Appropriate Material Properties for Advective–Diffusive Solute Flux in Membrane Soil

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Abstract: A generalized advective–diffusive equation for describing electrolytic solute transport in fine-grained soil (clay) membranes is presented. Clarification is made between the current theory and the widely cited coupled-flow theory by Yeung and Mitchell. Results of recently published experimental data are evaluated to demonstrate that the effective diffusion coefficient associated with Fick’s first law is not an appropriate independent material property for solute transport considerations in membrane soil. Three independent and experimentally attainable material properties are identified, specifically: osmotic efficiency, membrane diffusion coefficient, and hydraulic conductivity. Simple physical experiments by which these properties may be measured are described.

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Introduction

The ability of fine-grained soils to act as semipermeable membranes and restrict the passage of dissolved solutes is well documented. The mechanisms involved are responsible for a family of coupled transport phenomena that are generally referred to as “osmotic” or “membrane” phenomena, and specifically include electro-osmosis (flow of water in response to a gradient in electrical potential), chemico-osmosis (flow of water in response to a gradient in chemical potential), and ultrafiltration (restricted diffusive solute flux). The importance of these membrane phenomena and the consequent impact on water and solute flow in natural and engineered earthen materials has been investigated in the geologic, soil science, and geotechnical engineering disciplines for several decades.

Geotechnical engineers have explored formulations of irreversible thermodynamics in effort to provide more generalized advection–dispersion equations that take into account these membrane phenomena in soil. One formulation (Yeung 1990; Mitchell 1991; Yeung and Mitchell 1993) provides a comprehensive basis for analyzing the coupled fluxes of pore fluid, electrical current, and dissolved chemical species in response to hydraulic, electrical, and chemical gradients. Another formulation (Katchalsky and Curran 1965; Olsen et al. 2000; Olsen 2003) is more limited in that it only considers the mass fluxes of liquid and solute in response to hydraulic and chemical gradients, but can be used as a theoretical basis for a more generalized advection-dispersion equation.

This technical note examines the basic differences between these two formalisms in terms of the interrelationships employed among the fundamental thermodynamic phenomenological coefficients and the corresponding material properties more familiar to most geo-professionals, specifically: hydraulic conductivity, electro-osmotic conductivity, electrical conductivity, osmotic efficiency, and effective diffusion coefficient. Three independent and experimentally attractive material properties are identified by which fluid and solute transport may be effectively quantified in membrane soils.

Irreversible Thermodynamic Framework

Consider the simple membrane system illustrated in Fig. 1. Two reservoirs containing solutions of different chemical potential are separated by a membrane soil (e.g., compacted clay). Under the formalism of irreversible thermodynamics, the fluxes of water ($J_v$), electrical current ($J_I$), and diffusive solute ($J_s^f$) can be expressed in terms of the associated driving forces (gradients) and a series of phenomenological coefficients ($L_{ij}$) representing the material properties of the soil membrane:

$$J_v = L_{11} \nabla (-P) + L_{12} \nabla (-\psi) + L_{13} \nabla (-\pi)$$  \hspace{1cm} (1a)

$$J_I = L_{21} \nabla (-P) + L_{22} \nabla (-\psi) + L_{23} \nabla (-\pi)$$  \hspace{1cm} (1b)

$$J_s^f = L_{31} \nabla (-P) + L_{32} \nabla (-\psi) + L_{33} \nabla (-\pi)$$  \hspace{1cm} (1c)

The phenomenological coefficients may be functions of the state variables pressure $P$, electrical potential $\psi$, and solute con-
centrations $c$, but may not be functions of the driving forces causing flux (i.e., the gradients of $P$, $\psi$, and $c$). Dependency of the phenomenological coefficients on the driving forces is either a violation of the irreversible thermodynamic formalism or a failure in the choice of a proper energy dissipation function.

The phenomenological coefficients are correlated according to Onsager’s reciprocal principle, which states that the coupling matrix is symmetric ($L_{ij} = L_{ji}$). Under the special condition of zero net electric charge flux ($j_e = 0$) therefore, we may write

$$\nabla(-\psi) = -\frac{L_{11}}{L_{22}} \nabla(-P) - \frac{L_{23}}{L_{22}} \nabla(-\pi) \quad (2a)$$

$$J_s = \left[ L_{11} - \frac{L_{12}^2}{L_{22}} \right] \nabla(-P) + \left[ L_{13} - \frac{L_{12}L_{23}}{L_{22}} \right] \nabla(-\pi) \quad (2b)$$

$$\frac{J_s}{c} = \left[ \frac{L_{13}}{L_{22}} - \frac{L_{23}^2}{L_{22}} \right] \nabla(-P) + \left[ L_{33} - \frac{L_{23}^2}{L_{22}} \right] \nabla(-\pi) \quad (2c)$$

Eqs. (2b) and (2c) may be then simplified as follows:

$$J_s = L_P \nabla(-P) + L_{PD} \nabla(-\pi) \quad (3a)$$

$$\frac{J_s}{c} = L_{DP} \nabla(-P) + L_D \nabla(-\pi) \quad (3b)$$

where the coupling coefficients $L_P$, $L_{PD}$, and $L_D$ are as follows:

$$L_P = L_{11} - \frac{L_{12}^2}{L_{22}} \quad (4a)$$

$$L_{DP} = L_{PD} = L_{13} - \frac{L_{12}L_{23}}{L_{22}} \quad (4b)$$

$$L_D = L_{33} - \frac{L_{23}^2}{L_{22}} \quad (4c)$$

One important implication of the formalism resulting in Eqs. (3) and (4) is that three independent coupling coefficients are both necessary and sufficient for describing coupled water and solute flow in membrane soil with electrolyte solution ($L_P$, $L_{DP}$, and $L_D$). Each coefficient is required, yet no other coefficients are necessary.

**Transformation of Coupling Coefficients to Physical Parameters**

The coupling coefficients $L_P$, $L_{PD}$, and $L_D$ are not commonly used or measured in geotechnical engineering. However, transformation of these coefficients to familiar and experimentally attractive material parameters can be conducted within the established framework of irreversible thermodynamics so that the governing theories can be used to predict actual coupled flow behavior.

Parameters used in the field of geotechnical engineering to replace the coupled flow coefficients include hydraulic conductivity, electro-osmotic conductivity, electrical conductivity, osmotic efficiency, and effective diffusion coefficients. Three specific material properties are identified in the following: chemico-osmotic efficiency, membrane diffusion coefficient, and hydraulic conductivity.

**Chemico-Osmotic Efficiency**

Total solute flux includes both advective and diffusive components and can be obtained by combining Eqs. (3a) and (3b) as follows:

$$J_s = cJ_v + \frac{J_s}{c} = c(L_P + L_{DP}) \nabla(-P) + c(L_{PD} + L_D) \nabla(-\pi) \quad (5)$$

When a particular soil does not exhibit membrane behavior (e.g., sand), the coupling coefficients $L_{DP}$ (and $L_{PD}$) are equal to zero and Eq. (5) reduces to the widely used advective–diffusive equation for solute transport

$$J_s = cL_P \nabla(-P) + cL_D \nabla(-\pi) \quad (6)$$

where the coupling coefficient $L_P$ can be related to hydraulic conductivity $k$ and $L_D$ can be related to the effective diffusion coefficient $D^*$.  

Now consider a membrane system that permits the flow of water but completely prevents the passage of solute. The solute flux predicted by Eq. (5) for this “ideal” membrane should be zero, which leads to

$$L_P = -L_{DP} = -L_{PD} = L_D \quad (7)$$

If a physical experiment is devised for an ideal membrane where no water flux is permitted, then Eq. (3a) becomes

$$J_v = 0 = L_P \nabla(-P) + L_{PD} \nabla(-\pi) \quad (8)$$

Substituting Eq. (7) into the above equation, we have...
Fig. 2. Illustration of zero water volume flux experiment: (a) in ideal semimembrane soil with zero pressure boundary and (b) in ideal semimembrane soil with pressure boundary

\[
\nabla (-P) \bigg|_{I_p=0} = -\frac{L_{PD}}{L_p} = 1
\]

Two situations could satisfy the condition described by Eq. (9). Considering the conceptual systems shown as Fig. 2, these situations are: (1) that the applied osmotic pressure, \(\pi\), results in a rise of the water column in the left (i.e., high concentration) chamber [Fig. 2(a)] or (2) an external pressure (e.g., piston pressure) is applied to maintain the water levels in both containers at the same position in order to counter the osmotic pressure gradient [Fig. 2(b)].

On the other hand, if the soil is not an ideal membrane but rather is only able to partially block the passage of solute, an elevated water pressure smaller in magnitude than in Fig. 2(a) will be observed in the left chamber. The ratio in Eq. (9) in this case becomes less than unity, or

\[
\frac{\nabla (-P)}{\nabla (-\pi)} \bigg|_{I_p=0} = -\frac{L_{PD}}{L_p} < 1
\]

And finally, at the limiting case when a soil has no membrane capability, there will be no change in the water level under any osmotic pressure gradient and Eq. (9) becomes

\[
\frac{\nabla (-P)}{\nabla (-\pi)} \bigg|_{I_p=0} = -\frac{L_{PD}}{L_p} = 0
\]

Thus, the ratio of \(L_{PD}\) to \(L_p\) varies between 0 and 1 and provides an excellent measure for the efficiency of membrane behavior. Staverman (1952) defined this quantity as the membrane coefficient or chemico-osmotic efficiency

\[
\omega = -\frac{L_{PD}}{L_p}
\]

Membrane Diffusion Coefficient

A generalized advective-diffusive flux equation can be obtained following the approach by Katchalsky and Curran (1965). From Eq. (3a), the pressure gradient can be expressed as

\[
\nabla (-P) = J_s - L_{PD} \nabla (-\pi)
\]

Substituting the above equation into Eq. (5), the advective–diffusive solute flux becomes

\[
J_v = c(L_p + L_{DP}) \nabla (-P) + c(L_{PD} + L_D) \nabla (-\pi)
\]

\[
= c \left(1 + \frac{L_{DP}}{L_p}\right) J_v + c \frac{L_D L_p - L_{PD} L_{DP}}{L_p} \nabla (-\pi)
\]

Inserting the osmotic efficiency [Eq. (12)] into Eq. (14), we have

\[
J_v = c(1 - \omega) J_v + c(L_D - \omega^2 L_p) \nabla (-\pi)
\]

And from Eq. (3a), the water flux is

\[
J_w = L_p \nabla (-P) - \omega L_p \nabla (-\pi) = L_p [\nabla (-P) - \omega \nabla (-\pi)]
\]

The first term on the right-hand-side of Eq. (16) represents flux due to the applied hydraulic gradient and the second term represents osmotically induced water flow.

A simple physical experiment may be devised by actively maintaining a condition where the flux of water under an applied osmotic pressure gradient is zero \((J_v=0)\). Under this condition (conceptualized in Fig. 3), the total solute flux is due to the applied osmotic pressure gradient \(\nabla (-\pi)\) and Eq. (15) reduces to

\[
J_v = c(L_D - \omega^2 L_p) \nabla (-\pi)
\]

The terms preceding the osmotic pressure gradient in Eq. (17) can be combined into a single parameter describing the membrane diffusion coefficient under the condition of zero water volume flux, which Katchalsky and Curran (1965) referred to as \(\beta\)

\[
\beta = c(L_D - \omega^2 L_p)
\]

Given the membrane diffusion coefficient \(\beta\), we may now write the general advective–diffusive solute flux as follows:

\[
J_v = c(1 - \omega) J_v + \beta \nabla (-\pi)
\]
Hydraulic Conductivity

The remaining coupling parameter \( L_p \) can be transformed to hydraulic conductivity \( k \) by considering a physical experiment under boundary conditions of zero osmotic pressure gradient and a constant pressure gradient. Under these conditions, Eq. (16) becomes

\[
\frac{J_s}{\nabla (-P)} \bigg|_{\nabla (-\pi) = 0} = L_p
\]  

(20)

Comparison of Eq. (20) with Darcy’s law reveals the following:

\[
L_p = \frac{k}{\gamma_w n}
\]  

(21)

where \( k \)=hydraulic conductivity of the soil membrane; \( \gamma_w \)=unit weight of water, and \( n \)=porosity.

Summary of Transformed Coefficients

With Eq. (21), we complete the transformation of the coupling coefficients to three experimentally attainable material parameters. Specifically, we have gone from

\[
L_p = \frac{k}{\gamma_w n}
\]  

\[
L_D = \beta + \frac{\omega^2 k}{\gamma_w n}
\]  

(22a)

\[
L_{DP} = -\frac{\omega k}{\gamma_w n}
\]

to

\[
\omega = -\frac{L_{DP}}{L_p}
\]

\[
\beta = \frac{c(L_p L_D - L_{DP}^2)}{L_p}
\]  

(22b)

\[
k = \gamma_w n L_p
\]

and the coupled water and advective–diffusive solute flows can be fully quantified by the set of parameters defined by Eq. (22b)

\[
J_s = c(1-\omega)J_v + \beta \nabla (-\pi)
\]  

(23a)

\[
J_v = \frac{k}{\gamma_w n} \left[ \nabla (-P) - \omega \nabla (-\pi) \right]
\]  

(23b)

Comparison with Yeung and Mitchell’s Formalism

Substituting Eq. (23b) into Eq. (23a), applying the van’t Hoff approximation \( \pi = RTc \), and rearranging terms, we obtain the total solute flux under gradients of pressure and solute concentration

\[
J_s = c(1-\omega) \frac{k}{\gamma_w n} \nabla (-P) + \left[ \beta - c(1-\omega) \frac{\omega k RT}{\gamma_w n} \right] \nabla (-c)
\]  

(24)

In Yeung and Mitchell’s formalism (e.g., Yeung 1990; Yeung and Mitchell 1993), the following equation is derived:

\[
J_s = c(1-\omega) \frac{k}{\gamma_w n} \nabla (-P) + \left[ D^* - \frac{c\omega k RT}{\gamma_w n} \right] \nabla (-c)
\]  

(25)

where \( D^* \) is termed the effective diffusion coefficient of solute.

There are two differences in the bracketed coefficients preceding solute concentration gradient in Eqs. (24) and (25). First, \( D^* \) is defined and derived differently than \( \beta \). Second, there is an additional factor \((1-\omega)\) in the second term of the coefficient preceding solute concentration gradient in Eq. (24). The effective diffusion coefficient \( D^* \) may not be considered equal to \( \beta \), otherwise Eq. (25) does not account for the extra factor \((1-\omega)\).

In Yeung’s 1990 derivation, \( D^* \) is transformed by direct comparison of the phenomenological coefficients \( L_{ij} \) with Fick’s law, where \( D^* \) is equal to \( L_{ij} RT/c \). By drawing this direct analogy with Fick’s law, which explicitly deals with diffusive solute flux, the assumption that the soil does not exhibit membrane behavior must be imposed. Accordingly, Eq. (25) may not be suitable for advective–diffusive solute flux in membrane soils because the effective diffusion coefficient \( D^* \) is highly dependent on solute concentration \( c \) and the osmotic efficiency \( \omega \).

Eq. (24) may be more suitable for describing the solute flux in the membrane system shown in Fig. 1. If, for example, a thought experiment is conducted under conditions of zero pressure gradient, Eq. (3b) becomes

\[
\frac{J_s}{c} \bigg|_{\nabla (-P) = 0} = L_D \nabla (-\pi)
\]  

(26)

which by comparison with Fick’s law reveals

\[
D^* = cL_p RT
\]  

(27)

Substituting the above equation and \( L_D \) in Eq. (22a) into Eq. (18), we obtain

\[
\beta = cRT(L_D - \omega^2 L_p) = D^* - \frac{c\omega^2 k}{\gamma_w n}
\]  

(28)

Substituting Eq. (28) into Eq. (24), we have

\[
J_s = c(1-\omega) \frac{k}{\gamma_w n} \nabla (-P) + \left[ D^* - \frac{c\omega k RT}{\gamma_w n} \right] \nabla (-c)
\]  

(29)

which is identical in form to Eq. (25). However, according to Eq. (4c), \( L_D \) is not equal to \( L_{33} \) in general, but rather only if \( L_{33}=0 \).

Since \( D^* \) is widely considered a parameter that is not related to membrane properties, its direct usage for applications to membrane soils is misleading. Consider, for example, a recent experimental study on coupled solute and water flow in geosynthetic
Fig. 4. Characteristic functions of membrane properties of geosynthetic clay liner: (a) membrane diffusion coefficient or effective diffusion coefficient as functions of KCl concentration, (b) membrane diffusion coefficient or effective diffusion coefficient as functions of osmotic efficiency, and (c) osmotic efficiency as function of KCl concentration (data from Malusis and Shackelford 2002)
A general thermodynamic framework is presented for describing coupled liquid and solute flow in membrane soil. By examining irreversible thermodynamics and the current coupled flow theories, a general set of governing equations for liquid flow and advective–diffusive solute flow in membrane soils is derived. This equation set is recommended for future use in geotechnical engineering applications since it is consistent with the irreversible thermodynamics framework and is experimentally attractive. Three parameters are necessary and sufficient to fully describe simultaneous liquid and solute fluxes under the forces of pressure gradients and chemical concentration gradients: osmotic efficiency $\omega$, the membrane diffusion coefficient $\beta$, and the hydraulic conductivity $k$. Specific material properties such as the effective diffusion coefficient $D^*$ for a soil assumed to be nonselective to solute may not be preferable to infer or to identify parameters during parameter transformation because direct determination of $D^*$ for membrane soil is experimentally inconvenient, $D^*$ is inseparable from membrane behavior, and $D^*$ is not an independent material property.

References


