Theory of Ultrafiltration

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A theoretical study of ultrafiltration based on thermodynamics of irreversible processes is presented. A formula giving the efficiency of the ultrafiltration process in dilute solutions is derived. Relations between ultrafiltration and osmotic experiments are considered and a procedure for the experimental verification of Onsager reciprocal relations is indicated.

Recently there has been increased interest in the use of the process of ultrafiltration through membranes as a means of separating molecularly dispersed solutes. Especially its application to desalination of water and its use as a means of concentrating dilute solutions have been considered. Much of the progress in the experimental field has been due to novel techniques of membrane preparation, which has made membranes of high selectivity available, and has made the process of practical interest.

In the present article some theoretical aspects of the process are considered. The treatment is based on thermodynamics of irreversible processes and is closely related to earlier work on solute diffusion through osmotic membranes.

Symbols

\[ j_i \] = mass flow density of component \( i \)
\[ \mu_i \] = chemical potential of component \( i \)
\[ \Omega_{ij} \] = phenomenological coefficient
\[ L_{ij} \] = concentration independent phenomenological coefficient
\[ c_i \] = weight fraction of component \( i \)
\[ c \] = concentration of solute in solution (g/l)
\[ v_i \] = partial specific volume of component \( i \)
\[ M_i \] = molecular weight of component \( i \)
\[ p \] = hydrostatic pressure
\[ d \] = thickness of membrane
\[ \gamma \] = solubility factor
\[ \sigma \] = reflection coefficient
\[ \mathcal{P} \] = filtration pressure

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In the present treatment we will consider a two-component solution phase, where component 1 is the solvent and component 2 the solute. In the membrane phase, in addition, the membrane lattice is present as component 3.

The basic flow-equations then take the form

\[
\begin{align*}
    j_1 &= -\Omega_{11} \frac{d\mu_1}{dx} - \Omega_{12} \frac{d\mu_2}{dx} \\
    j_2 &= -\Omega_{21} \frac{d\mu_1}{dx} - \Omega_{22} \frac{d\mu_2}{dx}
\end{align*}
\]

(1)

where the reference frame is fixed in the membrane lattice.\(^{11}\)

For the phenomenological coefficients \(\Omega_{ij}\) the Onsager reciprocal relations (2) exist:

\[
\Omega_{12} = \Omega_{21}
\]

(2)

However, in order to provide a basis for an experimental verification of the reciprocal relations, the use of eqn. (2) will be refrained from in the present treatment.

In order to make the integration of eqns. (1) possible the concentration dependence of the phenomenological coefficients has to be taken explicitly into account. This is done by a series expansion of the coefficients. Observing that the flow of any component must vanish when its concentration is zero, the expansions of the coefficients do not contain constant terms and hence we may write

\[
\begin{align*}
    \Omega_{11} &= L_{11} c_1 + \text{higher terms} \\
    \Omega_{12} &= L_{12} c_1 c_2 + \text{higher terms} \\
    \Omega_{21} &= L_{21} c_1 c_2 + \text{higher terms} \\
    \Omega_{22} &= L_{22} c_2 + \text{higher terms}
\end{align*}
\]

(3)

Further, the chemical potential gradient is split into a pressure term and a purely chemical term:

\[
\frac{d\mu_i}{dx} = v_i \frac{dp}{dx} + \frac{d\mu_{ic}}{dx}; \quad i = 1, 2
\]

(4)

where the pressure-independent chemical potentials are connected via the Gibbs-Duhem equation:

\[
c_1 \frac{d\mu_{1c}}{dx} + c_2 \frac{d\mu_{2c}}{dx} + c_3 \frac{d\mu_{3c}}{dx} = 0
\]

(5)

For steady state conditions, with \(j_1\) and \(j_2\) constant across the membrane, solutions of (1) may be obtained by introducing (3) and (4) into (1) and integrating across the membrane. For dilute solutions we may neglect higher than first order terms in \(c_2\) and we then get

\[
\begin{align*}
    j_{1d} &= -L_{11}(1-c_3-c_2)(\Delta\mu_{1c}+v_1\Delta p) - L_{12}(1-c_3) \left(\frac{RT}{M_2} \Delta c_2 + v_2 c_2 \Delta p\right) \\
    j_{2d} &= -L_{21}(1-c_3)c_2(\Delta\mu_{1c}+v_1\Delta p) - L_{22} \left(\frac{RT}{M_2} \Delta c_2 + v_2 c_2 \Delta p\right)
\end{align*}
\]

(6)

We have here used the relations

\[ \int_0^d c_1 \left( \frac{d\mu_x}{dx} + v_1 \frac{dp}{dx} \right) dx = (1 - \bar{c}_3 - \bar{c}_2)(\Delta\mu_{1c} + v_1 \Delta p) \]  

(7)

\[ \int_0^d c_1 c_2 \left( \frac{d\mu_x}{dx} + v_1 \frac{dp}{dx} \right) dx = (1 - \bar{c}_3)\bar{c}_2(\Delta\mu_{1c} + v_1 \Delta p) \]  

(8)

\[ \int_0^d c_1 \bar{c}_2 \left( \frac{d\mu_x}{dx} + v_2 \frac{dp}{dx} \right) dx = (1 - \bar{c}_3) \left( \frac{RT}{M_2} \Delta c_2 + v_2 \bar{c}_2 \Delta p \right) \]  

(9)

\[ \int_0^d c_2 \left( \frac{d\mu_x}{dx} + v_2 \frac{dp}{dx} \right) dx = \frac{RT}{M_2} \Delta c_2 + v_2 \bar{c}_2 \Delta p \]  

(10)

In (9) and (10) we have used the following relation (expressed in weight units)

\[ \mu_x = \mu_{x0} + \frac{RT}{M_2} \ln f_2 \bar{c}_2 \]  

(11)

with

\[ f_2 = 1 + \alpha_c c_2 + \cdots \]  

(12)

In these equations the barred quantities are concentration averages across the membrane. Their exact evaluation requires detailed knowledge of concentration and pressure gradients in the membrane, but to a first order approximation they are equal to the mean concentration of the respective component in the membrane.

Further, we observe that $\Delta\mu_{1c}$ and $\Delta c_2$ refer to differences in $\mu_{1c}$ and $c_2$ between the membrane boundaries, inside the membrane. They are easily related to the differences in the corresponding quantities between the external solutions on the two sides of the membrane. We find that in the case of $\Delta\mu_{1c}$ the two quantities are equal if equilibrium conditions exist at the membrane interfaces. Then

\[ \Delta\mu_{1c} = - \frac{RT}{M_2} v_1 \Delta c \]  

(13)

In order to relate $\Delta c_2$ to the corresponding difference in concentration outside the membrane, we introduce the solubility factor $\gamma$ for dissolution of the solute in the membrane phase. For equilibrium conditions we define

\[ \gamma(1 - c_3) = \frac{c_2 \text{ (membrane)}}{c_2 \text{ (solution)}} \]  

(14)

We then get

\[ \Delta c_2 = \gamma(1 - \bar{c}_3)(c_2'' - c_2') = \gamma(1 - \bar{c}_3) v_1 \Delta c \]  

(15)

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where \( c'_2 \) and \( c''_2 \) refer to the weight fractions of solute in the external solutions on the two sides of the membrane. We have also

\[
\bar{c}_2 = \frac{1}{2} \gamma (1 - \bar{c}_3) (c'_2 + c''_2) \approx \gamma (1 - \bar{c}_3) v_1 \bar{c}
\]

(16)

where

\[
\bar{c} = c + \frac{1}{2} \Delta c
\]

(17)

is the mean external concentration of solute.

With (13), (15), and (16) eqns. (6) take the form

\[
j_1 d = -L_{11} v_1 (1 - \bar{c}_3) \left( \frac{\Delta p}{M_2} \Delta c \right) - L_{12} \gamma v_1 (1 - \bar{c}_3) \left( \frac{RT}{M_2} \Delta c + v_2 \bar{c} \Delta p \right)
\]

\[
j_2 d = -L_{21} \gamma v_1 (1 - \bar{c}_3) \left( \frac{\Delta p}{M_2} \Delta c \right) - L_{22} \gamma v_1 (1 - \bar{c}_3) \left( \frac{RT}{M_2} \Delta c + v_2 \bar{c} \Delta p \right)
\]

(18)

We will now specify the experimental conditions for ultrafiltration. We assume that the permeating solution on the low-pressure side immediately leaves the membrane surface. In practice this means that the solution compartment on the low-pressure side is very small (e.g. a membrane directly placed on a porous supporting medium). We then have the relation

\[
\frac{j_1}{j_2} = \frac{c''_2}{c''_2} = \frac{1}{c''_2} - 1 = \frac{1}{v_1 (c + \Delta c)} - 1
\]

(19)

Here the total mass flow \( j_1 + j_2 \) and the concentration \( c + \Delta c \) are easily measurable quantities. Hence, with the help of (19) the individual mass flows may also be readily determined.

We may now eliminate \( j_1 \) and \( j_2 \) between (18) and (19) and thus get an equation for the determination of \( \Delta c \). For dilute solutions and pressure differences considerably higher than the osmotic pressure \( |RT/M_2| \Delta c| < |\Delta p| \)  this equation takes a simple form:

\[
\frac{\Delta c}{c} = -2 \frac{L_{21} \gamma (1 - \bar{c}_3) - L_{22} \gamma (v_2/v_1)}{2L_{11} - L_{21} \gamma (1 - \bar{c}_3) - L_{22} \gamma (v_2/v_1) - 2L_{22} (RT/M_2)(\gamma/v_1) \Delta p}
\]

(20)

In analogy with the treatment in Ref. 12 we use the following expression for Staverman's reflexion coefficient \( \sigma \):

\[
\sigma = 1 - \frac{L_{21}}{L_{11}} \gamma (1 - \bar{c}_3) - \frac{L_{22}}{L_{11}} \gamma \frac{v_2}{v_1}
\]

(21)

Introducing further the filtration pressure \( P \), where

\[
P = -\Delta p
\]

(22)

we get

\[
\frac{\Delta c}{c} = -2 \sigma \left[ 1 + \sigma + 2 \frac{L_{22}}{L_{11}} \frac{RT}{M_2} \frac{\gamma}{v_1 P} \right]
\]

(23)

In the derivation of eqn. (23) the expression (17) for the mean concentration was used. If possible nonlinearity of the concentration gradient in the
membrane is taken into account, the concentration average may be written as follows
\[ c = c + (\frac{1}{2} + \varepsilon) Ac \]  
Instead of (23) we then get
\[ \frac{Ac}{c} = -2\sigma \left[ 1 + \sigma - 2\varepsilon(1-\sigma) + 2 \frac{L_{22}}{L_{11}} \frac{RT}{M_2} \frac{\gamma}{v_1 P} \right] \]

In these equations \( \varepsilon \) is a small quantity which may be evaluated if the concentration gradient is known.

Eqn. (23) gives a measure of the efficiency of ultrafiltration experiments. We find that the efficiency increases with increasing filtration pressure. This is due to the fact that the ordinary diffusion, which tends to smooth out the concentration difference across the membrane, is pressure independent and hence its effect becomes less pronounced at high pressures. At low pressures the effect of ordinary diffusion becomes dominant, however, and the efficiency declines accordingly.

Eqn. (23) also provides a means of verifying Onsager reciprocal relations. We have found that ultrafiltration and osmosis represent essentially different situations in adapting eqns. (18) to experimental conditions. In the case of osmotic experiments the pressure difference is small and hence in the dilute solution approximation of (18) only the term associated with \( L_{12} \) gives a significant contribution to the flow equations. The expression for \( \sigma \), derived in Ref. 12, therefore contains the coefficient \( L_{12} \). On the other hand, in the case of ultrafiltration with high filtration pressures, we see from (20) that only the term containing \( L_{21} \) is significant. Thus, comparing the values of \( \sigma \) obtained from osmotic experiments with those obtained from ultrafiltration (eqn. (23)) we may get an experimental check of the reciprocal relations.

Alternatively, eqns. (18) may be used directly. From ultrafiltration measurements with solutions of constant concentration but varying filtration pressure a system of equations is obtained which may be solved for the phenomenological coefficients. Although this method is less sensitive than the preceding one it has the advantage of using the same experimental arrangement in all experiments.

REFERENCES


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