PAPER

Estimating timescale of unstirred layer formation in osmotically driven flow

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Abstract

The osmotically driven flow across a semipermeable membrane under a constant static pressure difference is revisited with reference to previous reports on reverse osmosis. The osmosis due to the local solute concentration difference across the membrane induces solvent seeping flow, which advects solutes in a layer in contact with the membrane and reduces the osmosis itself as a result of nonlinear feedback. A few mathematical techniques for obtaining approximate solutions of the seeping flow and the layer thickness, such as that for inverse problems used in the field of heat transfer, are presented with an emphasis on nonlinear boundary conditions and the time-dependent solvent flow rate. We determined that the layer on the membrane forms rapidly and spontaneously through osmosis at a timescale of \( \sim O(\sqrt{t}) \) and that the layer thickness increases with no upper limit in an infinite time interval. Based on the obtained solution, we also discuss the thermodynamic output work in an irreversible process, which is extracted from the seeping flow as an osmotic engine.

1. Introduction

In membrane transport, osmosis is a physical mechanism underlying a variety of engineering or biological phenomena [1]. In the desalination process [2, 3], which is currently an essential requisite for supplying water to a rising global population, fresh water is produced by filtering seawater through a polymeric membrane using considerable external hydrostatic pressure applied against 'reverse' osmosis. During this process, the membrane experiences hydraulic viscous resistance proportional to the flow velocity and osmotic pressure depending on the solute concentration on the membrane. As water and salt are separated, a highly concentrated solution accumulates in a thin boundary layer close to the membrane on the high-pressure side. However, even when the flow is at rest, osmotic pressure, which is proportional to the local concentration difference, largely exceeds that expected from the bulk concentration of the filtered solution. This induces unfavourable virtual resistance to water filtration and eventually leads to membrane fouling, the mitigation of which is of considerable importance to recent engineering applications.

'Forward' osmosis implies spontaneous flow through a membrane that is mainly driven by the concentration difference across the membrane subject to a small external hydrostatic pressure difference, which leads to concentration relaxation attributed to the principle of increased entropy. Forward osmosis is practically utilised in all living creatures; for example, cells and organs, such as the epithelia of blood capillaries or intestinal membranes in animals, or the translocation of nutrition in phloem networks distributed in the entire bodies of plants [4], where any mechanical pumping system (such as a heart in animals) is absent. Forward osmosis has attracted significant attention in recent years as a new type of power generation or energy recovery system for future engineering innovation [5, 6].

Osmotically driven flow.— Here, we focus on osmotically driven flow, which is an ideal configuration of forward osmosis, to measure how quickly osmosis spontaneously drives the net fluid movement under no
external pressure difference across a membrane. Suppose that, initially, a pure solvent is partitioned from a solution of a nonelectrolyte with bulk concentration $c_s$ by a semipermeable membrane; for example, at the centre of a U-tube, which is frequently used to demonstrate osmotically driven flow for science education. From the microscopic viewpoint, the steric barrier effect selectively allows only the passage of solvent molecules but prevents solute molecules from leaking out through membrane pores.

The solvent spontaneously seeps across the membrane from the pure solvent side (trans side) to the solution side (cis side) owing to osmotic pressure, which virtually originates because of the Brownian motion of molecules from the microscopic viewpoint $[7–9]$. This transmembrane volume flux of the solvent from the trans side to the cis side is sustained until equilibrium is achieved, where the static hydraulic pressure difference across the membrane balances osmotic pressure. According to classical thermodynamics, the osmotic pressure, $P_o$, of an ideal solution is deduced from the balance of the chemical potentials across the membrane, and it is proportional to the product of temperature and the difference between the solute concentrations on the cis side and trans side. This is known as van’t Hoff’s law. However, note that in reality, osmotic pressure, which is the magnitude of macroscopic opposite pressure required to prevent solvent seepage to the cis side, is not stress transmitted through a bulk fluid in the mechanical sense. Thermodynamics is informative regarding the relaxation degree and the direction of the equilibrium in terms of free energy, but not with regard to the time scale and solvent flow velocity in a primary transient process. Seepage, as it pertains to this problem, is a nonequilibrium and irreversible process. As such, it is challenging to describe it with modern physics. Instead, we must use time-dependent continuum mechanics owing to the progress of the boundary concentration layer close to the membrane, as explained below.

As time elapses without increase in opposing hydraulic pressure, the resultant transmembrane volume flux of the solvent advects the solute away from the vicinity of the semipermeable membrane. Thus, a layer of less solute concentration is formed locally on the cis side of the membrane (During desalination with reverse osmosis, a layer of high solute concentration develops on the high-pressure side). In general, this layer, which is spatially localised on the semipermeable membrane, has been named either the concentration boundary layer $[6, 10]$ or the unstirred layer $[11, 12]$. The layer could be the cause of the aforementioned fouling in forward osmosis and reverse osmosis. In forward osmosis, the decrease in the solute concentration difference across the membrane is inevitably followed by the reduction in effective osmotic pressure and transmembrane volume flux, even though the development of the layer may be suppressed either by mechanical mixing through crossflow or by supplying solute molecules in the bulk region on the cis side.

**Objective.**—The unstirred layer has been accounted to be one of the unpredictable or unobservable factors in the desalination process in engineering problems, and thus, its thickness is implicitly assumed to be saturated. The presence of the unstirred layer is apparently plausible, but it remains hypothetical. This is partly because steady equilibrium has been mainly investigated from the practical viewpoint and partly because the unstirred layer is too thin to be observed without any disturbance in experiments and is otherwise disturbed by the external flow caused by bulk crossflow tangential to the membrane. In general, however, the layer thickness varies, owing to the time dependency of the osmosis. Thus, questions arise with regard to the unstirred layer formation. For example, it is unclear how quickly the layer develops and whether its thickness saturates within a finite timescale. The formation timescale and the increasing thickness of the layer have rarely been examined in detail in previous studies, although there are a few exceptions $[13, 14]$. In this study, considering the unsteadiness of flow and concentration next to the membrane, we revisit an analysis of the formation timescale and thickness.
of the layer by solving the time-dependent governing equation of the layer in the aforementioned ideal configuration.

2. Formulation

In what follows, the solute (number) concentration, solute flux, and solvent flow velocity are denoted by \( \tilde{c} \), \( \tilde{j} \), and \( \tilde{u} \), respectively, where the tilde indicates a dimensional variable. We restrict our attention to the case that these quantities are uniform along the membrane from the macroscopic point of view so that they depend only on time \( t \) and the distance, \( x \), from the membrane surface on the cis side. We neglect the effect of gravity in order to simplify the discussion, such that the natural convection due to the inhomogeneity of the density distribution does not occur. The macroscopic mass conservation rule is given by \( \frac{\partial \tilde{c}}{\partial t} + \nabla \cdot \tilde{j} = 0 \). Following Fick’s law, \( \tilde{j} \) is approximately given by the sum of advection and diffusion, \( \tilde{j} = \tilde{c} \tilde{u} - D \nabla \tilde{c} \), where \( D \) is the solute diffusivity in the solvent. The incompressibility of solvent flow may enable us to presume that \( \tilde{u} \) is independent of \( x \). We adopt two boundary conditions, i.e. \( \tilde{j} \times \tilde{n} = 0 \) (the impermeability of the membrane with normal vector \( \tilde{n} \) against solutes at \( \tilde{x} = 0 \)) and \( \tilde{c} = \tilde{c}_{\infty} \) (the uniform bulk concentration at \( \tilde{x} \rightarrow \infty \)). These conditions imply that no solute is supplied, i.e. \( \tilde{x} > 0 \). An initial condition is required for a fully posed initial-value problem.

Negligible inertia.—Van’t Hoff’s law is valid if the solute is extremely dilute; \( \tilde{I} = \tilde{c}_0 k_0 T \), where \( \tilde{I} \) and \( \tilde{c}_0 \) are the osmotic pressure and the concentration in the layer in contact with the membrane on the cis side, \( \tilde{c}(\tilde{x}, \tilde{x} = +0) \), respectively. It is empirically known that the solvent seepage velocity (volumetric flux) is proportional to the sum of osmotic pressure and the static hydraulic pressure difference, \( \tilde{p}_0 \), across the membrane under no electrostatic potential difference across the membrane [15]. This proportionality is known as the classic Starling principle of fluid exchange, \( \tilde{u} \cdot \tilde{n} = \sigma L_p (\tilde{I} - \tilde{p}_0) \). In the present study, the reflection coefficient of the membrane for solutes, \( \sigma \), is unity and the hydraulic conductance (osmotic permeability, filtration coefficient) of the membrane, \( L_p \), is a constant that is independent of the concentration or property of the impermeable solute. The reference of \( \tilde{p}_0 \) is taken at the trans side.

In general, the hydraulic pressure difference \( \tilde{p}_0 \) may be a time-dependent variable, for example, a function of the water level at time \( t \) on the cis side, which is calculated as \( \int_{0}^{t} \tilde{u}(\tau) d\tau \) in the case of a U-tube. Hereafter, \( \tilde{p}_0 \) is maintained steady, and it is zero unless otherwise noted. Starling’s relation may be practically satisfied in most experiments because the relaxation time constant calculated from fluid inertia and hydraulic conductance is too small to be observable compared to the experimental timescale in most cases. We can estimate the relaxation time constant, \( i_{\text{relax}} = ML_p/\tilde{S} \), from the total fluid mass, \( \tilde{M} \), and the membrane area, \( \tilde{S} \). Even though these variables vary considerably depending on membrane thickness and the material and size of solvent molecules, the magnitude of hydraulic conductance has been investigated experimentally for a variety of membranes: e.g. \( \tilde{O}(10^{-1}) \) [m/s/Pa] for frog mesentery, \( \tilde{O}(10^{-12}) \) [m/s/Pa] for the plasmalemma of Nitella translucens or Visking-dialysis tubing, and \( \tilde{O}(10^{-13}) \) [m/s/Pa] for toad skin [10, 16]. Even if we approximately overestimate fluid mass and membrane area, we find that \( \tilde{M} = \tilde{O}(1) \) [kg], \( \tilde{S} = \tilde{O}(1) \) [mm²], and the time constant is of the order of \( \tilde{O}(\mu s) \) at most. Thus, inertia is negligible in a practical sense. Hence, hereafter we presume that the solvent velocity is determined based on Starling’s relation.

Non-dimensional equation.—Assembling all aforementioned equations, non-dimensionalising time and length \( \left( \tilde{t}_0 \rightarrow \tilde{t}, \tilde{x}_0 \rightarrow \tilde{x} \right) \), and rescaling the dependent variable \( \left( \tilde{c}_0 \rightarrow \tilde{c} \right) \), we obtain the following second-order nonlinear partial differential equation:

\[
\frac{\partial \tilde{c}}{\partial \tilde{t}} + (\epsilon_0 - \tilde{p}_0) \frac{\partial \tilde{c}}{\partial \tilde{x}} = \frac{\partial^2 \tilde{c}}{\partial \tilde{x}^2}
\]

with the following two boundary conditions:

\[
\lim_{\tilde{x} \rightarrow \infty} \tilde{c} = 1 \quad \text{and} \quad \left. \frac{\partial \tilde{c}}{\partial \tilde{x}} \right|_{\tilde{x} = +0} = (\epsilon_0 - \tilde{p}_0) \epsilon_0
\]

where \( \epsilon_0 \) is defined by \( \epsilon_0 = \tilde{c}(t, x = +0) \) and \( \tilde{p}_0 = \tilde{p}_0/(\tilde{c}_0 k_0 T) \). The nonlinearity in the advection term and boundary conditions entangles an apparently trivial diffusion equation. The units of time and length are taken as \( \tilde{t}_0 = D/(L_p k_0 T \tilde{c}_{\infty})^2 \) and \( \tilde{x}_0 = D/(L_p k_0 T \tilde{c}_{\infty}) \), respectively, so that the coefficients of the advection and diffusion terms are unity. This nondimensionalisation was previously introduced by Nakano et al [13] or Liu and Williams [14], even though they mainly focused on reverse osmosis. A similar but different nondimensionalisation has been adopted in other studies [12, 17], where nondimensionalisation is determined by representative length or velocity units given by external conditions in individual cases, such as the constant thickness of the unstirred layer or the hydraulic pressure difference across the membrane. It should be noted that the present nondimensionalisation is the only possible method in our problem, where no external stirring factor is involved, that is, neither time nor length scale are given. For a variety of aqueous solutions, \( D \) is of the order of \( \tilde{O}(10^{-5}) \).
[m²/s]. Thus, the units can be estimated as $t_0 = O(10^{-3} \sim 10^{-7})[s]$ and $x_0 = O(10^{-6} \sim 10^{-1})[m]$ in the reasonable ranges of $\tilde{c}_\infty, \tilde{h}_T \sim O(10^3 \sim 10^7)[Pa]$ at room temperature ($\tilde{c}_\infty/N_b = O(10^2 \sim 10^6)[osmol/m^3]$).

3. Analysis

Hereafter, we will present numerical and theoretical approaches to the obtained deterministic equation. Pointing out the inconsistency of steadiness, we present the solution be integrated by numerical computation, then show two approximate solutions. One is polynomial procedure in previous reports on reverse osmosis by Nakano et al. The solution is complicated but provides an excellent overall agreement with the numerical solution, and implies the thickness of the layer principally diverges in an infinite time interval under no external stirring factor.

**pseudo steady solution.**— It is difficult to integrate the obtained deterministic equation with a uniform initial condition, $c(t = 0) = 1$. The steady equilibrium observed in experiments has been mainly examined in literature. This equilibrium is realised independently of the uncontrollable initial conditions in experiments. Based on [11, 18], let us consider the case that the thickness of the unstirred layer, $\theta$, saturates to a constant in equilibrium within a finite time interval. Eliminating the time derivative term, we obtain $\frac{\partial c}{\partial x} - (c_0 - p_0)c = \text{Const.}$ via the integration of equation (1) in $x$. This condition can be satisfied by the following expression regardless of the discontinuity of the first-order spatial differential:

$$c(x) = 1 + \Theta(\theta - x)(c_0 \exp((c_0 - p_0)x) - 1)$$

(3)

where $\Theta$ is the Heaviside step function. The steady concentration profile is the steepest at $x = \theta$, which is implausible in reality as previously pointed out by [12]. Even though the magnitude of $\theta$ is determined by the relation ($c_0 = e^{-\Theta(\theta)}$) deduced from the boundary condition at $x = +0$, the arbitrariness of $c_0$ still remains, which should be determined by introducing an external mixing effect in the bulk region. On the contrary, in the present deterministic system without any external mixing in the bulk region, the magnitude of $c_0$ should be determined self-consistently. As pointed out by Liu and Williams [14], who conducted the experimental observation of reverse osmosis, time dependency is essential for studying the present problem.

**Numerical solution by finite-difference method.**— To verify that the steady state is not realised in a strict sense, we examined the numerical time integration of the original time-dependent equation with the aforementioned initial condition and boundary conditions. Figure 2 shows the time series of the nondimensionalised concentration profile, which is numerically integrated using the fourth-order Runge–Kutta scheme. For reference, $c(t_0, x > 0.999$ is satisfied for $x > 4.62$ at $n = 0$ and $x > 101$ at $n = 8$, which implies that an artificial boundary at $x = 200$ provided in the simulation negligibly affects the result in a relatively early stage, $n \leq 8$. While the concentration in the layer in contact with the membrane, $c_0(t)$, is reduced to half of unity...
abruptly within one time unit \((t / t_0 \leq 1)\), the rate of decrease in \(c_0\) with time reduces considerably over the time unit \((t / t_0 \geq 1)\). The steady state does not appear to be realised in our system, where no length scale exists except \(\tilde{x}_0\). As time elapses further, the front of the unstirred layer proceeds far away from the membrane and the thickness of the layer increases asymptotically with no upper limit. This implies that the unstirred layer is not a boundary layer but can be thicker than experimentally expected. The finiteness of the characteristic thickness of the layer for reverse osmosis was comprehensively discussed in the appendix of \([14]\). The unsteadiness of the present system is related to the fact that the thickness of the unstirred layer is intrinsically undetermined. However, a finite length of the chamber or a finite measuring time interval as an experimental restriction would lead to the realisation of the steady state.

For comparison, the pseudo steady profile that satisfies both conditions, equation (3) and \(c_0 = e^{-\vartheta_0\vartheta}\) in the case of \(c_0 = c(t_0, 0)\), is additionally indicated by a dashed curve in the figure. The discrepancy between the dashed curve and solid curve for \(n = 5\) implies that the solute concentration on the membrane can be exaggerated (overestimated) through simple extrapolation based on the macroscopic concentration measured at a large distance from the membrane under the assumption of steady equilibrium.

**Polynomial profile approximation.**— The boundary condition at \(x = +0\) is not satisfied by the initial condition. The above numerical demonstration suggests that the unstirred layer develops in a relatively short time interval to rapidly regularise the singularity on the membrane. To refine the above mentioned expression of concentration, suppose that the thickness of the layer, \(\vartheta\), and the local concentration on the membrane on the cis side, \(c_0\), are dependent on time \(t\) instead of equation (3). Moreover, we assume that the profile of concentration, \(c(t, x)\), is expressed by the \(N\)-th order polynomials of \(x (N \geq 1)\) in the layer in contact with the membrane, \(0 < x < \vartheta(t)\):

\[
c(t, x) = 1 + \Theta(\vartheta(t) - x) \sum_{n=0}^{N} r_n(t)(\vartheta(t) - x)^n.
\]  

(4)

This expression is a refined version of equation (3). Furthermore, we assume the profile to be continuous and sufficiently smooth at \(x = \vartheta\), if considered in a strict sense, of differentiability class \(C^{N-1}\). Thus, we obtain \(r_n = (c_0(t_{n-1}) - \vartheta(t) - N)^n\) for \(n = N\); otherwise, \(r_n = 0\) \((0 \leq n \leq N - 1)\). Imposing that the governing equation is satisfied at \(x = 0\), we can deduce a first-order ordinary differential equation for \(c_0(t)\):

\[
\frac{dc_0}{dt} = -\frac{N - c_0 - (1 - c_0)p_0}{c_0N} - \frac{c_0}{N}
\]

which can be integrated analytically for any \(N\) and thus leads to

\[
\frac{-N - 1}{N^2} \ln \left(\frac{N - c_0}{(N - 1)c_0}\right) + \frac{1 - c_0}{2c_0} \left(1 - c_0 + 2\frac{c_0}{N}\right) = t,
\]

for \(p_0 = 0\). From the boundary condition at the origin, we can deduce \(\vartheta = \frac{N(t + c_0)}{c_0 - p_0}V_0\). That is, the thickness of the layer, \(\vartheta(t)\), is determined later using \(c_0(t)\).

The present problem is a quadratic second-order differential equation, equation (1). Thus, one would be particularly interested in the case of \(N = 3\) under the continuity conditions at \(x = \vartheta(t)\) for the first and second spatial derivatives and \(c\) for an arbitrary \(t\). The polynomial profile approximation, \(c_0(t_0)\), obtained for a finite \(N\) provides a qualitatively plausible time series of the concentration in the vicinity of the membrane surface but quantitatively distinct from the numerical result, \(c_0(t_0) = 0.50\); for example, \(c_0(t_0) \approx 0.44\) for \(N = 3\).

Moreover, one would be interested in the fact that the \(N\)-th order polynomial form addressed above converges to the simple expression at the limit \(N \rightarrow \infty\),

\[
c_0(t) = \frac{1}{1 + \sqrt{2t}}
\]  

(5)

despite \(\vartheta \rightarrow \infty\). Considering the original definition of the exponential function, \(\lim_{N \rightarrow \infty}(1 + \alpha/N) = e^\alpha\), the limit of the profile of concentration at time \(t\) is obtained as

\[
c(t, x) = 1 - (1 - c_0(t))\exp\left\{-\frac{c_0(t)}{1 - c_0(t)}x\right\}.
\]

In the previous studies, the accurate measurement of solute concentration in the vicinity of the membrane is performed by extrapolating the concentration measured in the outer region. As a measure of the thickness of the layer in literature, \(\Delta x\) is defined by \(\frac{\partial c}{\partial x}|_{x=0} \cdot \Delta x \equiv 1 - c_0\). In the present limit, \(\Delta x\) is also a function of time, i.e. \(\Delta x = \sqrt{2t} + 2t\). Figure 3 shows a comparison of the time series of the nondimensionalised solute concentration, \(c_0(t)\), at the origin given by equation (5) and the numerical solution.

The comparison suggests that a quantitative agreement is limited within the initial stage of layer formation, \(t \ll t_0\). However, we would like to note that equation (5) may be a lower bound of the numerical solution at
least. Considering that nondimensionalised solvent velocity is equal to \( c_0 - p_0 \), the solvent volume seepage in an infinite time interval may be calculated as \( \int_{0}^{\infty} u(t) dt \sim \int_{0}^{\infty} 1/(1 + 21) dt \to \infty \). Additionally, we note that the curve of \( c_0(t_n) \) obtained from a finite \( N \) exists between the numerical simulation and the limit case of \( N \to \infty \); for example, \( c_0(t_0) \approx 0.44 \) for \( N = 3 \) and 0.46 for \( N = 2 \) (not shown in the figure).

Nakano et al presented an analogous approach using a polynomial expression in the context of reverse osmosis in [13, 14], where the authors approximated the concentration profile as a cubic polynomial with time-varying thickness of the boundary layer. Substituting the polynomial expression, equation (4), with \( N = 3 \) into the integration of equation (1) in \( 0 < x < \partial(t) \), they obtained

\[
\frac{\partial}{\partial t} \int_{0}^{\partial(t)} c(t, x) dx + (c_0 - p_0) = 0 ,
\]

to deduce another first-order ordinary differential equation for \( c_0(t) \) instead of imposing that the governing equation is satisfied at \( x = 0 \). Following their procedure, we obtain the ordinary equation for an arbitrary \( N \) as

\[
\frac{d}{dt} \left( \frac{(1 - c_0)^2}{c_0 - p_0} \right) = \frac{N + 1}{N} (c_0 - p_0) ,
\]

and the implicit solution for \( p_0 = 0 \) is

\[
\frac{1}{3} \left( \frac{1 - c_0}{c_0} \right)^3 + \frac{1}{2} \left( \frac{1 - c_0}{c_0} \right)^2 = \frac{N + 1}{2N} t .
\]

For comparison, the above implicit expression of \( c_0 \) on \( t \) for \( N = 3 \) is indicated by the dash-dotted curve in figure 3.

**Approach in inverse problem.**— Finally, we apply a procedure of the inverse problem to the present problem, i.e. Equations (1) and (2). While leaving \( c_0(t) \) unsolved provisionally, we transform the frame of reference, \( x \to \xi \), where \( x = \xi - \xi_0(t) \) and \( \xi_0(t) \) is determined by

\[
\frac{d\xi_0}{dt} = -c_0(t) + p_0 .
\]

Through coordinate transformation, equation (1) is converted into the standard linear diffusion equation in the \( \xi - t \) space (\( -\infty < \xi < \infty \) and \( 0 < t < \infty \)), which is solvable analytically for a well-posed initial condition in terms of an appropriate Green function. However, it should be noted that the initial condition in \( \xi \leq 0 \) is arbitrary for the moment, while \( c(t, \xi)_{\xi=0} = 1 \) is given for \( \xi > 0 \) (see figure 4). Thus, for example, we may assume the initial condition expanded in \( -\infty < \xi < \infty \) is represented as

\[
c(t, \xi)_{\xi=0} = 1 + \Theta(-\xi) \sum_{n=1}^{\infty} a_n \xi^n ,
\]

in terms of unknown coefficients, \( a_n \), so that \( \lim_{\xi \to -0} c(t, \xi) = \lim_{\xi \to +0} c(t, \xi) \) is satisfied at \( t = 0 \). From the initial condition, the exact solution, \( c(t, \xi) \), for \( t > 0 \) is determined as
\[ c(t, \xi) = 1 + \sum_{n=1}^{\infty} a_n I_n(\tau, \eta) = c(\tau, \eta) \]  
(7)

where \((\tau, \eta) = (\sqrt{t}, \frac{\xi}{\sqrt{t}})\), and

\[ I_0(\tau, \eta) = \frac{1}{2} \text{erfc}(\eta) \],
\[ I_1(\tau, \eta) = 2\tau \eta I_0(\tau, \eta) - \frac{\tau}{\sqrt{\pi}} \exp(-\eta^2) \],
\[ I_n(\tau, \eta) = 2\tau \eta I_{n-1}(\tau, \eta) + 2(n-1)\tau^2 I_{n-2}(\tau, \eta) \quad \text{for} \ n \geq 2. \]

Considering that \(c_0(t)\) is a function of \(\sqrt{t}\) in the approximation discussed earlier (see equation (5)), we may suppose that the \(\xi_0(\xi)\) determined by equation (6) is expanded into a series as \(\xi_0(\xi) = \sum_{n=0}^{\infty} b_n t^n\), where 

\[ b_0 = b_1 = 0 \quad \text{and} \quad b_2 = -1 \quad \text{from} \quad \frac{d\xi_0}{dt}(0) = -c(0, 0) + p_0 = -1 + p_0. \]

Suppose 
\[ \eta_0(\tau) = \frac{\xi_0(\tau)}{\sqrt{4t}} = \sum_{n=2}^{\infty} b_n \tau^{n-1} \], then equation (6) is converted to

\[ c(\tau, \eta_0(\tau)) - p_0 + \frac{\eta_0(\tau)}{\tau} + \frac{d\xi_0}{d\tau} = 0 \quad , \]
(8)

which provides a family of restrictions on the unknown coefficients of the series, \(a_n \ (n \geq 1)\) and \(b_n \ (n \geq 3)\). The remaining boundary condition corresponding to equation (2), which should be satisfied at \(\xi = \xi_0(\xi)\), is

\[ c(\tau, \eta_0(\tau)) \{ c(\tau, \eta_0(\tau)) - p_0 \} = \frac{1}{2\tau} \frac{\partial c}{\partial \eta} \bigg|_{\eta_0(\tau)} \]
(9)

in the \((\tau, \eta)\) space. Equations (8) and (9) subject to equation (7) constitute a set of algebraic recurrence relations for the unknown coefficients of the series, \((a_n, b_n)\). The procedure may be classified as a so-called inverse problem, which generally does not ensure the convergence of the solution. The coefficients for the case of \(p_0 = 0\) can be determined as

\[ a_1 = 2, \quad a_2 = \frac{5}{2}, \quad a_3 = \frac{33\pi + 32}{18\pi}, \quad a_4 = \frac{819\pi + 896}{576\pi}, \quad \ldots \]
\[ b_3 = \frac{4}{3\sqrt{\pi}}, \quad b_4 = -\frac{3}{4}, \quad b_5 = \frac{27\pi + 128}{45\sqrt{\pi}}, \quad b_6 = -\frac{339\pi - 128}{288\pi}, \quad \ldots \]

It is numerically confirmed that the obtained form can be convergent only within a relatively small radius of convergence. The convergence may be viewed from the separation point around \((\eta, c_0) = (-2, 0.65)\), where the upper and lower thick dashed curves obtained by the truncation numbers (10 and 11) are separated from each other in figure (3). Following a mathematical procedure proposed in [19], we further perform an analytic continuation by
to improve the rate of convergence of the obtained alternating series. In figure 3, the intermediate dashed curve indicates the expression obtained from a procedure of the inverse problem, which is in excellent agreement with the numerically integrated solution.

**Mechanical work.**— We apply the present system to an osmotic engine that can convert osmotic energy to mechanical work or potential energy. The solvent volume seeped into the cist side is calculated as 
\[
|\xi_{pc}(t)| = \int_0^t (c_0(\tau) - p_0) d\tau \text{ per unit area of the membrane.}
\]
The nondimensionalised work output, \(\delta W\), for the initial time interval, \(t\), is a function of \(t\) and \(p_0\), which is equal to the product of \(p_0\) and \(|\xi_{pc}(t)|\) because the present seepage is an isobaric process in thermodynamics. Note that the process under the condition of \(p_0 = 0\) corresponds to irreversible free expansion and results only in increase in entropy (no work output, \(\delta W = 0\)), and it may complete in a relatively short time. In contrast, the flow under the condition of \(p_0 \neq 0\) corresponds to a reversible and quasi-static process, which requires a longer time interval to be completed. Based on these facts, we may conjecture that the maximum power, \(\delta W/t\), is realised at the optimal nondimensionalised pressure, \(p_0\) (0 < \(p_0 < 1\)). Based on equation (6) and \(c_0(0) = 1\), we obtain for a small \(t\),
\[
\delta W = \frac{dW}{dt} \bigg|_{t=0} - t + \frac{1}{2} \frac{dW}{dt} \bigg|_{t=0} t^2 + O(t^3) \approx -\left(p_0 - \frac{1}{2}\right) + \frac{1}{4} t + \frac{1}{2} \frac{dW}{dt} \bigg|_{t=0} t^2.
\]
From the equation, we can conclude that the initially instantaneous output power is the maximum (0.25) at \(p_0 = 0.5\) and that the average output power for a longer \(t\) is less than 0.25 because \(\frac{dW}{dt} \bigg|_{t=0} < 0\). The integration of equation (10) based on the numerically obtained \(c_0\) shows that \(\delta W/t\) decreases to 0.144 at \(t = 1\). Moreover, we can predict that the optimal value of \(p_0\) for a longer \(t\) is less than 0.5 because \(\frac{\partial \delta W}{\partial p_0} \bigg|_{t=0} < 0\).

**4. Summary**

In this study, we revisited a nonlinear partial differential equation describing the osmotically driven flow across a semipermeable membrane under a constant static pressure difference, which was previously investigated for reverse osmosis [13, 14]. First, we confirmed the following three points in the unstirred layer formed in osmotically driven flow: (1) inertia is practically negligible; (2) the layer formation timescale of the order of \(O(\tilde{t}_0)\) may be variable depending on parameters, and it may range from 1[ms]~1[year] based on the individual case studies; (3) layer thickness may increase with no limit in principle. Based on previous studies, the thickness of the layer, \(\vartheta\), was evaluated using the equation \(c_0 = e^{(p_0 - c_\infty)\vartheta}\), which was deduced under the assumption of the pseudo steady solution of equation (1).

In the present study, considering that the phenomenon is essentially time dependent, we applied a few mathematical procedures to the problem in order to measure the timescale of the development of the concentration boundary layer on the membrane. In particular, the last procedure of the inverse problem successfully provided an analytical expression of the time series of solute concentration, equation (10) with table 1 for the case of \(p_0 = 0\). From the result, we found that the localised concentration on the membrane decayed initially as \(-t^{\frac{1}{2}}\) and eventually as \(t^{\frac{-1}{2}}\). In fact, the latter asymptotic behaviour was confirmed experimentally in the previous studies [20, 21]. This implies that the thickness of the unstirred layer, \(\vartheta_1\), principally diverges with increase in \(t\) with no upper limit and the layer intrinsically never saturates. Finally, we considered the present system as an osmotic engine, and deduced the maximum power realised at the optimal nondimensionalised pressure.

We note that the initial condition in the present study is not artificial and that the present formulation can be tested experimentally as it is. For instance, solvent flow can be initially prevented by making static pressure equal to osmotic pressure, \(p_0 = c_\infty\). Then, the initial condition in the present study can be experimentally realised by eliminating \(p_0\) at an initial instant. The present system is determined by the only system parameter, \(p_0\), so that the obtained solution may be considered to be universal. As far as \(p_0 = 0\) mainly addressed in the present study, the time scale of the unstirred layer formation may be prescribed only in \(O(\tilde{t}_0)\) where \(\tilde{c}_0(t)/\tilde{c}_0(t = 0) \sim 1/2\). In physiology, it is known that such an abrupt change in solute concentration (or static pressure) leads to a certain dysfunction of the cell membranes. With the aid of mechanics, the cells and tissues in human bodies can respond to such an osmotic shock quickly, with the unstirred layer neutralising the shocked state of the cells. While we have here assumed spacial uniformity of quantities along the membrane for simplicity, in reality, such a biological membrane involves additional complexities. It demands us to consider the unstirred layer in higher dimensional space and furthermore to introduce non-uniform distribution of pores on the membrane to the model, which may provides inhomogeneous or unsteady development of the weakly correlated layers. This will be investigated in future studies.
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Table 1. Coefficient of the series \((a_n, b_n, q_n)\) solved in case of \(p_0 = 0\). The convergence of \(a_n\) and \(b_n\) is not excellent and is within a small radius of convergence. While \(b_n\) and \(c_n\) are alternating series, \(a_n\) is also a potentially alternating series because \(a_n\) is defined in equation (7) originating at algebraic series of \(\xi^n\) for \(\xi < 0\).

| \(n\) | \(a_n\) | \(b_n\) | \(q_n\) |
|------|--------|--------|--------|
| 0    | 0      | 0      | 1      |
| 1    | 2      | 0      | -1.128 4 |
| 2    | 2.5    | -1     | -0.371 6 |
| 3    | 2.399 2| 0.752 3| -0.251 7 |
| 4    | 1.917 0| -0.75  | 0.108 4 |
| 5    | 1.331 9| 0.849 3| -0.080 6 |
| 6    | 0.826 7| -1.035 6 | 0.033 7 |
| 7    | 0.467 0| 1.325 6 | -0.029 1 |
| 8    | 0.243 2| -1.756 1 | 0.010 1 |
| 9    | 0.118 0| 2.367 2 | -0.011 5 |
| 10   | 0.053 8| -3.310 4 | 0.002 5 |