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Critical Review of Coupled Flux Formulations for Clay Membranes Based on Nonequilibrium Thermodynamics

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Review article

Critical review of coupled flux formulations for clay membranes based on nonequilibrium thermodynamics

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ABSTRACT

Extensive research conducted over the past several decades has indicated that semipermeable membrane behavior (i.e., the ability of a porous medium to restrict the passage of solutes) may have a significant influence on solute migration through a wide variety of clay-rich soils, including both natural clay formations (aquifers, aquicludes) and engineered clay barriers (e.g., landfill liners and vertical cutoff walls). Restricted solute migration through clay membranes generally has been described using coupled flux formulations based on nonequilibrium (irreversible) thermodynamics. However, these formulations have differed depending on the assumptions inherent in the theoretical development, resulting in some confusion regarding the applicability of the formulations. Accordingly, a critical review of coupled flux formulations for liquid, current, and solutes through a semipermeable clay membrane under isothermal conditions is undertaken with the goals of explicitly resolving differences among the formulations and illustrating the significance of the differences from theoretical and practical perspectives. Formulations based on single-solute systems (i.e., uncharged solute), single-salt systems, and general systems containing multiple cations or anions are presented. Also, expressions relating the phenomenological coefficients in the coupled flux equations to relevant soil properties (e.g., hydraulic conductivity and effective diffusion coefficient) are summarized for each system. A major difference in the formulations is shown to exist depending on whether counter diffusion or salt diffusion is assumed. This difference between counter and salt diffusion is shown to affect the interpretation of values for the effective diffusion coefficient in a clay membrane based on previously published experimental data. Solute transport theories based on both counter and salt diffusion then are used to re-evaluate previously published column test data for the same clay membrane. The results indicate that, despite the theoretical inconsistency between the counter-diffusion assumption and the salt-diffusion conditions of the experiments, the predictive ability of solute transport theory based on the assumption of counter diffusion is not significantly different from that based on the assumption of salt diffusion, provided that the input parameters used in each theory are derived under the same assumption inherent in the theory. Nonetheless, salt-diffusion theory is fundamentally correct and, therefore, is more appropriate for problems involving salt diffusion in clay membranes. Finally, the fact that solute diffusion cannot occur in an ideal or perfect membrane is not explicitly captured in any of the theoretical expressions for total solute flux in clay membranes, but rather is generally accounted for via inclusion of an effective porosity, n_e , or a restrictive tortuosity factor, τ_r , in the formulation of Fick's first law for diffusion. Both n_e and τ_r have been correlated as a linear function of

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membrane efficiency. This linear correlation is supported theoretically by pore-scale modeling of solid–liquid interactions, but experimental support is limited. Additional data are needed to bolster the validity of the linear correlation for clay membranes.

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1. Introduction

The ability of clays to act as semipermeable membranes that inhibit the passage of solutes while allowing relatively unimpeded migration of the solvent (water) is well recognized and has been the subject of extensive research over the past several decades. For example, numerous experimental studies have been conducted to evaluate the effects of membrane behavior in clay-rich soils on agricultural processes (e.g., salt infiltration and soil salinization), groundwater flow through confining beds, salt-water intrusion, and mechanical behavior (Barbour, 1986; Barbour and Fredlund, 1989; Cey et al., 2001; Di Maio, 1996; Garavito, 2005; Garavito et al., 2007; Greenberg, 1971; Hanshaw, 1962; Keijzer, 2000; Keijzer et al., 1997; Kemper and Rollins, 1966; Kharaka and Berry, 1973; Kharaka and Smalley, 1976; McKelvey and Milne, 1960; Neuzil, 1986; Olsen, 1969; Rahman et al., 2005; Young and Low, 1965). In addition, recent experimental studies have indicated the existence of membrane behavior in engineered clay barriers used for hydraulic containment applications (e.g., landfills, surface impoundments, etc.), such as geosynthetic clay liners (GCLs), compacted clay liners, and soil-bentonite backfills for vertical cutoff walls (Di Emidio, 2010; Evans et al., 2008; Henning, 2004; Henning et al., 2006; Kang, 2008; Kang and Shackelford, 2009, 2010, 2011; Malusis, 2001; Malusis and Shackelford, 2002a, 2002b; Malusis et al., 2001; Mazzieri et al., 2003, 2005, 2010; Saindon and Whitworth, 2005; Shackelford, 2012; Shackelford and Lee, 2003; Van Impe, 2002; Yeo, 2003; Yeo et al., 2005). Collectively, this extensive body of research has

demonstrated that significant membrane behavior is possible in clay soils, particularly those soils rich in high swelling smectite minerals, such as bentonite (Di Emidio, 2010; Kang and Shackelford, 2010; Kemper and Quirk, 1972; Kemper and Rollins, 1966; Malusis and Shackelford, 2002a; Milne et al., 1964; Shackelford, 2012; Shackelford et al., 2003; Yeo et al., 2005).

In addition to the aforementioned experimental studies, several theoretical studies have been devoted to characterizing liquid flow and solute transport through clay membranes based on coupled flux theory derived from principles of nonequilibrium (irreversible) thermodynamics (Bader and Kooi, 2005; Dominijanni, 2005; Dominijanni and Manassero, 2012a; Garavito et al., 2002; Greenberg, 1971; Greenberg et al., 1973; Groenevelt and Bolt, 1969; Groenevelt and Elrick, 1976; Groenevelt et al., 1978, 1980; Kooi et al., 2003; Lu et al., 2004; Malusis, 2001; Malusis and Shackelford, 2002c; Manassero and Dominijanni, 2003; Mitchell et al., 1973; Olsen et al., 2000; Soler, 2001; Van Impe, 2002; Van Impe et al., 2003, 2006; Yeung, 1990; Yeung and Mitchell, 1993). However, the coupled flux formulations in these studies have differed, and the differences have not been elucidated in a comprehensive manner, which can lead to confusion over the validity or applicability of the various formulations. As a result, a critical review of these formulations was undertaken with the goal of explicitly resolving the differences among the formulations and illustrating the significance of these differences from both theoretical and practical perspectives.

2. Background

2.1. Solute exclusion and membrane efficiency

Membrane behavior in clay soils is characterized by two mechanisms, viz., (1) exclusion of charged solutes (ions) as a result of repulsive forces between the solutes and electric fields associated with the diffuse double layers (DDLs) of adjacent clay particles (Fritz, 1986; Hanshaw and Coplen, 1973; Shackelford et al., 2003), and (2) chemico-osmosis, or flow of water through the membrane in the direction from lower solute concentration (higher water activity) to higher solute concentration (lower water activity), i.e., opposite to the prevailing direction of solute diffusion. The extent to which these two mechanisms occur in clay membranes typically is referred to as membrane efficiency, which is quantified in terms of a reflection coefficient, σ , in the science literature (e.g., biophysics, geological science, soil science, etc.) (e.g., Kemper and Rollins, 1966; Staverman, 1952), and in terms of a chemico-osmotic efficiency coefficient, ω , in some engineering disciplines, such as geotechnical engineering (e.g., Fritz, 1986; Mitchell and Soga, 2005). Although σ and ω are equivalent parameters for quantifying membrane efficiency (i.e., $\sigma = \omega$), the latter designation is preferred in some engineering disciplines because σ historically has been used to denote mechanical stress. Also, σ has been used to designate soil electrical conductivity in previous theoretical developments for clay membranes (e.g., Mitchell and Soga, 2005; Yeung, 1990; Yeung and Mitchell, 1993). Thus, because the perspective of the theoretical developments reviewed herein has been derived largely from the viewpoint of engineered systems, ω is used herein to designate membrane efficiency. However, since ω also has been used to represent the coefficient of solute permeability at zero volume flow in the classical formulation of nonequilibrium thermodynamics (Katchalsky and Curran, 1965), the coefficient of solute permeability at zero volume flow is represented by β in this study in accordance with the theoretical development of Lu et al. (2004).

In general, values of ω may range from zero ($\omega = 0$) for a soil that exhibits no solute restriction due to membrane effects (i.e., no chemico-osmotic efficiency) to unity ($\omega = 1$) for a “perfect” or “ideal” membrane that completely restricts the passage of solutes. In an ideal membrane ($\omega = 1$), electric fields associated with the DDLs of adjacent clay particles overlap within all the pore spaces, such that all anions attempting to pass through the membrane are repelled across the entire width of the pore space. In this case, all of the accompanying cations also must be excluded to maintain electroneutrality (Fritz, 1986). However, clay membranes typically are “non-ideal” membranes (i.e., $0 < \omega < 1$), since the electric fields usually do not overlap completely in all pores. The actual value of ω for a clay membrane can vary widely within the range $0 < \omega < 1$ depending on several factors, including the mineralogy of the clay, the clay content of the soil, solution properties (e.g., size, charge, and concentration of solutes), and pore size (Shackelford et al., 2003). For example, the results of several experimental studies on clay membrane behavior in the presence of electrolyte solutions containing common salts (e.g., NaCl, KCl, and CaCl₂) have shown that ω generally decreases with increasing ion charge

and/or increasing salt concentration (Kemper and Quirk, 1972; Kemper and Rollins, 1966; Malusis and Shackelford, 2002a; Shackelford and Lee, 2003).

2.2. Nonequilibrium thermodynamics framework for clay membranes

The theoretical framework considered herein for describing coupled fluxes in clay membranes is based on the second law of thermodynamics, adapted for nonequilibrium systems in which irreversible processes occur (see Katchalsky and Curran, 1965). This approach is valid for irreversible processes provided that (1) local equilibrium is established such that any infinitesimal subsystem of the overall system is in equilibrium, (2) the fluxes are linearly related to the driving forces, and (3) Onsager's reciprocal law is valid for the system (Yeung and Mitchell, 1993). Within this framework, the dissipation of free energy by coupled fluxes under isothermal conditions is defined by a dissipation function, Φ , which can be expressed in general terms as follows (Mitchell and Soga, 2005):

$$\Phi = \sum_{i=1}^N J_i X_i \quad (1)$$

where J_i and X_i represent the i th of N different fluxes and driving forces, respectively. Based on Eq. (1), the linear relationship between the fluxes and driving forces can be written as follows:

$$\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 + \cdots + L_{1N}X_N \\ J_2 &= L_{21}X_1 + L_{22}X_2 + \cdots + L_{2N}X_N \\ &\vdots \\ &\vdots \\ J_N &= L_{N1}X_1 + L_{N2}X_2 + \cdots + L_{NN}X_N \end{aligned} \quad (2)$$

or, more concisely, as

$$J_i = \sum_{j=1}^N L_{ij}X_j; \quad i = 1, 2, \dots, N \quad (3)$$

where L_{ij} are phenomenological coefficients that relate the flux of type i to the gradient of type j .

Evaluation of the phenomenological coefficients in Eq. (3) is necessary to provide a complete description of coupled flux processes, but becomes increasingly more cumbersome as the numbers of fluxes and driving forces increase. For example, a set of equations with three fluxes and driving forces contains nine coefficients, whereas a set of equations with four fluxes and driving forces contains 16 coefficients. In general, a system with N fluxes and driving forces contains N^2 phenomenological coefficients that must be evaluated. However, in accordance with Onsager's reciprocal law, the cross (off-diagonal) phenomenological coefficients are equivalent, or

$$L_{ij} = L_{ji}. \quad (4)$$

As a result of Eq. (4), the number of independent coefficients in Eq. (3) is reduced from N^2 to $[(N+1)N]/2$. The validity of Eq. (4) with respect to electrical and chemical

coupling has been demonstrated experimentally in previous studies (Abd-el-Aziz and Taylor, 1965; Letey and Kemper, 1968; Miller, 1960; Olsen, 1969).

3. Theoretical development

In this review, coupled fluxes of liquid, current, and aqueous miscible chemical species (solutes) through a clay membrane under isothermal conditions are presented based on a conceptual model consisting of two compartments separated by a homogeneous charged membrane of thickness L , as illustrated in Fig. 1. Each compartment may contain a different pressure (P), electrical potential (Ψ), and chemical potential (μ) such that hydraulic, electrical, and chemical gradients, respectively, are maintained across the membrane. However, the compartments are assumed to be sufficiently mixed such that no gradients exist within either compartment (Katchalsky and Curran, 1965; Yeung, 1990).

In general, the charged membrane depicted in Fig. 1 can be considered as either a continuous or a discontinuous system for the purpose of describing the dissipation of free energy. The state variables (P , Ψ , and μ) in a continuous system are functions of both time and space, and the driving forces at any point within the membrane are represented by the gradients of the state variables at that location at a given time. In contrast, the state variables in a discontinuous system are represented by potential differences between the external solutions on either side of the membrane and are assumed to vary linearly within the membrane (Groenevelt and Bolt, 1969; Groenevelt and Elrick, 1976; Katchalsky and Curran, 1965; Olsen, 1969, 1972; Olsen et al., 2000; Sherwood and Craster, 2000). Thus, the discontinuous system approach is not applicable for computing point-wise fluxes within a membrane under transient conditions in which the gradients vary with both time and space, or under steady-state conditions in which the gradients are constant in time but not in space. As a result of this limitation in the discontinuous approach, the theoretical developments presented herein are based on the assumption of a continuous and homogenous system.

3.1. Coupled flux equations

The dissipation function (Eq. (1)) for a continuous system represented by the conceptual scenario in Fig. 1 can be written in general form for isothermal conditions as follows (Malusis and Shackelford, 2002c; Yeung, 1990):

$$\Phi = -q \frac{\partial P}{\partial x} - I \frac{\partial \Psi}{\partial x} - \sum_{i=1}^M J_i^d \frac{\partial \mu_i}{\partial x} \quad (5)$$

where q is the liquid (solution) flux, P is the liquid pressure, I is the electrical current, Ψ is the electrical potential, μ_i is the chemical potential of solute i , J_i^d is the molar diffusive flux of solute i , and M ($=N-2$) represents the total number of different solute species. Based on Eq. (5), the governing equations for coupled flux of liquid, current, and solutes are as follows (Malusis and Shackelford, 2002c):

$$q = -L_{11} \frac{\partial P}{\partial x} - L_{12} \frac{\partial \Psi}{\partial x} - \sum_{i=1}^M L_{1,i+2} \frac{\partial \mu_i}{\partial x} \quad (6a)$$

$$I = -L_{21} \frac{\partial P}{\partial x} - L_{22} \frac{\partial \Psi}{\partial x} - \sum_{i=1}^M L_{2,i+2} \frac{\partial \mu_i}{\partial x} \quad (6b)$$

$$J_j^d = -L_{j+2,1} \frac{\partial P}{\partial x} - L_{j+2,2} \frac{\partial \Psi}{\partial x} - \sum_{i=1}^M L_{j+2,i+2} \frac{\partial \mu_i}{\partial x}; \quad j = 1, 2, \dots, M. \quad (6c)$$

Furthermore, if the chemical solution is dilute such that ideal solution relationships are valid, $\partial \mu_i / \partial x$ is related to the molar concentration of species i , or C_i , as follows (Yeung, 1990; Yeung and Mitchell, 1993):

$$\frac{\partial \mu_i}{\partial x} = \frac{RT}{C_i} \frac{\partial C_i}{\partial x} \quad (7)$$

where R is the universal gas constant and T is absolute temperature. Substitution of Eq. (7) into Eqs. (6a)–(6c) yields the following expressions:

$$q = -L_{11} \frac{\partial P}{\partial x} - L_{12} \frac{\partial \Psi}{\partial x} - \sum_{i=1}^M L_{1,i+2} \frac{RT}{C_i} \frac{\partial C_i}{\partial x} \quad (8a)$$

$$I = -L_{21} \frac{\partial P}{\partial x} - L_{22} \frac{\partial \Psi}{\partial x} - \sum_{i=1}^M L_{2,i+2} \frac{RT}{C_i} \frac{\partial C_i}{\partial x} \quad (8b)$$

$$J_j^d = -L_{j+2,1} \frac{\partial P}{\partial x} - L_{j+2,2} \frac{\partial \Psi}{\partial x} - \sum_{i=1}^M L_{j+2,i+2} \frac{RT}{C_i} \frac{\partial C_i}{\partial x}; \quad j = 1, 2, \dots, M. \quad (8c)$$

Eqs. (8a)–(8c) represent a general formulation for isothermal, continuous membrane systems, in that the equations can be written to account for any number of different solutes. An increase in the number of solutes (M) increases the number of terms in each equation, thereby increasing the number of phenomenological coefficients that must be evaluated. In addition, a separate expression of Eq. (8c) is required for each solute species j . As a result of a desire to minimize the overall

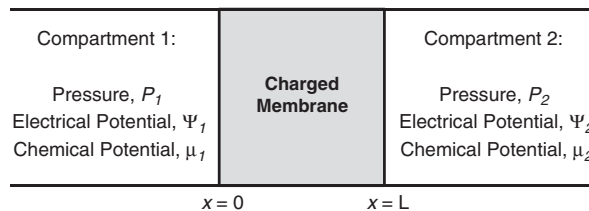


Fig. 1. Conceptual model for coupled fluxes through a homogeneous, charged membrane. Redrawn after Yeung (1990).

complexity of the system of equations, many previous theoretical developments have considered systems containing only a single solute or a single, binary salt (e.g., Greenberg et al., 1973; Groenevelt and Bolt, 1969; Groenevelt and Elrick, 1976; Lu et al., 2004; Manassero and Dominijanni, 2003; Olsen, 1969; Yeung, 1990; Yeung and Mitchell, 1993).

3.1.1. Single-solute formulation

Manassero and Dominijanni (2003) presented the following dissipation function for a system containing a single solute in the absence of applied or induced electrical gradients:

$$\Phi = -J_w V_w \frac{\partial P}{\partial X} - J_s^d \frac{RT}{C_s} \frac{\partial C_s}{\partial X} \quad (9)$$

where J_w is the flux of the solvent (H_2O), V_w is the partial molar volume of the solvent, J_s^d is the diffusive solute flux, and C_s is the molar solute concentration. For dilute solutions, $J_w V_w \approx q$ and Eq. (9) may be rewritten as follows:

$$\Phi = -q \frac{\partial P}{\partial X} - J_s^d \frac{RT}{C_s} \frac{\partial C_s}{\partial X}. \quad (10)$$

Thus, the resulting set of coupled flux equations can be written as follows:

$$q = -L_{11} \frac{\partial P}{\partial X} - L_{12} \frac{RT}{C_s} \frac{\partial C_s}{\partial X} \quad (11a)$$

$$J_s^d = -L_{21} \frac{\partial P}{\partial X} - L_{22} \frac{RT}{C_s} \frac{\partial C_s}{\partial X} \quad (11b)$$

Eqs. (11a) and (11b) represent a simplified form of Eqs. (8a)–(8c) for the case in which $M=1$. As a result, only three unique phenomenological coefficients need to be known, i.e., since $L_{12}=L_{21}$ (see Eq. (4)). However, because electrical coupling is ignored in Eqs. (11a) and (11b), these equations are applicable only for systems containing an uncharged (neutral) solute. For cases involving inorganic chemical species, the majority of solutes typically consist of electrolytes, or charged species (cations and anions), derived from dissolution of a parent compound (e.g., salt). Electrical coupling typically is included in formulations involving electrolyte solutions in order to model electrokinetic processes under an applied current (e.g., electro-osmosis and electrophoresis) or to account for induced electrical potentials among migrating ions.

3.1.2. Single-salt formulations

Yeung (1990) and Yeung and Mitchell (1993) considered a system containing a single cation and a single anion derived from complete dissociation of a strong, binary salt (e.g., NaCl). In their theoretical development, separate terms were included in the dissipation function for the salt cation (c) and the salt anion (a), as follows:

$$\Phi = -q \frac{\partial P}{\partial X} - I \frac{\partial \Psi}{\partial X} - J_c^d \frac{\partial \mu_c}{\partial X} - J_a^d \frac{\partial \mu_a}{\partial X}. \quad (12)$$

Thus, the resulting set of coupled flux equations may be written as follows:

$$q = -L_{11} \frac{\partial P}{\partial X} - L_{12} \frac{\partial \Psi}{\partial X} - L_{13} \frac{\partial \mu_c}{\partial X} - L_{14} \frac{\partial \mu_a}{\partial X} \quad (13a)$$

$$I = -L_{21} \frac{\partial P}{\partial X} - L_{22} \frac{\partial \Psi}{\partial X} - L_{23} \frac{\partial \mu_c}{\partial X} - L_{24} \frac{\partial \mu_a}{\partial X} \quad (13b)$$

$$J_c^d = -L_{31} \frac{\partial P}{\partial X} - L_{32} \frac{\partial \Psi}{\partial X} - L_{33} \frac{\partial \mu_c}{\partial X} - L_{34} \frac{\partial \mu_a}{\partial X} \quad (13c)$$

$$J_a^d = -L_{41} \frac{\partial P}{\partial X} - L_{42} \frac{\partial \Psi}{\partial X} - L_{43} \frac{\partial \mu_c}{\partial X} - L_{44} \frac{\partial \mu_a}{\partial X} \quad (13d)$$

or, upon substitution of Eq. (7), as follows:

$$q = -L_{11} \frac{\partial P}{\partial X} - L_{12} \frac{\partial \Psi}{\partial X} - L_{13} \frac{RT}{C_c} \frac{\partial C_c}{\partial X} - L_{14} \frac{RT}{C_a} \frac{\partial C_a}{\partial X} \quad (14a)$$

$$I = -L_{21} \frac{\partial P}{\partial X} - L_{22} \frac{\partial \Psi}{\partial X} - L_{23} \frac{RT}{C_c} \frac{\partial C_c}{\partial X} - L_{24} \frac{RT}{C_a} \frac{\partial C_a}{\partial X} \quad (14b)$$

$$J_c^d = -L_{31} \frac{\partial P}{\partial X} - L_{32} \frac{\partial \Psi}{\partial X} - L_{33} \frac{RT}{C_c} \frac{\partial C_c}{\partial X} - L_{34} \frac{RT}{C_a} \frac{\partial C_a}{\partial X} \quad (14c)$$

$$J_a^d = -L_{41} \frac{\partial P}{\partial X} - L_{42} \frac{\partial \Psi}{\partial X} - L_{43} \frac{RT}{C_c} \frac{\partial C_c}{\partial X} - L_{44} \frac{RT}{C_a} \frac{\partial C_a}{\partial X}. \quad (14d)$$

A total of nine unique phenomenological coefficients (i.e., three times more coefficients than for the single-solute system represented by Eqs. (11a) and (11b)) must be known in order to compute all of the fluxes given by Eqs. (14a)–(14d). However, if the salt cation and salt anion must migrate together to maintain electroneutrality in solution, the dissipation function given by Eq. (12) can be simplified by combining the separate terms for the salt cation and salt anion into a single term representing the salt as a whole (Greenberg et al., 1973; Letey et al., 1969; Mitchell et al., 1973; Olsen et al., 2000). For this case, the diffusive flux of the salt, J_s^d , is related to the individual diffusive fluxes of the salt cation, J_c^d , and the salt anion, J_a^d , as follows:

$$J_s^d = \frac{J_c^d}{\nu_c} = \frac{J_a^d}{\nu_a} \quad (15)$$

where ν_c and ν_a represent the numbers (or moles) of the cation and the anion, respectively, in each molecule (or mole) of the salt. Likewise, a similar stoichiometric relationship exists between the molar salt concentration, C_s , and the molar concentrations of the cation, C_c , and the anion, C_a , i.e.,

$$C_s = \frac{C_c}{\nu_c} = \frac{C_a}{\nu_a}. \quad (16)$$

Furthermore, the chemical potential of the salt, μ_s , can be expressed in terms of the individual chemical potentials of the cation, μ_c , and the anion, μ_a , as follows:

$$\mu_s = \nu_c \mu_c + \nu_a \mu_a \quad (17)$$

or, in differential form, as follows:

$$\frac{\partial \mu_s}{\partial x} = \nu_c \frac{\partial \mu_c}{\partial x} + \nu_a \frac{\partial \mu_a}{\partial x}. \quad (18)$$

Upon substitution of Eqs. (15) and (18) into Eq. (12), the dissipation function becomes (Olsen et al., 2000):

$$\Phi = -q \frac{\partial P}{\partial x} - I \frac{\partial \Psi}{\partial x} - J_s^d \frac{\partial \mu_s}{\partial x} \quad (19)$$

and the corresponding coupled flux equations can be written as follows:

$$q = -L_{11} \frac{\partial P}{\partial x} - L_{12} \frac{\partial \Psi}{\partial x} - L_{13} \frac{\partial \mu_s}{\partial x} \quad (20a)$$

$$I = -L_{21} \frac{\partial P}{\partial x} - L_{22} \frac{\partial \Psi}{\partial x} - L_{23} \frac{\partial \mu_s}{\partial x} \quad (20b)$$

$$J_s^d = -L_{31} \frac{\partial P}{\partial x} - L_{32} \frac{\partial \Psi}{\partial x} - L_{33} \frac{\partial \mu_s}{\partial x}. \quad (20c)$$

Alternative forms to Eqs. (19) and (20a)–(20c) also have appeared in the literature (e.g., Lu et al., 2004; Olsen, 2001), whereby the chemical potential gradients in the dissipation function (Eq. (19)) and the resulting flux expressions (Eqs. (20a)–(20c)) are replaced by gradients in chemico-osmotic pressure, π . These alternative forms result by first substituting Eqs. (7) and (16) into Eq. (18) to obtain the following expression for the gradient in chemical potential of the salt:

$$\frac{\partial \mu_s}{\partial x} = C_s \left(RT \frac{\partial C_c}{\partial x} + RT \frac{\partial C_a}{\partial x} \right) = C_s \left(\nu RT \frac{\partial C_s}{\partial x} \right) \quad (21)$$

where $\nu = \nu_a + \nu_c$. The parenthetical term in Eq. (21) is recognized as the differential form of the van't Hoff equation for π of a dilute solution containing a single, binary electrolyte. The van't Hoff equation may be written in general terms for a solution containing M ionic species as follows (Malusis and Shackelford, 2002c):

$$\pi = RT \sum_{i=1}^M C_i. \quad (22)$$

For the case of a single, binary electrolyte (i.e., $M=2$), Eq. (22) reduces to the following simplified form:

$$\pi = RT(C_a + C_c) = (\nu_a + \nu_c)RTC_s = \nu RTC_s. \quad (23)$$

Thus, substitution of Eq. (21) and the differential form of Eq. (23) into Eq. (19) yields the following alternative expression for the dissipation function:

$$\Phi = -q \frac{\partial P}{\partial x} - I \frac{\partial \Psi}{\partial x} - \frac{J_s^d \partial \pi}{C_s \partial x} \quad (24)$$

and the corresponding alternative forms of Eqs. (20a)–(20c) can be written as follows:

$$q = -L_{11} \frac{\partial P}{\partial x} - L_{12} \frac{\partial \Psi}{\partial x} - L_{13} \frac{\partial \pi}{\partial x} \quad (25a)$$

$$I = -L_{21} \frac{\partial P}{\partial x} - L_{22} \frac{\partial \Psi}{\partial x} - L_{23} \frac{\partial \pi}{\partial x} \quad (25b)$$

$$\frac{J_s^d}{C_s} = -L_{31} \frac{\partial P}{\partial x} - L_{32} \frac{\partial \Psi}{\partial x} - L_{33} \frac{\partial \pi}{\partial x}. \quad (25c)$$

Comparison of Eqs. (24) and (25a)–(25c) with Eqs. (19) and (20a)–(20c), respectively, reveals that Eqs. (24) and (25a)–(25c) are presented in terms of gradients in chemico-osmotic pressure, whereas Eqs. (19) and (20a)–(20c) are presented in terms of gradients in chemical potentials. Also, the diffusive salt flux terms in Eqs. (24) and (25c) are normalized with respect to the salt concentration, whereas those in Eqs. (19) and (20c) are not. Nonetheless, the two sets of equations are identical in the sense that the resulting fluxes will be the same regardless of whether the fluxes are computed based on the gradient in chemical potential or the gradient in chemico-osmotic pressure.

The single-salt formulations given by Eqs. (20a)–(20c) and Eqs. (25a)–(25c) are simplified relative to Eqs. (13a)–(13d) or (14a)–(14d) in that they consist of three equations with six unique phenomenological coefficients rather than four equations with nine unique phenomenological coefficients. When using the simplified formulations, the chemical potential of the salt, μ_s , in Eqs. (20a)–(20c) or the chemico-osmotic pressure, π , in Eqs. (25a)–(25c) must be defined properly to capture the contributions of both the cationic species and the anionic species (i.e., see Eqs. (17) and (23)). The individual diffusive fluxes of the cation and anion are not expressed directly in Eqs. (20a)–(20c) or Eqs. (25a)–(25c), but can be determined readily using Eq. (15).

Single-salt formulations such as those described above are valid only when no additional solutes are present in the free solution (i.e., the solution in the pore spaces available for solute migration). Such a condition does not exist when ion exchange of the salt cation and/or the salt anion is occurring within the membrane. Thus, while the single-salt formulations are applicable for describing the coupled fluxes in the absence of ion exchange processes, a more rigorous formulation is required for describing coupled fluxes under transient conditions for ion exchanging clay membranes in which the migrating salt ions exchange with other ions held electrostatically to the solid phase of the membrane (e.g., see Malusis and Shackelford, 2002c; Van Impe et al., 2003). In addition, electrolyte solutions passing through natural or engineered clay barriers often contain more than one cationic or anionic species. For these more complex cases, expanded formulations can be developed following the general framework given by Eqs. (6a)–(6c) or (8a)–(8c).

3.2. Relationships between phenomenological coefficients and soil properties

A practical limitation regarding the utility of the coupled flux equations expressed in terms of the phenomenological coefficients, L_{ij} , for describing solute migration through clay membranes is that the physical relevance of the various L_{ij} is not readily apparent. As a result, considerable effort has been devoted to expressing L_{ij} in terms of familiar and measurable soil properties, thereby rendering equations more amenable for direct application to practical problems involving natural or

engineered soil systems (e.g., Bader and Kooi, 2005; Dominijanni and Manassero, 2005; Lu et al., 2004; Malusis and Shackelford, 2002c; Manassero and Dominijanni, 2003; Yeung, 1990; Yeung and Mitchell, 1993). Thus, the purpose of this section is to provide a review of the various definitions for the L_{ij} that have been proposed. The review is presented chronologically with respect to the development in order to maintain some historical context upon which the various developments have been promulgated.

3.2.1. Single-salt (single-cation, single-anion) formulation of Yeung (1990)

The first comprehensive attempt to express the coefficients L_{ij} in terms of measurable soil properties was performed by Yeung (1990) for the single-salt system represented by Eqs. (14a)–(14d). Yeung (1990) developed relationships for L_{ij} by equating Eqs. (14a)–(14d) to fundamental flux laws (e.g., Darcy's law, Fick's law, Ohm's law, etc.) for special cases of laboratory tests in which specific fluxes and/or gradients were eliminated by design. These relationships may be written conveniently in matrix form as follows (Malusis and Shackelford, 2002c):

$$\begin{bmatrix} L_{11} & L_{12} & L_{13} & L_{14} \\ L_{21} & L_{22} & L_{23} & L_{24} \\ L_{31} & L_{32} & L_{33} & L_{34} \\ L_{41} & L_{42} & L_{43} & L_{44} \end{bmatrix} = \begin{bmatrix} \frac{k_h}{\gamma_w} + \frac{k_e^2}{n\sigma_e^*} & k_e & -\frac{\omega C_c k_h}{\gamma_w} + \frac{k_e C_c u_c^*}{\sigma_e^*} & -\frac{\omega C_a k_h}{\gamma_w} - \frac{k_e C_a u_a^*}{\sigma_e^*} \\ k_e & n\sigma_e^* & \frac{n C_c u_c^*}{RT} & -n C_a u_a^* \\ -\frac{\omega C_c k_h}{\gamma_w} + \frac{k_e C_c u_c^*}{\sigma_e^*} & n C_c u_c^* & \frac{n D_c^* C_c}{RT} & 0 \\ -\frac{\omega C_a k_h}{\gamma_w} - \frac{k_e C_a u_a^*}{\sigma_e^*} & -n C_a u_a^* & 0 & \frac{n D_a^* C_a}{RT} \end{bmatrix} \quad (26)$$

where k_h is hydraulic conductivity, γ_w is the unit weight of water ($=\rho_w g$, where ρ_w = density of water and g = gravitational acceleration), k_e is electro-osmotic conductivity, σ_e^* is the effective electrical conductivity of the porous medium, u_c^* and u_a^* are effective ionic mobilities of the cation and anion, D_c^* and D_a^* are effective self-diffusion coefficients for the cation and anion, and n is the total soil porosity. The expressions for L_{ij} in Eq. (26) have been modified from those presented by Yeung (1990) in that the expressions in Eq. (26) are defined based on the total cross-sectional area of the soil, whereas the original expressions for L_{ij} given by Yeung (1990) were defined based on the cross-sectional area of the voids (see also Mitchell and Soga, 2005). The original L_{ij} expressions of Yeung (1990) are obtained readily by dividing each L_{ij} in Eq. (26) by n . The relationship $L_{34}=L_{43}=0$ in Eq. (26) is based on the assumption of "infinite-dilution", whereby the solutes are dispersed within the solution such that no electrical interactions occur among the migrating solutes (Robinson and Stokes, 1959).

The "effective" coefficients (i.e., u^* , D^* , σ_e^*) in Eq. (26) account for the tortuous nature of solute migration pathways in porous media. These coefficients typically are defined relative to the corresponding aqueous or free-solution coefficients (i.e., u_o , D_o , and σ_{e_o}) as follows (Alshawabkeh and Acar, 1996):

$$u^* = \tau_a u_o; \quad D^* = \tau_a D_o; \quad \sigma_e^* = \tau_a \sigma_{e_o} \quad (27)$$

where τ_a is a dimensionless apparent tortuosity factor ($0 \leq \tau_a \leq 1$) that accounts for the geometry associated with the interconnection of the individual pores within the porous matrix as well as any other factors that may affect solute migration, including solute–solute and solute–solvent interactions (Shackelford and Daniel, 1991). Of course, as previously noted, solute–solute interactions should not exist for the limiting condition of infinite dilution. The self-diffusion coefficients of the cation and the anion, D_c^* and D_a^* , respectively, are related to the respective individual ionic mobilities, u_c^* and u_a^* , by the Nernst equation, which can be written in general form for any ionic species i as follows:

$$D_i^* = \frac{u_i^* RT}{F|z_i|} \quad (28)$$

where F is Faraday's constant ($=96,500$ C/equivalent) and z_i is the charge of species i . Also, the effective electrical conductivity, σ_e^* , may be expressed in general form for a system containing M ionic species as follows (Alshawabkeh and Acar, 1996):

$$\sigma_e^* = F \cdot \sum_{i=1}^M |z_i| C_i u_i^* \quad (29)$$

Therefore, Eq. (29) reduces to the following form for the single-cation and single-anion system:

$$\sigma_e^* = F (|z_c| C_c u_c^* + |z_a| C_a u_a^*) \quad (30)$$

The previously noted dependency of ω on salt concentration complicates the use of ω in practical applications, because chemico-osmosis occurs only when there is a concentration gradient in or across a membrane, such that ω generally also will vary spatially within the membrane (see Neuzil and Provost, 2009). As a result, values of ω used in Eq. (26) and all subsequent coupled flux expressions are actually apparent values that lie somewhere between the maximum and minimum ω that can occur based on the range of concentrations existing within or across the membrane.

3.2.2. Extension of Yeung (1990) formulation for general case of M solutes

As stated previously, the formulation of Yeung (1990) is applicable for systems containing a single cation and a single anion and does not account for any additional solutes that may be present in the source solution or introduced into the pore fluid as the result of ion exchange. However, Malusis and Shackelford (2002c) showed that the Yeung (1990) approach can be extended to account for the presence of additional ionic species by utilizing Eqs. (8a)–(8c) with the following general definitions of L_{ij} :

$$L_{11} = \frac{k_h}{\gamma_w} + \frac{k_e^2}{n\sigma_e^*} \quad (31a)$$

$$L_{12} = L_{21} = k_e \quad (31b)$$

$$L_{22} = n\sigma_e^* \quad (31c)$$

$$L_{1,j+2} = L_{j+2,1} = -\frac{\omega C_j k_h}{\gamma_w} \pm \frac{k_e C_j u_j^*}{\sigma_e^*} \quad (31d)$$

$$L_{2,j+2} = L_{j+2,2} = \pm nC_j u_j^* \tag{31e}$$

$$L_{j+2,i+2} \Big|_{i \neq j} = 0 \tag{31f}$$

$$L_{j+2,i+2} \Big|_{i=j} = \frac{nD_j^* C_j}{RT} \tag{31g}$$

where the “±” operator in Eqs. (31d) and (31e) is positive if species *j* is a cation and negative if species *j* is an anion.

3.2.3. Single-solute formulation of *Manassero and Dominijanni (2003)*

Subsequent to *Yeung (1990)* and simultaneous with *Malusis and Shackelford (2002c)*, *Manassero and Dominijanni (2003)* developed relationships for *L_{ij}* that are applicable for use in Eqs. (11a)–(11b) for a single-solute system. These relationships may be written for dilute solutions (i.e., *V_w ≈ 1*) as follows:

$$\begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} = \begin{bmatrix} \frac{k_h}{\gamma_w} & -\frac{\omega C_s k_h}{\gamma_w} \\ -\frac{\omega C_s k_h}{\gamma_w} & \frac{nD_s^* C_s}{RT} + \frac{C_s^2 k_h \omega^2}{\gamma_w} \end{bmatrix} \tag{32}$$

Substitution of the relationships in Eq. (32) into Eqs. (11a) and (11b) yields the following expressions for coupled liquid and solute flux (*Manassero and Dominijanni, 2003*):

$$q = -\frac{k_h}{\gamma_w} \frac{\partial P}{\partial x} + \frac{\omega k_h}{\gamma_w RT} \frac{\partial C_s}{\partial x} \tag{33a}$$

$$J_s^d = \frac{\omega C_s k_h}{\gamma_w} \frac{\partial P}{\partial x} - \left(\frac{nD_s^*}{RT} + \frac{C_s k_h \omega^2}{\gamma_w} \right) RT \frac{\partial C_s}{\partial x} \tag{33b}$$

3.2.4. Single-salt formulation of *Lu et al. (2004)* for zero-current condition

Eqs. (33a) and (33b) were developed for a system containing a single, uncharged solute, but are similar to those presented by *Lu et al. (2004)* for the single-salt formulation given by Eqs. (25a)–(25c) under the specific condition that no current is applied across the soil (i.e., *I = 0*). Under this condition, Eq. (25b) can be rearranged as follows:

$$\frac{\partial \Psi}{\partial x} \Big|_{I=0} = -\frac{L_{21}}{L_{22}} \frac{\partial P}{\partial x} - \frac{L_{23}}{L_{22}} \frac{\partial \pi}{\partial x} \tag{34}$$

Substitution of Eq. (34) into Eqs. (25a) and (25c) yields the following expressions (*Lu et al., 2004*):

$$q \Big|_{I=0} = -L_P \frac{\partial P}{\partial x} - L_{PD} \frac{\partial \pi}{\partial x} \tag{35a}$$

$$\frac{J_s^d}{C_s} \Big|_{I=0} = -L_{DP} \frac{\partial P}{\partial x} - L_D \frac{\partial \pi}{\partial x} \tag{35b}$$

where *L_P = L₁₁ - L₁₂²/L₂₂*, *L_{PD} = L_{DP} = L₁₃ - L₁₂L₂₃/L₂₂*, and *L_D = L₃₃ - L₁₂L₂₃/L₂₂*. The matrix of phenomenological coefficients given by *Lu et al. (2004)* for Eqs. (35a) and (35b) can be

expressed in terms of the total cross-sectional area of the soil as follows:

$$\begin{bmatrix} L_P & L_{PD} \\ L_{DP} & L_D \end{bmatrix} = \begin{bmatrix} \frac{k_h}{\gamma_w} & -\frac{\omega k_h}{\gamma_w} \\ -\frac{\omega k_h}{\gamma_w} & n\beta + \frac{k_h \omega^2}{\gamma_w} \end{bmatrix} \tag{36}$$

where *β* is the coefficient of solute permeability at zero volume flux, as defined by *Katchalsky and Curran (1965)*. Substitution of the relationships in Eq. (36) and the differential form of Eq. (23) into Eqs. (35a) and (35b) yields the following expressions:

$$q \Big|_{I=0} = -\frac{k_h}{\gamma_w} \frac{\partial P}{\partial x} - \frac{\omega k_h}{\gamma_w} \nu RT \frac{\partial C_s}{\partial x} \tag{37a}$$

$$J_s^d \Big|_{I=0} = -\frac{C_s \omega k_h}{\gamma_w} \frac{\partial P}{\partial x} - \left(n\beta C_s + \frac{C_s k_h \omega^2}{\gamma_w} \right) \nu RT \frac{\partial C_s}{\partial x} \tag{37b}$$

Under the condition of zero volume flux (i.e., *q = 0*), Eq. (37a) can be rearranged as follows:

$$\frac{\partial P}{\partial x} \Big|_{I=q=0} = -\omega \nu RT \frac{\partial C_s}{\partial x} \tag{38}$$

Thus, substitution of Eq. (38) into Eq. (37b) yields the following expression for *J_s^d* when *I = q = 0*:

$$J_s^d \Big|_{I=q=0} = -n\beta \nu RT C_s \frac{\partial C_s}{\partial x} \tag{39}$$

Furthermore, the form of Eq. (39) is the same as that of Fick’s first law for salt diffusion, or

$$J_s^d = -nD_s^* \frac{\partial C_s}{\partial x} \tag{40}$$

where *D_s^{*}* is the effective salt-diffusion coefficient as defined by the Nernst–Einstein equation, or (*Shackelford, 1989*):

$$D_s^* = \frac{D_c^* D_a^* (|z_c| + |z_a|)}{D_c^* |z_c| + D_a^* |z_a|} \tag{41}$$

Comparison of Eq. (40) with Eq. (39) reveals that *β* can be expressed in terms of *D_s^{*}* as follows:

$$\beta = \frac{D_s^*}{\nu RT C_s} \tag{42}$$

Lastly, substitution of Eq. (42) into Eq. (37b) yields the following set of coupled flux equations for the single-salt case under a zero-current condition (*I = 0*):

$$q \Big|_{I=0} = -\frac{k_h}{\gamma_w} \frac{\partial P}{\partial x} + \frac{\omega k_h}{\gamma_w} \nu RT \frac{\partial C_s}{\partial x} = -\frac{k_h}{\gamma_w} \frac{\partial P}{\partial x} + \frac{\omega k_h}{\gamma_w} \frac{\partial \pi}{\partial x} \tag{43a}$$

$$J_s^d \Big|_{I=0} = \frac{\omega C_s k_h}{\gamma_w} \frac{\partial P}{\partial x} - \left(\frac{nD_s^*}{\nu RT} + \frac{C_s k_h \omega^2}{\gamma_w} \right) \nu RT \frac{\partial C_s}{\partial x} \tag{43b}$$

Therefore, the single-salt formulation given by Eqs. (43a) and (43b) for the case in which $l=0$ is nearly identical to the formulation of Manassero and Dominijanni (2003) for a single, uncharged solute in Eqs. (33a) and (33b). The only difference between the two formulations is that the parameter ν is included in the second terms of Eqs. (43a) and (43b) (see Bader and Kooi, 2005; Dominijanni and Manassero, 2005), which reflects that a binary salt is not a single solute but rather is composed of two species (i.e., cation and anion).

4. Discussion

4.1. Counter diffusion versus salt diffusion

As noted by Manassero and Dominijanni (2003), the single-salt formulation of Yeung (1990) given by Eqs. (14a)–(14d) and the coefficients in Eq. (26) does not reduce to Eqs. (43a) and (43b) when $l=0$. This apparent discrepancy can be shown by first setting $l=0$ in Eq. (14b) and rearranging to yield the following expression for the gradient in electrical potential:

$$\frac{\partial \Psi}{\partial x} \Big|_{l=0} = -\frac{L_{21}}{L_{22}} \frac{\partial P}{\partial x} - \frac{L_{23} RT}{L_{22} C_c} \frac{\partial C_c}{\partial x} - \frac{L_{24} RT}{L_{22} C_a} \frac{\partial C_a}{\partial x}. \quad (44)$$

Substitution of Eq. (44) and the relationships for L_{ij} (Eq. (26)) into Eqs. (14a), (14c), (14d) yields

$$q \Big|_{l=0} = -\frac{k_h}{\gamma_w} \frac{\partial P}{\partial x} + \frac{\omega k_h}{\gamma_w} RT \left(\frac{\partial C_c}{\partial x} + \frac{\partial C_a}{\partial x} \right) \quad (45a)$$

$$J_c^d \Big|_{l=0} = \frac{\omega C_c k_h}{\gamma_w} \frac{\partial P}{\partial x} - \left(\frac{n D_c^*}{RT} - \frac{n C_c u_c^{*2}}{\sigma_e^*} \right) RT \frac{\partial C_c}{\partial x} - \left(\frac{n C_c u_c^* u_a^*}{\sigma_e^*} \right) RT \frac{\partial C_a}{\partial x} \quad (45b)$$

$$J_a^d \Big|_{l=0} = \frac{\omega C_a k_h}{\gamma_w} \frac{\partial P}{\partial x} - \left(\frac{n C_a u_a^* u_c^*}{\sigma_e^*} \right) RT \frac{\partial C_c}{\partial x} - \left(\frac{n D_a^*}{RT} - \frac{n C_a u_a^{*2}}{\sigma_e^*} \right) RT \frac{\partial C_a}{\partial x}. \quad (45c)$$

Furthermore, the requirement for electroneutrality in solution for the single-salt case can be expressed as follows:

$$|z_c| C_c = |z_a| C_a \quad (46)$$

or, in differential form,

$$|z_c| \frac{\partial C_c}{\partial x} = |z_a| \frac{\partial C_a}{\partial x}. \quad (47)$$

Also, based on Eq. (28), the effective ionic mobilities of the salt cation and salt anion can be written as follows:

$$u_c^* = \frac{D_c^* F |z_c|}{RT}; \quad u_a^* = \frac{D_a^* F |z_a|}{RT}. \quad (48)$$

Substitution of Eqs. (29), (41), (47), and (48) and the differential form of Eq. (23) into Eqs. (45a)–(45c) yields

$$q \Big|_{l=0} = -\frac{k_h}{\gamma_w} \frac{\partial P}{\partial x} + \frac{\omega k_h \nu RT}{\gamma_w} \frac{\partial C_s}{\partial x} = -\frac{k_h}{\gamma_w} \frac{\partial P}{\partial x} + \frac{\omega k_h}{\gamma_w} \frac{\partial \pi}{\partial x} \quad (49a)$$

$$J_c^d \Big|_{l=0} = \frac{\omega C_c k_h}{\gamma_w} \frac{\partial P}{\partial x} - n D_s^* \frac{\partial C_c}{\partial x} \quad (49b)$$

$$J_a^d \Big|_{l=0} = \frac{\omega C_a k_h}{\gamma_w} \frac{\partial P}{\partial x} - n D_s^* \frac{\partial C_a}{\partial x}. \quad (49c)$$

Finally, Eqs. (15) and (16) may be substituted into either Eqs. (49b) or (49c) to obtain the following expression for diffusive flux of the salt:

$$J_s^d \Big|_{l=0} = \frac{\omega C_s k_h}{\gamma_w} \frac{\partial P}{\partial x} - n D_s^* \frac{\partial C_s}{\partial x}. \quad (50)$$

The expressions for liquid flux (q) in Eqs. (49a) and (43a) are identical. However, the diffusive salt flux (J_s^d) expressions given by Eqs. (50) and (43b) differ in that the second part of Eq. (43b) includes both a Fickian diffusion term and a chemico-osmotic coupling term, whereas the second part of Eq. (50) includes only the Fickian term. This fundamental difference between Eqs. (43b) and (50) results from the difference between counter diffusion (or inter-diffusion) in which chemical species migrate in opposite directions, versus salt diffusion (or mutual diffusion) in which chemical species migrate in the same direction, as illustrated conceptually in Fig. 2 (e.g., also see Shackelford and Daniel, 1991).

Yeung (1990) defined L_{33} and L_{44} in Eq. (26) by considering a counter-diffusion experiment in the absence of hydraulic and electrical gradients (i.e., $\partial P/\partial x = \partial \Psi/\partial x = 0$), with two diffusion half-cells connected together as shown in Fig. 2a. Although the ion concentrations in the two half-cells are maintained equal (and, thus, $\partial \pi/\partial x = 0$), the cations or anions in the left half-cell are tagged with a radioactive isotope such that counter-diffusion of the radioactive and non-radioactive ions occurs across the boundary between the half-cells to balance the isotopic compositions (Yeung, 1990). Under these conditions, and given that $L_{43} = L_{34} = 0$ (Eq. (26)), Eqs. (14c)–(14d) reduce to the following:

$$J_c^d \Big|_{\frac{\partial P}{\partial x} = \frac{\partial \Psi}{\partial x} = 0} = -L_{33} \frac{RT}{C_c} \frac{\partial C_c}{\partial x} \quad (51a)$$

$$J_a^d \Big|_{\frac{\partial P}{\partial x} = \frac{\partial \Psi}{\partial x} = 0} = -L_{44} \frac{RT}{C_a} \frac{\partial C_a}{\partial x}. \quad (51b)$$

Thus, Eqs. (51a) and (51b) share the same form as Fick's first law, which may be written in general form for the counter-diffusion test conditions assumed by Yeung (1990) as follows:

$$J_j^d = -n D_j^* \frac{\partial C_j}{\partial x} \quad (52)$$

where D_j^* is the effective self-diffusion coefficient of solute species j . Substitution of Eq. (52) into Eqs. (51a) and (51b) yields the definitions of L_{33} and L_{44} given in Eq. (26), i.e.:

$$L_{33} = \frac{n D_c^* C_c}{RT}; \quad L_{44} = \frac{n D_a^* C_a}{RT}. \quad (53)$$

Likewise, the definition of $L_{j+2,i+2}$ (where $i=j$) in Eq. (31g) can be derived using a similar approach as above, since Eq. (31g) represents an extension of the Yeung (1990) formulation for M species.

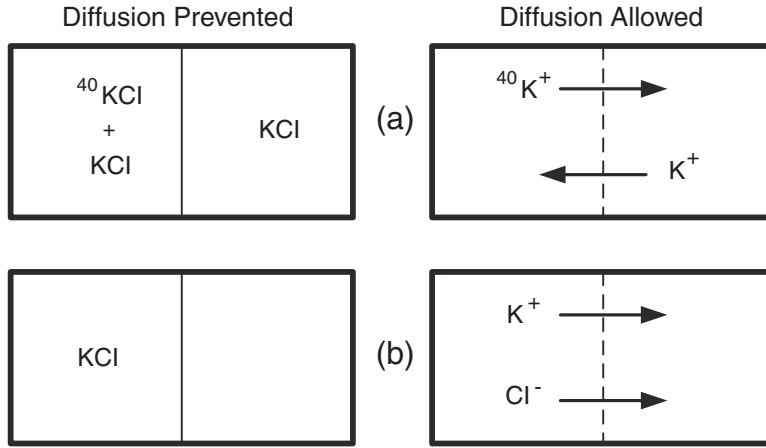


Fig. 2. Difference between (a) counter or self diffusion and (b) salt or mutual diffusion in aqueous systems. Redrawn after Shackelford and Daniel (1991).

Under the counter-diffusion test conditions of Yeung (1990), $\partial P/\partial x$ and $\partial \pi/\partial x$ are both zero. Therefore, the net flux of liquid through the system in Fig. 4a also must be zero (i.e., $q=0$) based on Eq. (49a). However, in a salt-diffusion experiment, such as that illustrated in Fig. 2b, different salt concentrations are maintained on each side of the membrane, such that $\partial \pi/\partial x \neq 0$. As noted by Manassero and Dominijanni (2003) and Lu et al. (2004), both $q=0$ and $\partial P/\partial x=0$ cannot be achieved simultaneously when $\partial \pi/\partial x \neq 0$, unless the soil does not exhibit membrane behavior (i.e., $\omega=0$). This reality is easily illustrated by considering a case in which the salt diffusion experiment in Fig. 2b is conducted with no applied current ($I=0$) and in a closed system, such that liquid flux through the membrane is prohibited ($q=0$). Under these conditions, a hydraulic (pressure) gradient will be induced in response to the applied chemical gradient, as is shown by setting $q=0$ in Eq. (35a) and rearranging to yield the following:

$$\frac{\partial P}{\partial x} \Big|_{q=I=0} = -\frac{L_{PD}}{L_P} \frac{\partial \pi}{\partial x} \quad (54)$$

or, upon substitution of the relationships for L_{PD} and L_P in Eq. (36), as follows:

$$\frac{\partial P}{\partial x} \Big|_{q=I=0} = \omega \frac{\partial \pi}{\partial x} \quad (55)$$

Furthermore, upon substitution of Eq. (42) into Eq. (36), the coefficient L_D may be written as follows:

$$L_D = \frac{nD_s^*}{\nu RT} + \frac{C_s k_h \omega^2}{\gamma_w} \quad (56)$$

The expression for L_D in Eq. (56) differs from the definitions of L_{33} and L_{44} in Eq. (53) in that L_D includes both a Fickian diffusion term and a chemico-osmotic coupling term, whereas L_{33} and L_{44} include only the Fickian term. This difference between Eqs. (56) and (53) represents a fundamental difference between the counter-diffusion formulation of Yeung (1990) and the salt-diffusion formulation of Lu et al. (2004).

The significance of the discrepancy noted above may be examined by considering the results of laboratory experiments conducted by Malusis et al. (2001) and Malusis and Shackelford (2002a,b) for simultaneous measurement of ω and effective diffusion coefficients in the absence of electrical current ($I=0$) for a manufactured, bentonite-based hydraulic containment barrier known as a geosynthetic clay liner (GCL). The testing conditions utilized in these studies were identical to those of the theoretical salt-diffusion experiment considered in the derivation of Eqs. (55) and (56). The GCL specimens were confined in a closed testing cell with fixed-volume reservoirs at the specimen boundaries. Diffusion testing was performed by flushing a salt (KCl) across the top specimen boundary and de-ionized water across the bottom specimen boundary using customized syringe pumps with custom actuators designed to prevent liquid flux through the specimens (i.e., $q=0$). Once steady-state conditions were achieved in the experiments, the differential pressures induced across the GCL specimens (ΔP) in response to the known differences in chemico-osmotic pressure ($\Delta \pi$) were used to compute steady-state values of ω (i.e., ω_{ss}) using the following form of Eq. (54) (Malusis and Shackelford, 2002a):

$$\omega_{ss} = \frac{\Delta P}{\Delta \pi} \Big|_{q=I=0} \quad (57)$$

However, effective diffusion coefficients for the salt cation (K^+) and salt anion (Cl^-) at steady state were determined based on the counter-diffusion formulation given by Eqs. (49a)–(49c), rather than the salt-diffusion formulation given by Eqs. (43a) and (43b) (Malusis and Shackelford, 2002b). Under steady-state conditions, the differentials in Eqs. (49b) and (49c) can be replaced with differences, as follows:

$$J_{c,ss}^d \Big|_{I=0} = \frac{\omega_{ss} C_c k_h \Delta P}{\gamma_w \Delta x} - nD_s^* \frac{\Delta C_c}{\Delta x} \quad (58a)$$

$$J_{a,ss}^d \Big|_{I=0} = \frac{\omega_{ss} C_a k_h \Delta P}{\gamma_w \Delta x} - nD_s^* \frac{\Delta C_a}{\Delta x} \quad (58b)$$

Also, since $q=0$, Eq. (57) may be substituted into Eqs. (58a), (58b) to yield the following equations for diffusive flux at steady state (Malusis and Shackelford, 2002b):

$$J_{c,ss}^d \Big|_{I=q=0} = -nD_{\omega}^* \frac{\Delta C_c}{\Delta X}; \quad J_{a,ss}^d \Big|_{I=q=0} = -nD_{\omega}^* \frac{\Delta C_a}{\Delta X} \quad (59)$$

where D_{ω}^* is a coupled salt-diffusion coefficient given by

$$D_{\omega}^* = D_s^* - \frac{\omega^2 (\bar{C}_a + \bar{C}_c) k_h RT}{n\gamma_w} \quad (60)$$

The concentrations $\bar{C}_a (= \Delta C_a/2)$ and $\bar{C}_c (= \Delta C_c/2)$ in Eq. (60) are the arithmetic mean molar concentrations of the anion and cation, respectively, across the membrane (Fritz, 1986; Katchalsky and Curran, 1965; Whitworth and Fritz, 1994).

Eqs. (59) and (60) suggest that salt-diffusion coefficients measured for clay membranes under no-flow ($q=0$) and zero-current ($I=0$) conditions are not true salt-diffusion coefficients, D_s^* , but rather are coupled diffusion coefficients, D_{ω}^* . On the basis of Eq. (60), D_{ω}^* would always be less than D_s^* when $\omega > 0$. For example, D_{ω}^* values for the GCL specimens tested by Malusis and Shackelford (2002b) are lower than the corresponding D_s^* values for a given membrane efficiency, as shown in Fig. 3a. However, Eq. (60) is derived from the counter-diffusion formulation given by Eqs. (49a)–(49c) and, therefore, is not the proper expression for the salt-diffusion conditions imposed in the experiments.

A more appropriate formulation for salt-diffusion testing conditions is the salt-diffusion formulation given by Eqs. (43a) and (43b). For experiments in which $q=I=0$, Eqs. (15), (16), and (43a) may be substituted into Eq. (43b) to yield the following diffusive flux equations for the cation and anion:

$$J_c^d \Big|_{q=I=0} = -nD_s^* \frac{\partial C_c}{\partial X}; \quad J_a^d \Big|_{q=I=0} = -nD_s^* \frac{\partial C_a}{\partial X} \quad (61)$$

Thus, at steady state, Eq. (61) becomes

$$J_{c,ss}^d \Big|_{q=I=0} = -nD_s^* \frac{\Delta C_c}{\Delta X}; \quad J_{a,ss}^d \Big|_{q=I=0} = -nD_s^* \frac{\Delta C_a}{\Delta X} \quad (62)$$

On the basis of Eq. (62), salt-diffusion coefficients measured for a clay membrane at steady state under $q=I=0$ conditions are, in fact, true salt-diffusion coefficients, D_s^* , rather than coupled-diffusion coefficients, D_{ω}^* , as defined in Eq. (59). Therefore, the values of D_{ω}^* in Fig. 3a are the true D_s^* values for the GCL specimens, whereas the D_s^* values in Fig. 3a (which were computed using Eq. (60)) are artifacts of the counter-diffusion assumption inherent in Eq. (59). Although the differences between D_{ω}^* and D_s^* for the GCL specimens in Fig. 3a increased as the source KCl concentration, C_o , decreased, due to an increase in ω with decreasing C_o (see Fig. 3b), the overall differences between D_{ω}^* and D_s^* were relatively small (<12%; see Fig. 3c) for the range of ω exhibited by the specimens ($\omega \leq 0.63$).

4.2. Generalized salt-diffusion formulation

A generalized formulation for M solutes that is based on the assumption of salt diffusion rather than counter diffusion can

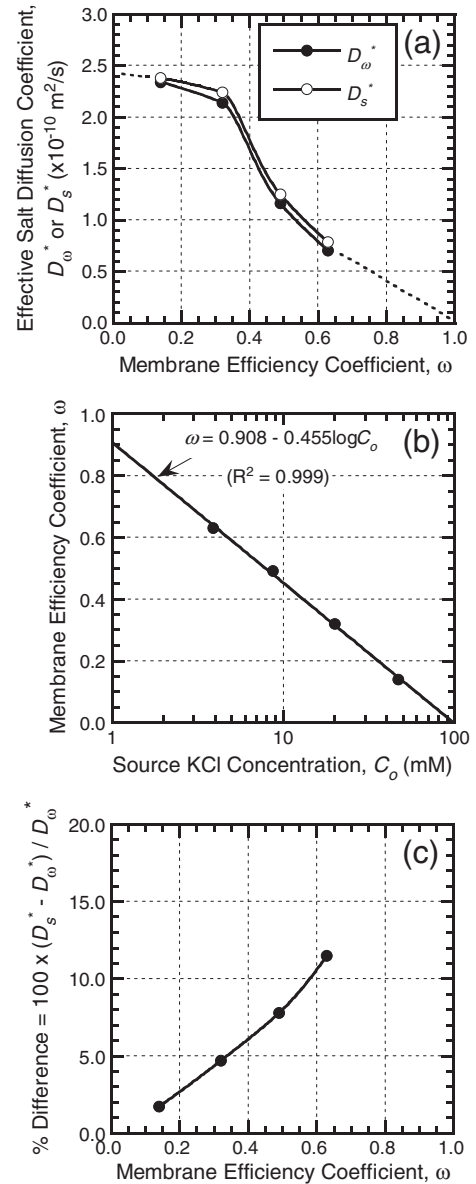


Fig. 3. Diffusion test results for GCL specimens with KCl solutions: (a) D_{ω}^* and D_s^* values (derived from the counter-diffusion formulation given by Eqs. (59)–(60)) as a function of membrane efficiency, ω ; (b) relationship between ω and source KCl concentration, C_o ; and (c) percent differences between D_{ω}^* and D_s^* as a function of ω . Replotted after Malusis and Shackelford (2002b).

be obtained by deriving an alternative definition for $L_{j+2,i+2}$ (where $i=j$) in Eq. (31g) based on the experimental conditions of Malusis et al. (2001) and Malusis and Shackelford (2002a,b) described above. Specifically, we set $I=0$ in Eq. (8b) and rearrange to yield the following expression for $\partial \Psi / \partial x$:

$$\frac{\partial \Psi}{\partial x} \Big|_{I=0} = -\frac{L_{21}}{L_{22}} \frac{\partial P}{\partial x} - \sum_{i=1}^M \frac{L_{2,i+2}}{L_{22}} \frac{RT}{C_i} \frac{\partial C_i}{\partial x} \quad (63)$$

Substitution of Eqs. (31a)–(31e) and Eq. (63) into Eqs. (8a), (8c) yields

$$q|_{l=0} = -\frac{k_h}{\gamma_w} \frac{\partial P}{\partial x} + \left(\frac{\omega k_h RT}{\gamma_w} \right) \sum_{i=1}^M \frac{\partial C_i}{\partial x} \quad (64a)$$

$$J_j^d|_{l=0} = \frac{\omega C_j k_h}{\gamma_w} \frac{\partial P}{\partial x} - \sum_{i=1}^M \left[\left(L_{j+2,i+2} \pm \frac{n C_j C_i u_j^* u_i^*}{\sigma_e^*} \right) \frac{RT}{C_i} \frac{\partial C_i}{\partial x} \right] \quad (64b)$$

where the “±” operator is positive when species *j* and species *i* have opposite charges (i.e., species *j* is a cation and species *i* is an anion, or vice versa) and negative when species *j* and species *i* have like charges (i.e., species *j* and species *i* are both cations or both anions). Furthermore, setting *q* = 0 in Eq. (64a) results in the following expression for ∂*P*/∂*x*:

$$\frac{\partial P}{\partial x} \Big|_{q=0} = \omega \frac{\partial \pi}{\partial x} = \omega \left[RT \sum_{i=1}^M \frac{\partial C_i}{\partial x} \right] \quad (65)$$

where the term in brackets represents the differential form of the van't Hoff expression for chemico-osmotic pressure (*π*) of a solution containing *M* species (see Eq. (23)). Thus, when *q* = 0, Eq. (64b) becomes

$$J_j^d \Big|_{l=0} = \frac{\omega^2 C_j k_h}{\gamma_w} \frac{\partial \pi}{\partial x} - \sum_{i=1}^M \left[\left(L_{j+2,i+2} \pm \frac{n C_j C_i u_j^* u_i^*}{\sigma_e^*} \right) \frac{RT}{C_i} \frac{\partial C_i}{\partial x} \right]. \quad (66)$$

Comparison of Fick's first law with Eq. (66) yields the following expression:

$$-n D_{sj}^* \frac{\partial C_j}{\partial x} = \frac{\omega^2 C_j k_h}{\gamma_w} \frac{\partial \pi}{\partial x} - \sum_{i=1}^M \left[\left(L_{j+2,i+2} \pm \frac{n C_j C_i u_j^* u_i^*}{\sigma_e^*} \right) \frac{RT}{C_i} \frac{\partial C_i}{\partial x} \right] \quad (67)$$

where *D_{sj}^{*}* is the effective salt-diffusion coefficient of species *j* that accounts for the interaction between species *j* and oppositely charged solutes traveling together such that electro-neutrality is maintained. This interaction is characterized by electrical potential gradients generated between cations and anions in response to the different ionic mobility of each species, which slows the faster moving ions and speeds the slower moving ions (Robinson and Stokes, 1959; Shackelford and Daniel, 1991). In general, *D_{sj}^{*}* for any species *j* may be expressed in general form as a function of the self-diffusion coefficients of all species as follows (Malusis and Shackelford, 2004a):

$$D_{sj}^* = D_j^* \pm \frac{D_j^* C_j |z_j|}{\partial C_j} \times \frac{(\sum D_-^* |z_-| \partial C_- - \sum D_+^* |z_+| \partial C_+)}{(\sum D_-^* |z_-|^2 C_- + \sum D_+^* |z_+|^2 C_+)} \quad (68)$$

where the subscripts + and – represent cations and anions, respectively, and the “±” operator is positive when species *j* is

a cation. Substitution of Eqs. (28) and (29) into Eq. (68) yields the following expression:

$$D_{sj}^* \frac{\partial C_j}{\partial x} = D_j^* \frac{\partial C_j}{\partial x} \pm \sum_{i=1}^M \frac{C_j u_j^* u_i^* RT}{\sigma_e^*} \frac{\partial C_i}{\partial x} \quad (69)$$

where the “±” term is positive when species *j* and species *i* have opposite charges and negative when species *j* and species *i* have like charges. Finally, substitution of Eqs. (31f) and (69) into Eq. (67) yields the following generalized expression:

$$L_{j+2,i+2} \Big|_{i=j} = \frac{n D_j^* C_j}{RT} + \frac{\omega^2 C_j^2 k_h}{\gamma_w RT} \frac{\partial \pi}{\partial C_j} = \frac{n D_j^* C_j}{RT} + \frac{\omega^2 C_j^2 k_h}{\gamma_w} \sum_{i=1}^M \frac{\partial C_i}{\partial C_j}. \quad (70)$$

Thus, Eq. (70) replaces Eq. (31g) for use in Eq. (6c) when describing the general case of salt diffusion of *M* solutes through clay membranes, provided that *L_{j+2,i+2}* = 0 for *i* ≠ *j*, as defined by Eq. (31f). Alternatively, Eqs. (31f) and (70) can be replaced by a single expression for *L_{j+2,i+2}* as follows:

$$L_{j+2,i+2} = \delta_{ij} \frac{n D_j^* C_j}{RT} + \frac{\omega^2 C_j C_i k_h}{\gamma_w} \quad (71)$$

where *δ_{ij}* is the Kronecker or Dirac delta function (i.e., *δ_{ij}* = 1 when *i* = *j* and *δ_{ij}* = 0 when *i* ≠ *j*). Eq. (71) is consistent with the definition of *L_{j+2,i+2}* given by Van Impe et al. (2003) for fluxes expressed in terms of the cross-sectional area of the voids.

For the single-cation, single-anion formulation given by Eqs. (14a)–(14d), Eq. (70) can be simplified to obtain new definitions for *L₃₃* (for the cation) and *L₄₄* (for the anion) for salt diffusion applications. In this case, the stoichiometric relationships given by Eqs. (15) and (16) may be substituted into Eq. (70), which yields the following expressions:

$$L_{33} = \frac{n D_c^* C_c}{RT} + \frac{\omega^2 C_c^2 k_h \nu}{\gamma_w \nu_c} \quad (72a)$$

$$L_{44} = \frac{n D_a^* C_a}{RT} + \frac{\omega^2 C_a^2 k_h \nu}{\gamma_w \nu_a}. \quad (72b)$$

These new definitions of *L₃₃* and *L₄₄* replace those in Eq. (26) when modeling problems involving salt diffusion rather than counter diffusion (the remaining coefficients in Eq. (26) do not change).

4.3. Total solute flux expressions

The total solute flux, *J_j*, of a species *j* in the absence of electrical current (i.e., *l* = 0) and mechanical dispersion may be expressed as the combination of advective (hydraulic) flux, *J_j^a* (= *qC_j*) and diffusive flux, *J_j^d*, as follows:

$$J_j = J_j^a + J_j^d = q C_j + J_j^d. \quad (73)$$

In the case of clay membranes, expressions for *J_j* based on Eq. (73) depend upon whether counter diffusion or salt diffusion is assumed in the coupled-flux formulation and whether the formulation is written for individual ionic species, a binary salt, or an uncharged solute. For example, the total molar solute

flux equation presented by [Manassero and Dominijanni \(2003\)](#) for an uncharged solute (denoted by subscript s) may be obtained by substituting Eqs. (33a)–(33b) into Eq. (73), which yields:

$$J_s = (1-\omega)q_h C_s + (1-\omega)q_\pi C_s - nD_s^* \frac{\partial C_s}{\partial x} \quad (74)$$

where q_h and q_π represent hydraulic and chemico-osmotic liquid fluxes, respectively, as follows:

$$q_h = -\frac{k_h}{\gamma_w} \frac{\partial P}{\partial x} \quad (75a)$$

$$q_\pi = \omega \frac{k_h}{\gamma_w} \frac{\partial \pi}{\partial x} = \omega \frac{k_h}{\gamma_w} RT \frac{\partial C_s}{\partial x} \quad (75b)$$

The first term in Eq. (74) is a conventional advective term representing solutes carried by the hydraulic component of the liquid flux, whereas the second term is a chemico-osmotic advective term representing solutes carried by the chemico-osmotic component of the liquid flux. Both of these advective terms are reduced by a factor $1-\omega$ that represents the degree of exclusion of the solute from the membrane pores. The third term is a conventional Fickian diffusive term, where D_s^* is the effective diffusion coefficient for the uncharged solute.

For the case of a single, binary salt (also denoted by subscript s), the total molar flux of salt based on the salt-diffusion formulation of [Lu et al. \(2004\)](#) may be obtained by substituting Eqs. (43a)–(43b) into Eq. (73), which yields an expression identical to Eq. (74). However, in this case, D_s^* is the effective salt-diffusion coefficient as defined by the Nernst–Einstein equation (Eq. (41)), and q_π is given as follows:

$$q_\pi = \omega \frac{k_h}{\gamma_w} \frac{\partial \pi}{\partial x} = \omega \frac{k_h}{\gamma_w} RT \left(\frac{\partial C_c}{\partial x} + \frac{\partial C_a}{\partial x} \right) = \omega \frac{k_h}{\gamma_w} \nu RT \frac{\partial C_s}{\partial x} \quad (76)$$

where ν accounts for the contributions of both the salt cation and the salt anion to the chemico-osmotic pressure of the solution, as discussed previously. Thus, for a given concentration gradient $\partial C_s/\partial x$, q_π for a binary salt is greater than q_π for an uncharged solute by a factor of ν . Alternatively, separate total flux equations for the salt cation (c) and salt anion (a) may be expressed by substituting Eqs. (15) and (16) into Eq. (74), which yields the following expressions:

$$J_c \Big|_{l=0} = (1-\omega)q_h C_c + (1-\omega)q_\pi C_c - nD_s^* \frac{\partial C_c}{\partial x} \quad (77a)$$

$$J_a \Big|_{l=0} = (1-\omega)q_h C_a + (1-\omega)q_\pi C_a - nD_s^* \frac{\partial C_a}{\partial x} \quad (77b)$$

where q_π is as defined in Eq. (76), but also can be expressed solely in terms of the salt cation or salt anion (based on Eq. (16)), as follows:

$$q_\pi = \omega \frac{k_h}{\gamma_w} \frac{\nu}{\nu_c} RT \frac{\partial C_c}{\partial x} = \omega \frac{k_h}{\gamma_w} \frac{\nu}{\nu_a} RT \frac{\partial C_a}{\partial x} \quad (78)$$

Therefore, Eqs. (77a)–(77b) can be written as follows:

$$J_c \Big|_{l=0} = (1-\omega)q_h C_c + (1-\omega) \frac{\omega C_c k_h RT}{\gamma_w} \frac{\nu}{\nu_c} \frac{\partial C_c}{\partial x} - nD_s^* \frac{\partial C_c}{\partial x} \quad (79a)$$

$$J_a \Big|_{l=0} = (1-\omega)q_h C_a + (1-\omega) \frac{\omega C_a k_h RT}{\gamma_w} \frac{\nu}{\nu_a} \frac{\partial C_a}{\partial x} - nD_s^* \frac{\partial C_a}{\partial x} \quad (79b)$$

For the general case of M solutes, the general salt-diffusion formulation for the $l=0$ condition, given by Eqs. (64a) and (64b), may be used to derive a general expression for the total molar flux of a solute species j . Substitution of Eqs. (31f), (69), and (70) into Eq. (64b) yields the following diffusive flux expression:

$$J_j^d \Big|_{l=0} = \frac{\omega C_j k_h \partial P}{\gamma_w \partial x} - nD_{sj}^* \frac{\partial C_j}{\partial x} - \frac{\omega^2 C_j k_h RT}{\gamma_w} \sum_{i=1}^M \frac{\partial C_i}{\partial x} \quad (80)$$

where D_{sj}^* is the effective salt-diffusion coefficient as defined by Eq. (68). Thus, substitution of Eqs. (64a) and (80) into Eq. (73) yields the following expression for the total flux:

$$J_j \Big|_{l=0} = (1-\omega)q_h C_j + (1-\omega)q_\pi C_j - nD_{sj}^* \frac{\partial C_j}{\partial x} \quad (81)$$

where

$$q_\pi = \omega \frac{k_h}{\gamma_w} \frac{\partial \pi}{\partial x} = \omega \frac{k_h}{\gamma_w} RT \sum_{i=1}^M \frac{\partial C_i}{\partial x} \quad (82)$$

Eq. (81), defined here as the molar solute flow per unit total cross-sectional area, is consistent with the general expression given by [Van Impe et al. \(2003\)](#) for total solute flux defined as the molar solute flow per unit cross-sectional area of the voids. In contrast to Eq. (81), the general expression for total solute flux under zero current based on the counter-diffusion formulation of [Yeung \(1990\)](#) is given as follows ([Malusis and Shackelford, 2002c](#)):

$$J_j \Big|_{l=0} = (1-\omega)q_h C_j + q_\pi C_j - nD_{sj}^* \frac{\partial C_j}{\partial x} \quad (83)$$

The difference between the flux expression given by Eq. (81) and the flux expression given by Eq. (83) is that the factor $1-\omega$ is present in the second term (i.e., the q_π term) of Eq. (81), but is absent from the second term of Eq. (83). As a result of this difference, the contribution of chemico-osmotic advection to the total solute flux in Eq. (81) is less than that in Eq. (83) for a clay membrane (i.e., since $1-\omega < 1$).

The significance of the difference between Eqs. (81) and (83) can be examined by considering the column test data reported by [Malusis and Shackelford \(2004b\)](#) for three GCL specimens (length, $L = 10$ mm) using 8.7-mM KCl solutions. The column experiments were conducted in an apparatus similar to that used in the diffusion experiments conducted earlier by [Malusis and Shackelford \(2002b\)](#), except that the apparatus was an open system as opposed to a closed (no-flow) system. The upper and lower specimen boundaries were flushed with

the source KCl solution ($C_o = 8.7$ mM) and distilled water ($C = 0$), respectively, mimicking a constant-source boundary condition at the top and a perfectly-flushing boundary condition at the bottom. Flux breakthrough curves (FBCs) defined by $J_j(x=L,t)$ were determined by measuring the masses of the chemical species (K^+ and Cl^-) emanating from the specimen into the distilled water flushed across the lower boundary (Malusis and Shackelford, 2004b). No pressure was applied at the lower specimen boundary. However, different pressures were applied at the top boundary in each test (0, 6.9, and 69 kPa), resulting in different applied hydraulic gradients, $i_h (= \Delta P/L)$, across the specimens ($i_h = 0, 70.3, \text{ and } 703$).

Predicted FBCs were developed herein for comparison against the measured FBCs of Malusis and Shackelford (2004b) by applying the following continuity expressions for the liquid and solute, respectively (Manassero and Dominijanni, 2003):

$$\frac{\partial q}{\partial x} = 0 \quad (84a)$$

$$-\frac{\partial J_j}{\partial x} = R_{dj} \omega \frac{\partial C_j}{\partial t} \quad (84b)$$

where R_{dj} is the dimensionless retardation factor for species j that accounts for linear, instantaneous, and reversible sorption (e.g., see Shackelford and Daniel, 1991). Substitution of Eq. (49a) into Eq. (84a) yields the following:

$$\frac{\partial}{\partial x} \left(-\frac{k_h}{\gamma_w} \frac{\partial P}{\partial x} + \omega \frac{k_h}{\gamma_w} \frac{\partial \pi}{\partial x} \right) = 0. \quad (85)$$

Also, substitution of Eqs. (75a), (81), and (82) into Eq. (84b) yields the following continuity expression for each solute based on salt diffusion:

$$R_{dj} \omega \frac{\partial C_j}{\partial t} = -\frac{\partial}{\partial x} \left[-(1-\omega) C_j \frac{k_h}{\gamma_w} \frac{\partial P}{\partial x} + (1-\omega) C_j \omega \frac{k_h}{\gamma_w} \frac{\partial \pi}{\partial x} - n D_{sj}^* \frac{\partial C_j}{\partial x} \right] \quad (86)$$

whereas substitution of Eqs. (75a), (82), and (83) into Eq. (84b) yields the following continuity expression for each solute based on counter diffusion:

$$R_{dj} \omega \frac{\partial C_j}{\partial t} = -\frac{\partial}{\partial x} \left[-(1-\omega) C_j \frac{k_h}{\gamma_w} \frac{\partial P}{\partial x} + C_j \omega \frac{k_h}{\gamma_w} \frac{\partial \pi}{\partial x} - n D_{sj}^* \frac{\partial C_j}{\partial x} \right]. \quad (87)$$

This approach differs slightly from that of Malusis and Shackelford (2004b), who developed predicted FBCs using Eq. (87) but assumed a linear pressure distribution within the soil (i.e., $\partial^2 P / \partial x^2 = 0$) and, therefore, did not satisfy the liquid continuity expression given by Eq. (85).

Predicted concentration profiles within the specimens (as a function of time) were determined by simultaneously solving Eqs. (22), (68), (85), and (86) (i.e., the salt-diffusion model) or Eqs. (22), (68), (85) and (87) (i.e., the counter-diffusion model), subjected to the following initial and boundary conditions: $C_j(x,0) = 0$, $C_j(0,t) = C_o$; $C_j(L,t) = 0$; $P(x,0) = 0$, $P(0,t) = P_o$; and $P(L,t) = 0$. The solutions were obtained using the MATLAB (Mathworks, Inc., Natick, MA) partial differential equation solver (pdepe), which converts PDEs to ordinary

differential equations (ODEs) using a piecewise nonlinear Galerkin/Petrov-Galerkin method that is second-order accurate in space (Skeel and Berzins, 1990). The time integration was performed by an ODE solver (ode15s) that changes the time step dynamically. The predicted FBCs then were computed from the predicted concentration profiles using Eq. (81) for the salt-diffusion model and Eq. (83) for the counter-diffusion model.

The FBCs measured for K^+ and Cl^- in each of the three column experiments described above are shown in Fig. 4. Each measured FBC in Fig. 4 is compared against two predicted FBCs based on the salt-diffusion model and one predicted FBC based on the counter-diffusion model, developed using the input parameters summarized in Table 1. The input parameters for the counter-diffusion model simulations are the same as those reported by Malusis and Shackelford (2002c) for $C_o = 8.7$ mM KCl, and include a membrane efficiency coefficient, ω , of 0.49, and an apparent tortuosity factor, τ_a , of 0.063. In order to directly compare the differences between the salt-diffusion model and the counter-diffusion model, salt-diffusion model simulations were conducted using all of the same input parameters as for the counter-diffusion model simulations. However, the value $\tau_a = 0.063$ is based on $D_s^* = 1.25 \times 10^{-10} \text{ m}^2/\text{s}$ for $\omega = 0.49$ as reported by Malusis and Shackelford (2002b) (see Fig. 3a) and a free-solution salt diffusion coefficient, D_{so} , of $19.9 \times 10^{-10} \text{ m}^2/\text{s}$ for KCl (Shackelford and Daniel, 1991). As discussed previously, the D_s^* values in Fig. 3a are not the true D_s^* values for the GCL specimens, but rather are artifacts of the counter-diffusion formulation employed by Malusis and Shackelford (2002b) to analyze the diffusion test data. The true D_s^* for $C_o = 8.7$ mM KCl is the D_ω^* value in Fig. 3a, which is $1.16 \times 10^{-10} \text{ m}^2/\text{s}$ (see Malusis and Shackelford, 2002b). Based on $D_s^* = 1.16 \times 10^{-10} \text{ m}^2/\text{s}$ and $D_{so} = 19.9 \times 10^{-10} \text{ m}^2/\text{s}$, the true τ_a for salt diffusion is 0.058 rather than 0.063. Therefore, a second set of predicted FBCs were developed from the salt-diffusion model using $\tau_a = 0.058$.

The results in Fig. 4 show that the predicted FBCs provide a reasonable match to the measured FBCs, particularly for Cl^- and for the experiments conducted at $i_h = 70.3$ and 703. Also, the predicted FBCs based on the salt-diffusion model do not differ substantially from those based on the counter-diffusion model, regardless of i_h . For example, predicted exit fluxes of the solutes at steady state based on the counter-diffusion model were only slightly lower (i.e., <12%) relative to those based on the salt-diffusion model for the same $\tau_a (= 0.063)$, as illustrated for Cl^- in Fig. 5. Since the only difference between the two models is that the chemico-osmotic advective term in the salt-diffusion model (see Eq. (81)) is reduced relative to the same term in the counter-diffusion model (see Eq. (83)), the minor differences in predicted steady-state solute flux obtained from the two models (using the same τ_a) indicate that chemico-osmotic advection was not a dominant transport process in the column experiments conducted by Malusis and Shackelford (2004b).

The results in Fig. 5 also show that the counter-diffusion model generally yielded more accurate predictions of steady-state solute flux relative to the salt-diffusion model when the τ_a derived from the counter-diffusion formulation given by Eqs. (59)–(60) (i.e., $\tau_a = 0.063$) was used in both models. However, steady-state fluxes given by the salt-diffusion model using τ_a derived from the salt-diffusion formulation given

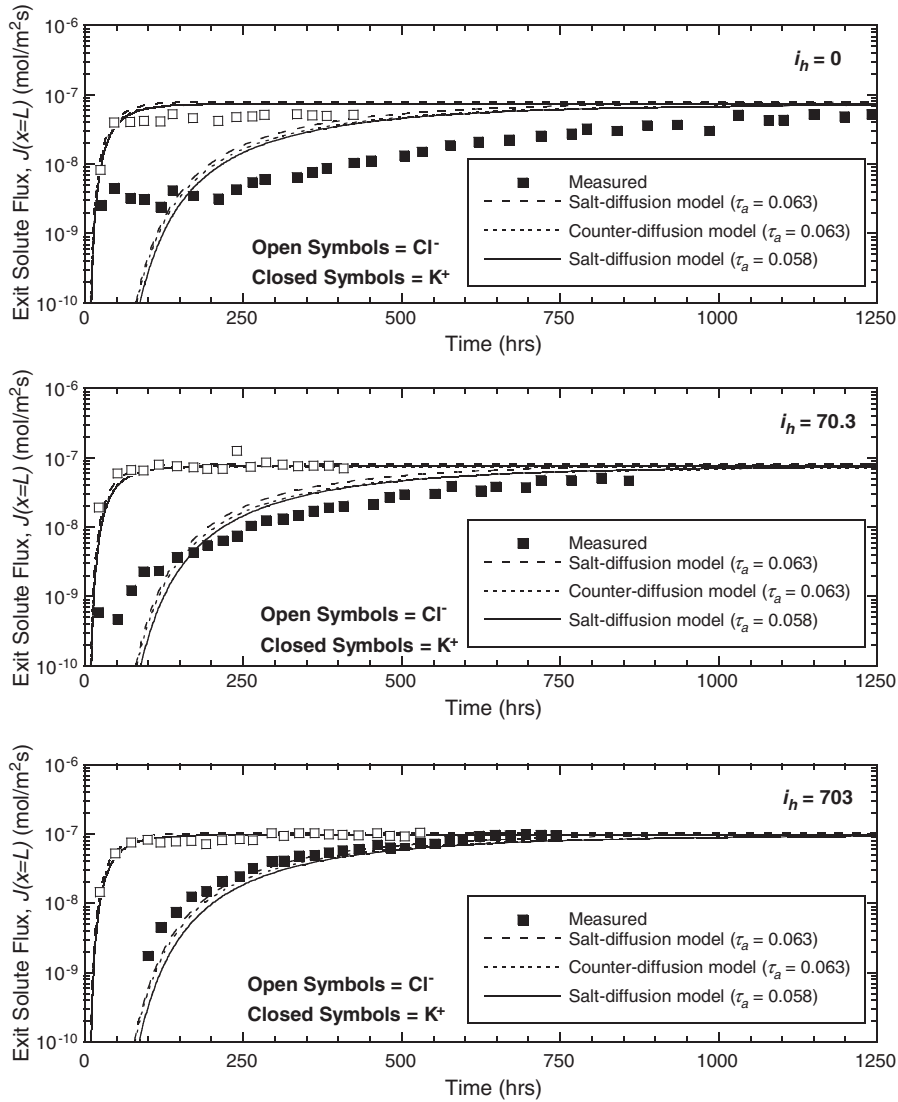


Fig. 4. Measured and predicted solute fluxes for different hydraulic gradients (i_h) based on salt- and counter-diffusion models with values for the apparent tortuosity factor based on counter-diffusion theory ($\tau_a=0.063$) or salt-diffusion theory ($\tau_a=0.058$). Measured data from Malusis and Shackelford (2004b).

by Eq. (62) (i.e., $\tau_a=0.058$) are nearly identical to those given by the counter-diffusion model for $\tau_a=0.063$.

The findings above illustrate that the predictive ability of a solute transport model for clay membranes based on the assumption of counter diffusion is not significantly different from that of a model based on the assumption of salt diffusion, provided that the input parameters used in each model are derived under the same assumption inherent in the model. However, this similarity is due to the balancing of competing errors associated with the counter-diffusion approach. Use of counter-diffusion theory to interpret salt-diffusion test data results in overestimation of D_s^* (e.g., see Fig. 3a, where D_{os}^* is the true D_s^*), which in turn causes overprediction of the diffusive component of solute transport. This overprediction is balanced by overprediction of chemico-osmotic advection, due to the absence of the reductive factor $1 - \omega$ from the chemico-osmotic

term (second term) in Eq. (83). The two errors are competing errors, because diffusion and chemico-osmotic advection occur in opposite directions. Thus, despite the similar predictive abilities of the counter-diffusion and salt-diffusion models, the two models are not equally appropriate. Salt-diffusion theory is fundamentally correct and, therefore, is more appropriate for modeling problems involving salt diffusion in clay membranes.

4.4. Restrictive tortuosity versus effective porosity

The results in Figs. 4 and 5 suggest that the influence of chemico-osmotic advection on solute transport in clay membranes is likely to be minor, even for clay membranes with relatively high membrane efficiencies. However, this observation is not meant to suggest that membrane behavior has little

Table 1

Summary of input parameters used to develop predicted flux breakthrough curves (FBCs) for comparison against measured FBCs presented by Malusis and Shackelford (2004b) for GCL specimens with KCl solutions ($C_o=8.7$ mM, $\omega=0.49$, $L=10$ mm, $T=25^\circ\text{C}$, $R_{d,\text{Cl}}=1.53$, $R_{d,\text{K}}=12.6$, $D_{o,\text{Cl}}=1.96\times 10^{-9}$ m²/s, $D_{o,\text{K}}=2.03\times 10^{-9}$ m²/s).

Column test no.	i_h	P_o (kPa)	n	k_h (m/s)	Model type	τ_a
1	0	0	0.81	1.5×10^{-11}	Salt diffusion	0.063
					Counter diffusion	0.063
					Salt diffusion	0.058
2	70.3	6.9	0.79	2.0×10^{-11}	Salt diffusion	0.063
					Counter diffusion	0.063
					Salt diffusion	0.058
3	703	69	0.81	1.4×10^{-11}	Salt diffusion	0.063
					Counter diffusion	0.063
					Salt diffusion	0.058

i_h =hydraulic gradient; P_o =applied pressure; n =total porosity; k_h =hydraulic conductivity; and τ_a =apparent tortuosity factor.

impact on the rate of solute migration in clay soils. In fact, as indicated by the results shown in Fig. 3a, a marked decrease in D_s^* occurs with increasing ω such that $D_s^*\rightarrow 0$ in the limit as $\omega\rightarrow 1$ as required by the definition of an ideal membrane (i.e., no solute can enter the membrane). Because the requirement for decreasing D_s^* with increasing ω is not explicitly captured in the theoretical development of coupled flux equations such as Eqs. (81) and (83), Malusis and Shackelford (2004a) referred to this effect as “implicit coupling” and attributed the effect to a decrease in the apparent tortuosity factor, τ_a , with increasing ω .

According to Shackelford and Daniel (1991), τ_a in Eq. (30) can be defined as the product of a matrix tortuosity factor, τ_m , and a restrictive tortuosity factor, τ_r , as follows (Malusis and Shackelford, 2004a):

$$\tau_a = \tau_m \tau_r = \tau_m \prod_{i=1}^N \tau_i \tag{88}$$

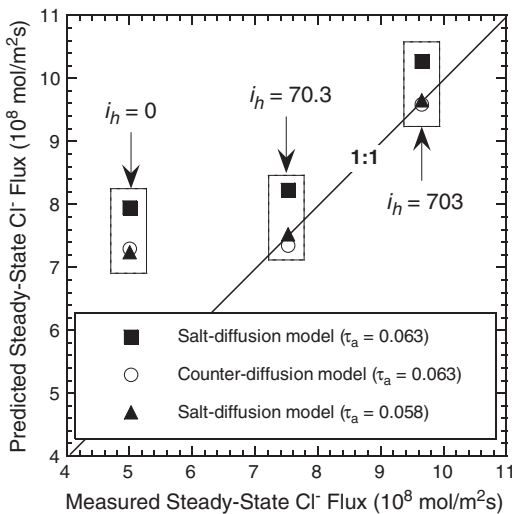


Fig. 5. Measured versus predicted steady-state fluxes of chloride for different hydraulic gradients (i_h) based on salt- and counter-diffusion models with values for the apparent tortuosity factor based on counter-diffusion theory ($\tau_a=0.063$) or salt-diffusion theory ($\tau_a=0.058$). Measured data from Malusis and Shackelford (2004b).

where τ_m accounts for the tortuosity associated with the geometry of the interconnected pores and τ_r is a lumped parameter that accounts for any number, N , of other mechanisms, represented individually by τ_i , that restrict the diffusive solute flux, such as solute exclusion and solute drag near the surfaces of clay particles (e.g., see Kemper et al., 1964). Based on Eq. (88), the effective salt-diffusion coefficient, D_s^* , may be expressed to reflect the separate influences of matrix tortuosity and restrictive tortuosity as follows (Oscarson et al., 1992):

$$D_s^* = \tau_a D_{so} = \tau_m \tau_r D_{so} \tag{89}$$

where D_{so} is the free-solution salt-diffusion coefficient. Since τ_m represents the tortuosity associated entirely with the geometric interconnectivity of the pores, τ_m generally is considered a constant for a given arrangement of soil particles and, therefore, independent of solute concentration. In contrast, τ_r for clay membranes may vary with solute concentration insofar as changes in solute concentration cause a change in ω (e.g., see Fig. 3b). Theoretically, $\tau_r=0$ for ideal membranes (i.e., $\omega=1$) that completely exclude solutes. However, higher solute concentrations generally cause shrinkage of the diffuse-double layers and an increase in τ_r , such that τ_r would approach unity as the membrane efficiency approaches zero ($\tau_r\rightarrow 1$ as $\omega\rightarrow 0$), assuming that all other potentially restrictive effects are insignificant. Under this assumption, τ_m would be equivalent to τ_a at zero membrane efficiency (i.e., $\tau_a=\tau_m$ when $\omega=0$) based on Eq. (88).

Approaches similar to that described by Eqs. (88) and (89) have been utilized to account for the influence of solute exclusion on diffusion in clay membranes (e.g., Grathwohl, 1998; Kemper and van Schaik, 1966; Manassero and Dominijanni, 2003; Porter et al., 1960). For example, Manassero and Dominijanni (2003) represented τ_r in Eq. (89) by a factor θ to account for membrane effects, and further defined θ as the ratio of the effective porosity, n_e , to the total porosity, n , or

$$\theta = \tau_r = \frac{n_e}{n} \tag{90}$$

where n_e is the portion of n that allows solute migration (i.e., the free solution in the membrane pores). Thus, based on Eq. (90), Eq. (89) may be expressed as follows:

$$D_s^* = \frac{n_e}{n} \tau_m D_{so} \tag{91}$$

With this definition for D_s^* , Fick’s first law for salt diffusion may be written in the following general form (e.g., see Pearson, 1999):

$$J_j^d = -n D_{si}^* \frac{\partial C_i}{\partial X} = -n \left(\frac{n_e}{n}\right) \tau_m D_{so,i} \frac{\partial C_i}{\partial X} = n_e D_{se,i} \frac{\partial C_i}{\partial X} \tag{92}$$

where $D_{se,i} (= \tau_m D_{so,i})$ is an effective salt-diffusion coefficient that accounts only for the matrix tortuosity. The alternative expression for Fick’s first law given by Eq. (92) may be preferred over that given by Eq. (40), since D_{se} may be treated as a constant and the effect of membrane behavior is explicitly represented by n_e rather than implicitly embedded in D_s^* .

However, a practical difficulty associated with expressing diffusive flux in Eq. (92) based on n_e is that n_e generally cannot be measured independently, whereas n is easily measured, and neither n_e nor τ_r are explicitly correlated with membrane behavior. To resolve this issue, Manassero and Dominijanni (2003) proposed that τ_r be approximated by the following linear relationship with ω , which was supported largely on the basis of the data shown in Fig. 3:

$$\tau_r = \frac{n_e}{n} = 1 - \omega \tag{93}$$

Eq. (93) provides a means to replace n_e with a simple function that is based on an independently measurable property (i.e., ω) and explicitly accounts for the implicit coupling effect illustrated by the GCL diffusion test data in Fig. 3a. Based on Eq. (93), Eq. (92) may be written as follows:

$$J_i^d = -n_e \tau_m D_{so,i} \frac{\partial C_i}{\partial X} = -(1 - \omega) n D_{se,i} \frac{\partial C_i}{\partial X} \tag{94}$$

Furthermore, Eqs. (91) and (93) may be substituted into Eqs. (81) and (83) to obtain the following total solute flux expressions based on salt diffusion and counter diffusion, respectively:

$$J_j \Big|_{l=0} = (1 - \omega) q_h C_j + (1 - \omega) q_n C_j - (1 - \omega) n \tau_m D_{so,j} \frac{\partial C_j}{\partial X} \tag{95a}$$

$$J_j \Big|_{l=0} = (1 - \omega) q_h C_j + q_n C_j - (1 - \omega) n \tau_m D_{so,j} \frac{\partial C_j}{\partial X} \tag{95b}$$

As discussed by Manassero and Dominijanni (2003), Eq. (95a) is considered more fundamentally correct relative to Eq. (95b) if one considers the specific case of an ideal membrane ($\omega = 1$), because substitution of $\omega = 1$ into Eq. (95a) reduces the total solute flux to zero (as required for an ideal membrane). Conversely, substitution of $\omega = 1$ into Eq. (95b) yields the following:

$$J_j(\omega = 0) \Big|_{l=0} = q_n C_j \tag{96}$$

Thus, the solute flux given by Eq. (95b) does not reduce to zero for an ideal membrane (i.e., unless one considers that C_j must be zero for $\omega = 1$), which is unsettling from a theoretical standpoint.

Bader and Kooi (2005) and Garavito et al. (2007) indicate that the linear relationship between τ_r and ω given by Eq. (93) is reasonable on the basis of theoretical considerations given in Katchalsky and Curran (1965). Although neither Bader and Kooi (2005) nor Garavito et al. (2007) elucidate the nature or extent of these theoretical considerations, Dominijanni (2005) showed that Eq. (93) can be derived using a physical modeling approach to describe the phenomenological coefficients on the basis of physical and chemical interactions between the solid and liquid phases at the pore scale. As noted in a more recent study by Dominijanni and Manassero (2012b), the theoretical basis for Eq. (93) is valid under the condition that pore-scale variations in hydraulic pressure, ion concentrations, and water velocity within the membrane are negligible. However, Eq.

(93) is experimentally supported by only a limited amount of measured data and may not be universally applicable.

For example, τ_a and τ_r values reported by Malusis and Shackelford (2002b) for the GCL specimens in Fig. 3 are re-plotted in Figs. 6a and b, respectively, along with τ_a and τ_r values derived from experimental data recently reported by Di Emidio (2010) for specimens of Na bentonite and a polymer-treated bentonite (HYPER clay) tested using a similar approach to that described by Malusis and Shackelford (2002b), but using CaCl₂ solutions ($C_0 = 1$ mM and 5 mM) rather than KCl solutions. The τ_a values for the Na bentonite and HYPER clay specimens in Fig. 6a are based on steady-state D_s^* values reported by Di Emidio (2010) for Cl⁻ and a free-solution salt diffusion coefficient, $D_{so} = 13.4 \times 10^{-10}$ m²/s for CaCl₂ at 25 °C (Shackelford and Daniel, 1991). Values of $\tau_m = 0.17, 0.15,$ and 0.12 for the Na bentonite, HYPER clay, and GCL specimens, respectively, may be inferred from the trends in Fig. 6a, on the basis that $\tau_m = \tau_r$ at $\omega = 0$.

The results in Fig. 6b illustrate that the measured τ_r values for the GCL and HYPER clay specimens, collectively, generally follow the linear trend defined by Eq. (93), to the extent that Eq. (93) may be considered a reasonable representation of the relationship between τ_r and ω for clay membranes. In contrast, the τ_r for the Na bentonite specimen with $\omega = 0.29$

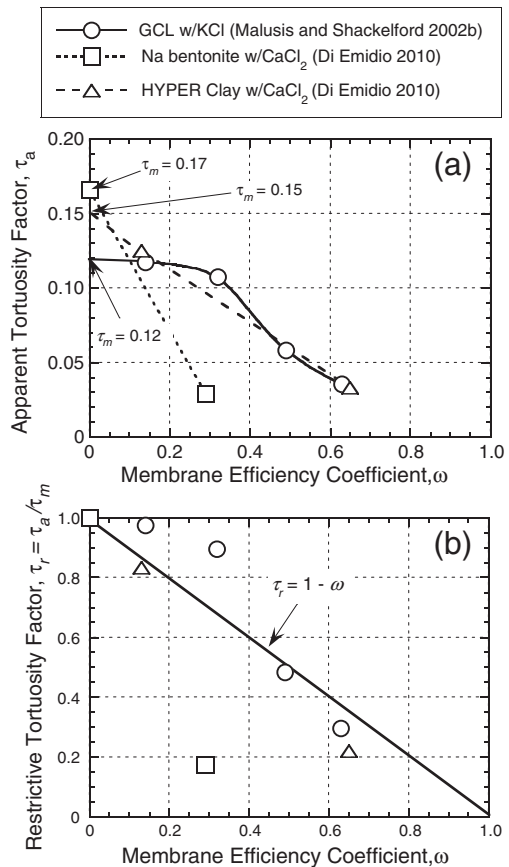


Fig. 6. Correlations between tortuosity factors and membrane efficiency coefficients based on measured diffusion coefficients for different clays and salt solutions: (a) apparent tortuosity factor; and (b) restrictive tortuosity factor.

lies well below the trend line defined by Eq. (93), suggesting that Eq. (93) is not reasonable in this case. Given these conflicting results and the limited amount of data in Fig. 6, additional measured data are needed to bolster the validity of the linear relationship between τ_r and $1 - \omega$ given by Eq. (93).

5. Summary and conclusions

A critical review of coupled flux formulations for liquid, current, and aqueous miscible chemical species (solutes) through a clay membrane under isothermal conditions based on the principles of nonequilibrium (irreversible) thermodynamics was undertaken. The goals of the review were to explicitly resolve differences among the formulations and to illustrate the significance of these differences from both theoretical and practical perspectives.

The fundamental coupled flux formulations for continuous systems considering a single (uncharged) solute and single dissociating salt were developed from first principles directly from the relevant form of the dissipation function and expressed in terms of phenomenological coefficients, L_{ij} . For the single-salt system, the resulting coupled flux equations can be presented in terms of gradients in either chemico-osmotic pressure or chemical potentials, resulting in slightly different forms of the equations. Nonetheless, the two sets of equations are shown to be identical in the sense that the resulting values for the fluxes will be the same regardless of whether the values are based on the gradient in chemical potential or the gradient in chemico-osmotic pressure. Also, the coupled flux expressions for the single-salt system consisting of four equations with nine unique phenomenological coefficients can be presented in a more simplified form consisting of three equations with six unique phenomenological coefficients, provided the chemical potential of the salt, μ_s , or the chemico-osmotic pressure, π , is properly defined to capture the contributions of both the cationic species and the anionic species.

Considerable effort has been devoted to expressing L_{ij} in terms of familiar and measurable soil properties, such as the hydraulic conductivity, k_h , and effective diffusion coefficient, D^* , in order to render the coupled flux equations more suitable for direct application to natural or engineered soil systems. The resulting definitions of the L_{ij} in terms of soil properties are shown to vary depending on whether the solutes are neutral or charged, the number of solutes considered in the system, and the assumption of whether the solutes are subjected to counter diffusion or salt diffusion. With respect to counter versus salt diffusion, the assumption of counter diffusion is shown to result in the theoretical formulation of a coupled-diffusion coefficient, D_{ω}^* , which consists of the difference between true salt-diffusion coefficient, D_s^* , and a coupling term which is a function of the membrane efficiency coefficient, ω , the mean molar concentrations of the salt ions, and k_h , whereas the assumption of salt diffusion results directly in D_s^* . As a result, application of the counter-diffusion theory to previously published results of diffusion-membrane experiments performed under salt-diffusion boundary conditions was shown to result in misinterpretation of the true values for the salt-diffusion coefficient, D_s^* , although the resulting errors in D_s^* were relatively small (<12%) for the range of membrane efficiencies ($\leq 63\%$) encountered in the experiments.

In the case of clay membranes, expressions for the total solute flux, J_j , depend upon whether counter diffusion or salt diffusion is assumed in the coupled-flux formulation and whether the formulation is written for individual ionic species, a binary salt, or an uncharged solute. A primary difference between the expression for J_j based on the salt-diffusion assumption versus that based on the counter-diffusion assumption is that the factor $1 - \omega$ is present in the chemico-osmotic advection component of J_j in the case of salt diffusion, but absent in the case of counter diffusion. As a result of this difference, the contribution of chemico-osmotic advection to the total solute flux based on salt diffusion is less than that based on counter diffusion for a clay membrane (i.e., since $1 - \omega < 1$). The potential significance of this difference was evaluated on the basis of the results of previously published column experiments conducted on a clay membrane. Measured flux breakthrough curves (FBCs) for K^+ and Cl^- based on column tests conducted at three applied hydraulic gradients of 0, 70.3, and 703 were compared with predicted FBCs based on the counter- and the salt-diffusion theories using independently measured flow and transport parameters. The differences between the steady-state fluxes based on the two diffusion theories were found to be minor, suggesting that chemico-osmotic advection was not a dominant transport process in the column experiments. Overall, both theories provided reasonably accurate predictions of the steady state fluxes when the input parameters used in each theory were derived under the same assumption inherent in the theory. Thus, the predictive ability of solute transport for clay membranes based on the assumption of counter diffusion was found to be not significantly different from that based on the assumption of salt diffusion. Nonetheless, salt diffusion theory is fundamentally correct and, therefore, is more appropriate than counter-diffusion theory for modeling problems involving salt diffusion in clay membranes.

Finally, the fact that solute diffusion cannot occur in an ideal or perfect membrane (i.e., $\omega = 1$) is not explicitly indicated in any of the theoretical expressions for J_j , but rather is generally accounted for via inclusion of an effective porosity, n_e , or a restrictive tortuosity factor, τ_r , in the formulation of Fick's first law for salt diffusion in clay membranes, both of which have been correlated as a linear function of membrane behavior (i.e., $\tau_r = n_e/n = 1 - \omega$). Although this correlation has been supported theoretically on the basis of physical modeling at the pore scale, experimental support is limited. Additional data are needed to bolster the validity of the linear correlation for clay membranes.

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