Temperature Dependence of Thermo-osmosis

A Solution Model

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A model has been proposed to study the temperature dependence of the permeation and the thermo-osmosis of a single substance through a membrane. The model takes into account the dependence on temperature of the molar volume of permeant, the enthalpy of transfer from the permeant phase to the membrane phase, and the phenomenological coefficients defined for a thin slab of membrane. The empirical phenomenological coefficients, permeability and thermo-osmotic permeability of the discontinuous system are obtained as integral formulae of the abovementioned properties. A method has been proposed to evaluate the transport phenomenological coefficients, true for a thin slab of membrane, from the experimental data of the enthalpies of dissolution of permeant in the membrane, of the permeability and of the thermo-osmotic permeability. The experimental data reported in the literature and those obtained from our previous work fit well with this theoretical model, but it is recognized that new experimental results are needed to apply this model completely.

Thermo-osmosis, the flow of matter through a membrane due to a difference in temperature, has been studied in a wide variety of experimental situations. The common feature shown by all the results of the experiments is that thermo-osmotic permeability is a function of temperature, changing with the average temperature and difference in temperature of the external solutions. From a theoretical point of view thermo-osmosis has been given considerable attention. The mechanisms of thermo-osmosis in charged membranes were studied by different authors. In non-charged membranes they were discussed by others, using (completely or in part) the local formulation of thermodynamics of irreversible processes. There are also authors who assume an unconventional point of view in their theoretical analysis of the physical nature of the forces driving non-isothermal fluids transport in porous membranes.

The works more related to the present paper study thermo-osmosis only under the effect of small and constant pressure and temperature gradients, not explaining, therefore, any dependence of thermo-osmotic permeability on temperature. In addition, they do not include in the dissipation function the term due to viscous forces. The proposed model explains the dependence of permeability and thermo-osmotic permeability on temperature reported elsewhere. These data do not allow an entire applicability of the model. Therefore, new experimental results are needed to apply it completely.

The Model

Particularizing eqn (26) of ref. (18) to the case of a system composed of the membrane matrix and a monocomponent permeant fluid (which will be taken as water), on which no external forces will act \( F_i = 0 \), we obtain for the average dissipation function

\[
\langle \Phi \rangle = - \langle J_w^m \rangle \cdot (\text{grad} \mu_w^m)_T - \langle J_q \rangle \cdot \frac{\text{grad} T^m}{T^m}
\]  

\(1\)
where the angular brackets indicate the average values for the cross-section of the membrane, (for example, 

$$\langle \Phi \rangle = \frac{1}{A \delta z} \int \Phi \, d\tau$$

where $\tau$ is the volume of a thin cross-sectional slab of membrane of thickness $\delta z$ at position $z$, and $A$ is the area of cross-section of the membrane), $\langle J^m_w \rangle$ is the molar flux of water relative to the membrane matrix, whose velocity is $v^m = 0$, $\langle J^q \rangle$ is the reduced heat flux, $(\text{grad} \mu^w)_T$ is the gradient of chemical potential of water at constant temperature and $(\text{grad} \ T^m)$ is the gradient of the thermodynamic temperature. The superscript $m$ indicates that the quantity affected by it is within the membrane.

Eqn (1) is true for an isotropic, non-reacting system containing two species $i$ (water and membrane matrix) under steady-state conditions, with inertial terms neglected (terms in $u^2$). Even then, viscous contributions to the fluxes can still occur, but they have become implicit ones, so that dissipation is absorbed by the force required to keep the membrane stationary. Eqn (1) can be applied to a continuous membrane phase, where the distances between adjacent parts of the membrane matrix are of the same order of magnitude as the diameter of a permeating molecule, which gives us reason to suppose that the membrane component is interspersed at a molecular level among the components of the permeating fluid and therefore partakes intimately in the processes occurring.

If we suppose that the membrane has plane-parallel faces and that all the gradients in the membrane are in the $z$ direction, which is perpendicular to the lateral surfaces of the membrane, then eqn (1) would be

$$\langle \Phi \rangle = -\langle J^m_w \rangle \left( \frac{d\mu^m_w}{dz} \right)_T - \langle J^q \rangle \left( \frac{dT^m}{dz} \right)$$

where $\langle J^m_w \rangle$ and $\langle J^q \rangle$ are the components in the $z$ axis of the corresponding fluxes $\langle J^m_w \rangle$ and $\langle J^q \rangle$.

The phenomenological equations corresponding to eqn (2) are

$$\langle J^m_w \rangle = -l_w \left( \frac{d\mu^m_w}{dz} \right)_T - l_{wT} \left( \frac{dT^m}{dz} \right)$$

$$\langle J^q \rangle = -l_{T^m} \left( \frac{d\mu^m_w}{dz} \right)_T - l_T \left( \frac{dT^m}{dz} \right)$$

where $l_w$, $l_{T^m}$, $l_{wT}$ and $l_T$ are the phenomenological transport coefficients for a thin slab of the membrane parallel to the faces of the membrane and perpendicular to the direction of the average flow (the $z$ direction). The coefficient $l_w$ is a pseudo-coefficient of diffusion in which the viscosity coefficient is concealed.

Integrating eqn (3), taking into account that the flow $\langle J^m_w \rangle$ is constant in the steady state, between the surfaces of the membrane (i.e. between $z = 0$ and $z = \Delta z$) we obtain

$$\langle J^m_w \rangle = \frac{1}{\Delta z} \left[ -\int_0^{\Delta z} l_w \left( \frac{d\mu^m_w}{dz} \right)_T \, dz - \int_0^{\Delta z} l_{wT} \left( \frac{dT^m}{dz} \right) \, dz \right].$$

In order to carry out the integrations which appear in the above equation it is necessary to know the dependence of the phenomenological coefficients on the intensive state variables (which characterize the intensive thermodynamic state of each slab of the membrane) and the profile of these in the membrane, that is the dependence of the intensive variables on $z$, as well as the gradients and their dependence on $z$.

The solution to this general problem is almost impossible, therefore in practice it recurs to postulate a model of behaviour of the membrane. The model which we are
going to use to integrate eqn (5) is based on the ideas of those already established, but allows for the strong dependence of thermo-osmotic permeability on temperature. Imagine our membrane as a continuous system with macroscopic overall dimensions and well defined properties. The system is formed by two components: the structural substance of macromolecules of the membrane, which form the matrix, and which we consider as the solvent, and the permeant substance, which we take as the solute. We take the pressure, \( P^m \), the temperature, \( T^m \), and the composition of the binary system, which is characterized by the mole fraction, \( x \), of the permeant, varying continuously from point to point and in the perpendicular direction of the lateral surfaces of the membrane.

Under steady-state conditions it is possible to imagine the binary system divided into slabs, characterized by \( P^m(z) \), \( T^m(z) \) and \( x(z) \), each of which is found in a separate saturation equilibrium with the pure permeant liquid with the same values of pressure and temperature \( (P, T) \). This implies that temperature, pressure and chemical potential of the permeant are the same inside and outside of the slab. Considering all this and using the expression for the differential of the chemical potential, we obtain

\[
\left( \frac{d\mu^m}{dz} \right)_T = \frac{\overline{\Delta H^s}}{T} \left( \frac{dT}{dz} \right) + \overline{\nu_w} \left( \frac{dP}{dz} \right)
\]

where \( \overline{\nu_w} \) is the partial molar volume of the pure permeant (water) and \( \overline{\Delta H^s} \) is the molar enthalpy change for the dissolution of permeant in the slab, which is by definition

\[
\overline{\Delta H^s} \overset{\text{def}}{=} \overline{H^w} - \overline{H_w}
\]

and \( \overline{H_w} \) and \( \overline{H^w} \) are the partial molar enthalpies of the water and of the water in the binary system, respectively.

Substituting eqn (6) into eqn (5) gives

\[
\langle J^m \rangle = -\frac{1}{\delta} \left[ \int_0^{\Delta z} l_w \overline{\nu_w} \left( \frac{dP}{dz} \right) dz + \int_0^{\Delta z} \left( \frac{l_w \overline{\Delta H^s}}{T} + \frac{l_w T}{T} \right) \left( \frac{dT}{dz} \right) dz \right].
\]

In this equation \( \Delta z = \delta \), the thickness of the membrane. In order to solve the integrals which appear in eqn (8) it is necessary to know the functions \( l_w[T(z), P(z), \overline{\nu_w}[T(z), P(z)], \overline{\Delta H^s}[T(z), P(z)], l_w T[T(z), P(z)] \) as well as the gradients \( (dP/dz) \) and \( (dT/dz) \). The problem is simplified if we take into account the fact that in condensed phases the thermodynamic properties are practically independent of the pressure, except for very high values. In the study of thermo-osmosis the differences in pressure usually reach only a few centimetres of mercury, in a way that the above statement is true in the present case. Consequently, eqn (8) can be expressed as

\[
\langle J^m \rangle = -\frac{1}{\delta} \left[ \int_0^{\Delta z} l_w[T(z)] \overline{\nu_w}[T(z)] \left( \frac{dP}{dz} \right) dz + \int_0^{\Delta z} \left( \frac{l_w[T(z)] \overline{\Delta H^s}[T(z)]}{T(z)} + \frac{l_w T[T(z)]}{T(z)} \right) \left( \frac{dT}{dz} \right) dz \right].
\]

Two particular cases can be presented.

(1) If the temperature is kept constant eqn (9) becomes

\[
\langle J^m_w \rangle = -\frac{l_w(T)}{\delta} \frac{\overline{\nu_w}(T)}{\Delta P} \Delta P
\]

where we have put \( \Delta P = P(\Delta z) - P(0) \).
(2) With a constant pressure we obtain
\[
\langle J_w^* \rangle = -\frac{1}{\delta} \int_{T(0)}^{T(\Delta t)} \left( \frac{l_w(T) \Delta H^*(T)}{T} + \frac{l_w(T)}{T} \right) dT.
\]

Comparing eqn (9), or its particular cases which are given by eqn (10) and (11), with the global empirical description given by Haase\textsuperscript{21} we obtain for the permeability
\[
A(T) = l_w(T) \dot{V}_w(T)
\]
and for the thermo-osmotic permeability
\[
B = \frac{1}{\Delta T} \int_{T_1}^{T_2} \left( \frac{l_w(T) \Delta H^*(T)}{T} + \frac{l_w(T)}{T} \right) dT
\]
where \(T_1\) and \(T_2\) are the temperatures at the surfaces of the membrane.

Eqn (12) and (13) relate the phenomenological coefficients, which are determined experimentally, with the average coefficients \(l_w\) and \(l_wT\). Eqn (12) allows us to determine the function \(l_w(T)\) from measurements of permeation at different temperatures. From eqn (13) it follows that if we know \(l_w(T)\) from measurements of permeation and \(\Delta H^*(T)\) after calorimetric measurements, we can calculate \(l_wT(T)\) from thermo-osmotic measurements.

**Application of the Theoretical Analysis**

As stated above, eqn (12) evaluates the \(l_w(T)\) coefficient from the permeability values at different temperatures. The values obtained from \(l_w(T)\) can be fitted to a development in the form of power series:
\[
l_w(T) = a_0 + a_1 T + a_2 T^2 + \ldots
\]
where \(a_0, a_1, a_2, \ldots\) are constants. The values of \(\Delta H^*\) for different temperatures can be fitted to another power series
\[
\Delta H^*(T) = b_0 + b_1 T + b_2 T^2 + \ldots
\]
where \(b_0, b_1, b_2, \ldots\) are constants.

It is also possible to suppose that the \(l_w(T)\) coefficient can allow a development in the form of power series of the absolute temperature in such a way that
\[
l_wT(T) = c_0 + c_1 T + c_2 T^2 + \ldots
\]
where \(c_0, c_1, c_2, \ldots\) are constants. All the constants \(a_n, b_n,\) and \(c_i\) are characteristics of the permeant-membrane system.

Substituting eqn (14)–(16) in eqn (13) and after carrying out the integration, we obtain
\[
B = B_0 \ln \left( \frac{T_2}{T_1} \right) + B_1 + B_2(T_2 + T_1) + B_3(T_2^2 + T_2 T_1 + T_1^2) + \ldots
\]
where
\[
B_0 = a_0 b_0 + c_0
B_1 = a_0 b_1 + a_1 b_0 + c_1
B_2 = \left( \frac{1}{2} \right) (a_0 b_2 + a_1 b_1 + a_2 b_0 + c_2)
B_3 = \left( \frac{1}{3} \right) (a_0 b_3 + a_1 b_2 + a_2 b_1 + a_3 b_0 + c_3)
\]

Eqn (17) is a general expression for the thermo-osmotic permeability as a function of the surface temperature of the membrane. The experimental data, in the systems where the hypothesis of our model are true, should be well described by such an equation.
Table 1. Optimal fit to eqn (17) for the thermo-osmotic permeability divided by membrane thickness, \( B/\delta \), for the different membranes

<table>
<thead>
<tr>
<th>membrane</th>
<th>( [B(T_1, T_2)/\delta] ) mol m(^{-2}) s(^{-1}) K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>cellophane 600(^3)</td>
<td>(-2.42 \times 10^{-1} \ln(T_2/T_1)/(T_2 - T_1) + 1.7 \times 10^{-3} - 1.47 \times 10^{-4}(T_2 + T_1))</td>
</tr>
<tr>
<td>cellophane 600(^4)</td>
<td>(4.8 \ln(T_2/T_1)/(T_2 - T_1) - 2.96 \times 10^{-2} + 2.3 \times 10^{-5}(T_2 + T_1))</td>
</tr>
<tr>
<td>cellophane 600P(^7)</td>
<td>(3.4 \times 10^{-4} \ln(T_2/T_1)/(T_2 - T_1) - 1.02 \times 10^{-4})</td>
</tr>
<tr>
<td>cellophane 500P(^7)</td>
<td>(2.1 \ln(T_2/T_1)/(T_2 - T_1) - 1.34 \times 10^{-2} + 1.06 \times 10^{-5}(T_2 + T_1))</td>
</tr>
<tr>
<td>C.A. mem. no. 1(^{6a})</td>
<td>(-4.9 \times 10^{-2} \ln(T_2/T_1)/(T_2 - T_1) + 3.0 \times 10^{-4} - 2.2 \times 10^{-7}(T_2 + T_1))</td>
</tr>
<tr>
<td>C.A. mem. no. 2(^{6a})</td>
<td>(-7.7 \times 10^{-3} \ln(T_2/T_1)/(T_2 - T_1) + 3.16 \times 10^{-5})</td>
</tr>
</tbody>
</table>

\(^a\) The values reported for this membrane have been obtained from steady state.

The experimental results given by Haase et al.,\(^3\) Rastogi et al.,\(^4\) and Fernández-Pineda and Vázquez-González,\(^7\) who used different cellophane membranes and water as the permeant, like those of Mengual et al.,\(^6\) who used cellulose acetate membranes with 2.7 degree of acetylation and water as permeant, have been analysed using eqn (17). The procedure followed consisted of fitting the experimental results to an equation with the form of eqn (17) by multiple regression analysis. To select the optimum fits, the same procedure as indicated in ref. (7) was followed. The results of the optimal fits are shown in table 1, where the functions \( B(T_1, T_2)/\delta \) appear, in mol m\(^{-2}\) s\(^{-1}\) K\(^{-1}\), to permit a comparative analysis.

Inspection of table 1 suggests that in all the fits, terms with coefficients \( B_0 \) and \( B_1 \) appear to be statistically different from zero; this indicates that the sum \( (l_w \Delta H^s + l_w T) \) depends, at least linearly, on the thermodynamic temperature. In four of the six fits, terms with coefficients \( B_0 \), \( B_1 \), and \( B_2 \) appear to be statistically different from zero; this indicates that the sum \( (l_w \Delta H^s + l_w T) \) depends quadratically on the thermodynamic temperature for the stated experimental systems. This quadratic dependence on temperature is notable in the fit of the experimental results obtained by Fernández-Pineda and Vázquez-González\(^7\) for the membrane 500P, where the average temperature and the difference in temperature between the faces of the membrane vary within small intervals (between 308 and 317 K and between 2 and 6 K, respectively).

In order to complete the application of the theoretical analysis to the experimental results, the dependence of the coefficient \( l_w \) and the heat of dissolution \( \Delta H^s \) on temperature must be determined. However, values for \( \Delta H^s \) have not been reported for the experimental systems described above. Experimental measurements of the heat of dissolution and its dependence on temperature are of great importance for the application of the present model. Values of \( \Delta H^s \) have been estimated for the 600P and 500P membranes in ref. (7) from microcalorimetric measurements\(^8\) and determinations of membrane water content at saturation. Only two temperatures were studied (33 and 45 °C) and the results obtained were fitted to a linear dependence on \( T \).

\[
\begin{align*}
\Delta H^s/\text{J mol}^{-1} &= 374.6 - 1.973T \\
\Delta H^s/\text{J mol}^{-1} &= 97.7 - 1.104T
\end{align*}
\]

for the 600P and 500P membranes, respectively.

Eqn (12), the values of permeability \( A \),\(^7\) the values of the specific volume of water,\(^22\) and the values of the molecular mass of the water have been used to determine the values of \( l_w(T) \). These values have been fitted to a power series of absolute temperature. The best fits obtained, within the temperature range studied, are

\[
\begin{align*}
l_w/\text{mol}^2 \text{ s kg}^{-1} \text{ m}^{-3} &= 1.254 \times 10^{-7} - 4.13 \times 10^{-11}T \\
l_w/\text{mol}^2 \text{ s kg}^{-1} \text{ m}^{-3} &= 2.208 \times 10^{-7} - 7.71 \times 10^{-11}T
\end{align*}
\]

for the 600P and 500P membranes, respectively.
The dependence on temperature of the transport coefficient, $I_{wT}$, is calculated by substituting eqn (19) and (20) into eqn (18) and by solving the system of equations found for $c_i$. Note that the values of $B_0, B_1, \ldots$ etc. used here were obtained from the direct fit of the experimental data to eqn (17), and not those which would be obtained from the values appearing in table 1 multiplied by the thickness of the membranes, since a small discrepancy exists between these, this being caused by the arithmetic precision of the microcomputer we have used. The dependences on temperature found are:

$$I_{wT}(600P)/\text{mol m}^{-1}\text{s}^{-1} = -4.5 \times 10^{-5} + 2.56 \times 10^{-7}T - 8.15 \times 10^{-11}T^2$$

and

$$I_{wT}(500P)/\text{mol m}^{-1}\text{s}^{-1} = 8.6 \times 10^{-9} - 4.30 \times 10^{-7}T + 9.91 \times 10^{-10}T^2.$$  

(21)

The constant coefficients $a_0, b_0$ and $c_0$ which appear in eqn (19), (20) and (21) do not allow a simple interpretation. For this reason the dependence on temperature has been referred to its lowest value in the range in which the experimental data are available. The selected temperature is $T_c = 306.15 \text{ K}$. By using some elemental algebraic manipulations eqn (19)-(21) are transformed for the 600P membrane into

$$I_w/\text{mol}^2\text{s}^{-1} - 1.127 \times 10^{-7} - 4.13 \times 10^{-11}(T - T_0)$$

$$\Delta H_w/\text{J mol}^{-1} = -229.5 - 1.973(T - T_0)$$

and for the 500P membrane into

$$I_w/\text{mol}^2\text{s}^{-1} = 1.971 \times 10^{-7} - 7.71 \times 10^{-11}(T - T_0)$$

$$\Delta H_w/\text{J mol}^{-1} = -240.3 - 1.104(T - T_0)$$

(22)

(23)

The constant terms which appear in eqn (22) and (23) are now the values of $I_w, \Delta H_w$ and $I_{wT}$ for the temperature of 306.15 K (33 °C). For the 600P membrane the term $c_0^2(T - T_0)^2$ in the coefficient $I_{wT}$ can be neglected when looking at the other two within the temperature range in which there is experimental data. For the 500P membrane this term can also be neglected, in the abovementioned conditions, but the errors are greater than those for the 600P membrane (in this one the difference ranges between $1 \times 10^{-9}$ and $1 \times 10^{-8}$, while in the other it varies between $-1 \times 10^{-9}$ and $2 \times 10^{-7}$). In both cases outside of the range of temperature indicated above, the discrepancies can be noticed.

The behaviour of the numerator of the integrand in eqn (13) for the 600P membrane, from the procedure followed in obtaining eqn (22), is reduced to a linear dependence on temperature. The extrapolation, with all the risks it entails, permits us to expect its annulment at ca. 60 °C, this would be the temperature at which the direction of the thermo-osmosic flow would be inverted, i.e. instead of going from hot to cold it would go from cold to hot. With a 600P membrane different from the previous one the thermo-osmosic coefficient has been determined at a stirring rate of 260 rev min$^{-1}$ and at 65 and 70 °C bulk temperatures. The flow observed was from cold to the hot side, obtaining a value for the corrected thermo-osmotic permeability $B_{corr} = 2.4 \times 10^{-10}$ mol m$^{-1}$ s$^{-1}$ K$^{-1}$. Taking this value and the $B_{corr}$ values obtained at the highest average temperatures from ref. (7) and following the procedure mentioned there, the differential thermo-osmotic coefficient $b(t)$ is calculated. This coefficient is annulled at ca. 57.4 °C. In contrast to the above, the numerator of the integrand in eqn (13) for the 500P membrane is a quadratic function of the temperature; the extrapolation does not reveal a real value of the intercept with the axis of temperatures; however, this function has a minimum value at a temperature of ca. 43.5 °C. This temperature is approximately equal to the mean temperature at which the experimental data present the lowest value.

In summary, a model has been developed to describe the dependence of the thermo-osmotic permeability on temperature. The model is applied to the transport under
steady-state conditions of one solute, driven by a temperature gradient, assuming that the membrane-permeant system can be described as a non-electrolyte solution. The experimental data reported in the references were analysed and fitted with this model, but it is recognized that new studies are needed to apply it completely: to measure equilibrium parameters (like those which allow us to know the states and the enthalpies of dissolution of the permeant into the membrane) and likewise to measure transport parameters (like the permeability and the thermo-osmotic permeability in a broad temperature range, with the aim of determining with accuracy their dependencies on temperature).

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References

23. M. I. Paz-Andrade, personal communication.