å in diameter; the membranes are 0.09 mm thick.

The two systems on which measurements are reported here are (i) methanol (CH₃OH)/water and (ii) formamide (HCONH₂)/water. These chemicals were obtained commercially and used without further purification.

The osmosis cell is made of glass and consists of two halves with a volume of 55 ml each. The two halves have polished edges between which the membrane is held so that the effective membrane area is 16 cm². The whole assembly is kept at a constant temperature of 25 ± 0.01 °C by immersing in a thermostated water bath. Both compartments of the osmosis cell are stirred by means of glass rods with plane ends inserted through the glass walls of the cells. The fluid in both halves is constantly pumped around a circuit cell-concentration measuring apparatus-storage vessel-cell, the storage vessel being necessary to absorb an eventually occurring volume flux through the membrane.
The concentration measuring apparatus (CMA) operates by means of a method developed by Kratky et al. This method is based on the density dependence of the eigenfrequency of a bent glass capillary filled with the fluid. By calibrating this eigenfrequency with mixtures of known composition, the apparatus can be used to measure the mole fraction of the nonelectrolyte directly. The accuracy obtained by this procedure is $\pm 3.5 \times 10^{-4}$ as error in the mole fraction. Since with this method no fluid has to be removed from the apparatus, the experiments can be continued over large time intervals, typically of the order of 500—3000 minutes.

The CMA's are, of course, also kept at 25 ± 0.01°C. In addition, thermistors measure the temperatures of the fluids before entering the CMA's and these temperatures are continuously recorded.

Measurements are taken automatically at preset times by starting and stopping a counting apparatus for the vibrational motion of the capillaries in the CMA's. When the CMA's stop counting a signal causes the data transfer unit to punch the time and the data serially on tape.

The set up described above is shown schematically in Figure 1. For more details the reader is referred to Reference 5.

**Fig. 1. Schematic overview of the measuring apparatus.**

3. **Theoretical Aspects and Data Handling**

A. **Theoretical Description of the Experiments**

Two cells separated by a membrane are filled with approximately equal volumes of mixtures of two substances $S_1$ and $S_2$, in general water ($S_2$) and a nonelectrolyte ($S_1$). These are then allowed to come into equilibrium under isothermal and isobaric conditions. We arbitrarily call the water the solvent and the nonelectrolyte the solute and describe the state of a phase by the mole fraction of solute molecules. The two phases are distinguished by a prime and a double prime, respectively. We then have, if $n_1'(t)[n_2'(t)]$ and $n_1''(t)[n_2''(t)]$ are the numbers of moles $S_1[S_2]$ in the two phases at time $t$,

$$x'(t) = n_1'(t)[n_1'(t) + n_2'(t)]^{-1};$$
$$x''(t) = n_1''(t)[n_1''(t) + n_2''(t)]^{-1},$$

(1)

$$n_1'(t) + n_1''(t) = N_1;$$
$$n_2'(t) + n_2''(t) = N_2. \quad (2)$$

Here Equations (2) express the conservation of mole number $N_i$ of substance $S_i$ throughout the experiment. The four equations (1) and (2) can now be solved for the four numbers of moles $n_i'(t)$, $n_i''(t)$ ($i=1,2$). The result is especially simple if one introduces the equilibrium mole fraction $c_{oo}$, given as

$$x_{oo} = N_1[N_1 + N_2]^{-1}, \quad (3)$$

and reads for the normalized quantities

$$v_1' = n_1'[N_1 + N_2]^{-1}$$

and

$$v_1'' = n_1''[N_1 + N_2]^{-1}$$

as follows (here and in the rest of this section, the time dependence of all quantities which are not explicitly declared to be constant is implicit):

$$v_1' = x'(x_{oo} - x')(x' - x'')^{-1};$$
$$v_2' = (1 - x')(x_{oo} - x'')(x' - x'')^{-1};$$
$$v_1'' = x''(x' - x_{oo})(x' - x'')^{-1};$$
$$v_2'' = (1 - x'')(x' - x_{oo})(x' - x'')^{-1}. \quad (4)$$

We now introduce new variables $y = x' - x_{oo}$; $z = x_{oo} - x'$ which are always positive for the initial condition $x'(0) > x''(0)$. Equations (4) then look even simpler:

$$v_1' = P + x_{oo}Q;$$
$$v_2' = -P + (1 - x_{oo})Q;$$
$$v_1'' = -P + x_{oo}(1 - Q);$$
$$v_2'' = P + (1 - x_{oo})(1 - Q), \quad (5)$$

$$P = yz[y + z]^{-1}; \quad Q = z[y + z]^{-1}. \quad (6)$$
We now define normalized fluxes \( \varphi_1 \) and \( \varphi_2 \) by
\[
\varphi_1 = -\frac{d\varphi_1'}{dt} = \frac{d\varphi_1''}{dt}, \quad \varphi_2 = -\frac{d\varphi_2'}{dt} = \frac{d\varphi_2''}{dt},
\]
so that we have
\[
\varphi_1 = -\frac{dP}{dt} - x_\infty \frac{dQ}{dt} ; \quad \varphi_2 = \frac{dP}{dt} - (1 - x_\infty) \frac{dQ}{dt} , \tag{7}
\]
\[
\frac{dP}{dt} = \left[ y^2 \frac{dz}{dt} + z^2 \frac{dy}{dt} \right] (y + z)^{-2} ; \quad \frac{dQ}{dt} = \left[ y \frac{dz}{dt} - z \frac{dy}{dt} \right] (y + z)^{-2}. \tag{9}
\]
With these equations, the ratio \( \varphi_1 = \frac{\varphi_1}{\varphi_2} = \frac{1}{1 - x_\infty} \) is identical to the one derived by Schlögl\(^1\). We remark that the “exchange” flow \( \varphi_A \),
\[
\varphi_A = \frac{\varphi_1}{x_\infty} - \frac{\varphi_2}{1 - x_\infty} = -\left( \frac{dP}{dt} \right) [x_\infty(1 - x_\infty)]^{-1},
\]
is always positive if \( dP/dt \) is always negative, i.e., if \( y \) and \( z \) are monotone decreasing functions of the time.

The usual procedure for evaluating the measured data would now be to evaluate the derivatives \( d\varphi/\varphi \) and \( dz/\varphi \) in some way numerically from the measured \( y(t) \) and \( z(t) \) \( (x_\infty \) may be supposed to be known either a priori by weighing the substances or a posteriori by measuring it). This method, however, may introduce large errors in the values of these derivatives, especially in the neighbourhood of equilibrium. We therefore want to make use of the known form of the fluxes \( \varphi_1 \) and \( \varphi_2 \) to predict the form of the \( y(t) \) and \( z(t) \) functions and then compare these with experiment. How this is done in detail is described in the next subsection.

**B. Solution of the Equations in the Linear Regime**

The fluxes \( \varphi_i \) can only depend on the difference \( w = y + z = x' - x'' \). Since these fluxes are certainly well-behaved functions of \( w \) and since they vanish in equilibrium, they may be expanded into a Taylor series in \( w \):
\[
\varphi_i(w) = w \frac{d\varphi_i}{dw} \bigg|_{w=0} + \frac{1}{2} w^2 \frac{d^2\varphi_i}{dw^2} \bigg|_{w=0} + \frac{1}{6} w^3 \frac{d^3\varphi_i}{dw^3} \bigg|_{w=0} + \cdots. \tag{10}
\]
Such a Taylor series may be approximated by its first term for \( w \) small enough, especially if the membrane is symmetric which implies that \( \varphi_i(-w) = -\varphi_i(w) \) and then the quadratic term has to be zero exactly.

We are, of course, aware of the fact that linear irreversible thermodynamics predicts that the fluxes \( \varphi_i \) are proportional to the differences in chemical potential of the two substances in the two phases. The point is, that these differences have to be proportional to \( w \) in the neighbourhood of equilibrium. Explicit expressions for the proportionality constants are given in the Appendix, Equations (A.10).

Assuming now that the \( \varphi_i \) depend linearly on \( w \), we can introduce transport coefficients \( \alpha \) and \( \beta \) as follows:
\[
\frac{d}{dt} \left( \frac{yz}{y + z} \right) = -\frac{d}{dt} \left( \frac{(w - z) z}{w} \right) = \alpha w , \tag{11}
\]
\[
\frac{d}{dt} \left( \frac{y}{y + z} \right) = \frac{d}{dt} \left( \frac{w - z}{w} \right) = \beta w \tag{12}
\]
which implies for the fluxes
\[
\varphi_1 = [-\alpha + x_\infty \beta] w ; \quad \varphi_2 = [\alpha + (1 - x_\infty) \beta] w . \tag{13}
\]
Equations (11) and (12) give two differential equations for \( z \) and \( w \) (a prime means time-differentiation):
\[
z' = -\frac{w'}{w} z + \beta w^2 = 0 , \tag{14}
\]
\[
z' = -2 \frac{2z z'}{w} + \frac{z^2 w'}{w^2} - \alpha w = 0 . \tag{15}
\]
The first of these Equations (14) has as formal solution \( z = -\beta f' f \), where \( f \) is a primitive function of \( w \), i.e., \( f' = w \). Insertion of this result in Eq. (15) gives a nonlinear differential equation for \( f \):
\[
f'' f + \beta f' f^2 + f^2 + 2 \beta f^2 f + (\alpha \beta) f' = 0 . \tag{16}
\]
Since the time does not explicitly occur in this equation, it can be transformed into a differential equation of first order by defining \( p(f) = f' \) so that \( f'' = p'(f) p(f) \). This procedure yields a linear equation for \( p \):
\[
p' + \frac{1 + 2 \beta f}{f(1 + \beta f)} p + \frac{\alpha}{\beta} \frac{1}{f(1 + \beta f)} = 0 . \tag{17}
\]
with the solution (c an integration constant)

\[ p = \frac{df}{dt} = -\frac{\alpha}{\beta} f + c. \]  

(18)

This final equation is easily solved to give for

\[ h = \beta (f + c) \]

\[ F(h) = \frac{1}{2} h^2 + (1 - 2 \beta c) h + [(\beta c)^2 - \beta c] \ln |h| \]

\[ = -\alpha t + D, \]

(19)

where D is another integration constant.

The deviations y and z may be expressed in
terms of h by using the formal solution of Eq. (14),

\[ z = -\beta f', \]

Eq. (18) for f' in terms of f and the
definition \( w = y z - f' \) as

\[ y = -\frac{\alpha}{\beta} \frac{h}{h - \beta c}; \quad z = \frac{\alpha}{\beta} (1 - \beta c) + h. \]

(20)

C. Evaluation of the Data

The experimentally measured values of \( x' \) and \( x'' \)
are used in the following way to obtain z and \( \beta \) from
Eqs. (19) and (20). First of all, it is remarked that
Eqs. (20) imply upon elimination of h:

\[ y = \frac{1}{\alpha c} y z + \left( \frac{1}{\beta c} - 1 \right) z. \]

(21)

Close to equilibrium, the quadratic term in Eq. (21)
may be neglected; this equation then becomes

\[ x' = \left( 1 - \frac{1}{\beta c} \right) x'' + \frac{1}{\beta c} x_\infty. \]

(22)

Therefore, a plot of \( x' \) versus \( x'' \) should be asymptotically straight in the neighbourhood of equilibrium. This is shown for an example of the system formamide (component 1) and water (component 2) in Figure 2. From this asymptotically straight line the parameters \( x_\infty \) and \( \beta c \) may easily be obtained.

Farther from equilibrium, the ratio \( y/z \) is seen to be measurable with sufficient accuracy (note that \( x_\infty \) is now known!) and satisfies

\[ \frac{y}{z} = \frac{1}{\alpha c} y + \left( \frac{1}{\beta c} - 1 \right). \]

(23)

Therefore, a plot of \( y/z \) versus y should give a straight line in this region. This is shown again for the example quoted earlier in Figure 3. This yields the values of \( \alpha c \) and \( \beta c \) and the ratio \( \alpha/\beta \) is now known. To obtain \( z \) independently, \( h \) is calculated from y (or z) by

\[ h = (\beta c) \frac{y}{z} [y + \alpha c/\beta], \]

(24)

and a plot of \( F(h) \) of Eq. (19) versus t should give
a straight line with slope \(-\alpha\). This is shown for the
same example as above in Figure 4. Now both the values \( \alpha \) and \( \beta \) are known. From these the permeabilities \( p_1 \) and \( p_2 \), i.e., the ratios of particle number
flux (in moles per unit area of membrane) and mole
fraction difference are obtained by means of
Eqs. (13) as

\[ p_1 = (N_1 + N_2) (-\alpha + x_\infty \beta)/A; \]

\[ p_2 = -(N_1 + N_2) \{x + (1 - x_\infty) \beta\}/A, \]

(25)

where \( A \) is the membrane area.

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Fig. 2. The mole fraction \( x' \) versus the mole fraction \( x'' \)
as an illustration of Equation (22). The system is formamide/water, the initial conditions were \( x'(0) = 0.2923, \quad x''(0) = 0.0381 \). The cross denotes the equilibrium concentration \( x = 0.1508 \).

Fig. 3. A plot of \( y/z \) versus y (see text for definitions) as an illustration of Equation (23). Same system as used for Figure 2.
4. Results and Discussion

In Figures 5 and 6 the results of permeability measurements on the mixtures methanol-water and formamide-water, respectively, are given. As is clear from these figures, the permeabilities increase strongly for $x_{\infty} \rightarrow 0$ and weakly (or not at all for formamide) for $x_{\infty} \rightarrow 1$. This is obviously due to the explicit dependence of the permeabilities on $x_{\infty}$ as given by the formulae (see the Appendix for the derivation)

$$p_1 = kT q \left( \frac{L_{11}}{x_{\infty}} - \frac{L_{12}}{1 - x_{\infty}} \right), \quad p_2 = p_{\text{M or P}},$$

$$p_2 = kT q \left( - \frac{L_{12}}{x_{\infty}} + \frac{L_{22}}{1 - x_{\infty}} \right), \quad p_2 = p_{\text{W}}$$

since the dependence of the factor $q$ and the phenomenological coefficients $L_{ij}$ on $x_{\infty}$ could scarcely produce such an effect. It is, however, easy to see that the assumption that $q$ and the $L_{ij}$ do not depend on $x_{\infty}$ at all cannot reproduce the data. What is clearly seen from Figs. 5 and 6 is that $L_{12}$ is negative, since else the positive values of $p_{\text{W}}$ for small $x_{\infty}$ cannot be explained, and that $q$ is positive, since else $p_{\text{M}}$ and $p_{\text{F}}$ would be negative for small $x_{\infty}$ because of the fact that $L_{11}$ and $L_{22}$ are positive.

Since the ratio $p_1/p_2$ does not contain the factor $q$ a test was done to investigate whether this ratio can be explained by means of $x_{\infty}$-independent $L_{ij}$ values:

$$R(x_{\infty}) = \frac{p_1}{p_2} = \frac{(1 - x_{\infty}) L_{11} - x_{\infty} L_{12}}{(1 - x_{\infty}) L_{12} + x_{\infty} L_{22}}.$$

The first part of this test consists in checking the derivative of $R(x_{\infty})$ at the point $x_{\infty} = 1/2$; it follows from Eq. (28) that this derivative has, for $x_{\infty}$-independent $L_{ij}$, the form

$$\frac{d}{dx_{\infty}} R(x_{\infty}) \bigg|_{x_{\infty} = \frac{1}{2}} = 4 \frac{L_{12}^2 - L_{11} L_{22}}{(L_{22} - L_{12})^2},$$

Fig. 4. A plot of $F(t)$ (see text for definition) versus $t$ as an illustration of Equation (19). Same system as used for Figure 2.

Fig. 5. Permeabilities of the methanol/water system as functions of $x_{\infty}$. •: permeability of water, $p_{\text{W}}$; ▲: permeability of methanol, $p_{\text{M}}$.

Fig. 6. Permeabilities of the formamide/water system as functions of $x_{\infty}$. •: permeability of water, $p_{\text{W}}$; ▲: permeability of formamide, $p_{\text{F}}$. 

$$L_{ij}$$ values:
and this has to be negative for the entropy production to be positive. As is clear from Fig. 7 in which \( p_1/p_2 \) for the two mixtures are plotted versus \( x_{\infty} \), this is not true for the methanol-water system, excluding the possibility of \( x_{\infty}\)-independent \( L_{ij} \) values for this system. For the formamide-water system, the derivative is negative; we can then try to fit the points with a curve of the form

\[
\frac{p_1}{p_2} = \left[ \mu \left( \frac{1 - x_{\infty}}{x_{\infty}} \right) + \nu \left( \frac{1 - x_{\infty}}{x_{\infty}} \right) + 1 \right]^{-1},
\]

where \( \mu = L_{11}/L_{22} \) and \( \nu = -L_{12}/L_{22} \). It turns out that no curve of the form (30) fits the measured values for the formamide-water system in a reasonable way.

It is actually not surprising to find a strong dependence of the \( L_{ij} \) on \( x_{\infty} \). Such a result has also been found by Krämer and Sauer for the system ethylene glycol-methanol and may also be expected on the basis of a number of theoretical approaches, even in the absence of interactions between the membrane and the molecules of the solutions. We have performed the above test notwithstanding these results since no simple and manifestly correct physical picture exists which predicts the dependence of \( L_{ij} \) on \( x_{\infty} \). Such a result has also been found by Krämer and Sauer for the system methanol-water as compared to formamide-water cannot be interpreted theoretically as yet. We do, however, feel inclined to believe that the bonding of molecules to the membrane with hydrogen bridges may play a role.

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Appendix

Permeabilities and Linear Phenomenological Laws

The general phenomenological laws for the experiments described in this article are

\[
\begin{align*}
\varphi_1 &= L_{11} \Delta \mu_1 + L_{12} \Delta \mu_2, \\
\varphi_2 &= L_{21} \Delta \mu_1 + L_{22} \Delta \mu_2,
\end{align*}
\]

where the \( L_{ij} \) are phenomenological coefficients satisfying the Onsager relation \( L_{12} = L_{21} \) and \( \Delta \mu_i \) is the difference in chemical potential of component \( i \) across the membrane. In this appendix the relation between Eqs. (A.1) and the linear laws used in Sect. 3 will be made explicit via a statistical mechanical argument.

The configurational grand canonical partition function for a mixture of two types of molecules in a volume \( V \) is

\[
Z = \sum_{m_1=0}^{\infty} \sum_{m_2=0}^{\infty} \frac{1}{m_1! m_2!} \exp(m_1 \beta \mu_1 + m_2 \beta \mu_2) \\
\cdot \left\{ \exp \left[ -\beta U(x_1, \ldots, x_{m_1}; y_1, \ldots, y_{m_2}) \right] \right\},
\]

where \( \beta = (kT)^{-1} \), \( \mu_i \) is the chemical potential of component \( i \) and \( U(x_1, \ldots, x_{m_1}; y_1, \ldots, y_{m_2}) \) is the potential energy of an assembly of \( m_1 \) molecules of type 1 at \( x_1, \ldots, x_{m_1} \) and of \( m_2 \) molecules of type 2 at \( y_1, \ldots, y_{m_2} \). The pressure \( p \) and number densities

\[
\begin{align*}
\frac{p_{\text{M}}}{p_{\text{W}}} &\quad \bigcirc \quad \text{of methanol-water as compared to formamide-water cannot be interpreted theoretically as yet. We do, however, feel inclined to believe that the bonding of molecules to the membrane with hydrogen bridges may play a role.}
\end{align*}
\]

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\frac{p_{\text{M}}}{p_{\text{W}}} &\quad \bigcirc \quad \text{of methanol-water as compared to formamide-water cannot be interpreted theoretically as yet. We do, however, feel inclined to believe that the bonding of molecules to the membrane with hydrogen bridges may play a role.}
\end{align*}
\]
\( q_i \) are then given as
\[
\beta p = f(\beta \mu_1, \beta \mu_2) \equiv V^{-1} \ln \Xi, \quad (A.3)
\]
\[
q_i = \frac{\langle m_i \rangle}{V} = \frac{\partial}{\partial \beta \mu_i} f(\beta \mu_1, \beta \mu_2). \quad (A.4)
\]

In the neighbourhood of a reference state \((\mu_{1\infty}, \mu_{2\infty})\), \(f\) can be expanded in a Taylor series as
\[
f(\beta \mu_1, \beta \mu_2) = f(\beta \mu_{1\infty}, \beta \mu_{2\infty})
+ \frac{1}{2} \beta^2 (\mu_1 - \mu_{1\infty})^2 a_{11} + \frac{1}{2} \beta^2 (\mu_2 - \mu_{2\infty})^2 a_{22}
+ \beta (\mu_1 - \mu_{1\infty})(\mu_2 - \mu_{2\infty}) a_{12}, \quad (A.5)
\]
where the \(a_{ij}\) are given as
\[
a_{ij} = \frac{\partial^2 f}{\partial \beta \mu_i \partial \beta \mu_j} \bigg|_{\infty}
= \frac{1}{V} \left( \langle m_i m_j \rangle_{\infty} - \langle m_i \rangle_{\infty} \langle m_j \rangle_{\infty} \right). \quad (A.6)
\]

Now we have two such states, distinguished by a prime and a double prime. These are under equal pressures. This implies, from Eqs. (A.5) and (A.3)
\[
(\mu_1 - \mu_{1''}) \theta_{1\infty} + (\mu_2 - \mu_{2''}) \theta_{2\infty} = 0. \quad (A.7)
\]

We further have for the number density in the ('')-phase
\[
q_i' = q_{i\infty} + \beta a_{i1}(\mu_1' - \mu_{1\infty})
+ \beta a_{i2}(\mu_2' - \mu_{2\infty}) \quad (A.8)
\]
and an analogous equation for the ("")-phase. Now remembering that \(x = q_1[q_1 + q_2]^{-1}\) and expanding this ratio up to linear terms in \(\mu_1 - \mu_{1\infty}\) allows us to obtain for \(x' - x''\) the expression that follows:
\[
x' - x'' = \left[ q_{1\infty} + q_{2\infty} \right]^{-1} \beta \left( (\mu_1' - \mu_{1''})
\times [a_{11} (1 - x_{\infty}) - a_{12} x_{\infty}] + (\mu_2' - \mu_{2''})
\times [- a_{22} x_{\infty} + a_{12} (1 - x_{\infty})] \right). \quad (A.9)
\]

Using also Eq. (A.7), we can express \(\Delta \mu_i = \mu_i' - \mu_i''\) in \(x' - x''\) as
\[
\Delta \mu_1 = (1 - x_{\infty})[\beta Q]^{-1}(x' - x'');
\Delta \mu_2 = - x_{\infty}[\beta Q]^{-1}(x' - x''), \quad (A.10)
\]
where \(Q\) is given by
\[
Q = (1 - x_{\infty})^2 a_{11} - 2 x_{\infty} (1 - x_{\infty}) a_{12} + x_{\infty}^2 a_{22}.
q_{1\infty} + q_{2\infty}. \quad (A.11)
\]

It is easily seen, that \(Q\) has the value
\[
Q_0 = x_{\infty}(1 - x_{\infty})
\]
in case the molecules do not interact, since then \(a_{11} = q_{1\infty}, a_{12} = 0, a_{22} = q_{2\infty}\), as is easily ascertained by a direct calculation for \(\Xi\) in this case. Defining then \(q = Q_0/Q\), it may be seen that a comparison of Eqs. (25), (A.1), and (A.10) yields the permeabilities in terms of the \(L_{ij}\) as
\[
p_1 = kT q \left( \frac{L_{11}}{x_{\infty}} - \frac{L_{12}}{1 - x_{\infty}} \right);
p_2 = kT q \left( - \frac{L_{12}}{x_{\infty}} + \frac{L_{22}}{1 - x_{\infty}} \right). \quad (A.12)
\]

These equations follow also from the work of Krämer and Sauer.

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1. R. Schlögl, Stofftransport durch Membranen, Steinkopff Verlag, Darmstadt 1964.