

Effects of sodium chloride on constitutive relations in variably saturated porous media

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[1] Though many arid and contaminated sites have high salinity, prediction of effects of salinity on water movement in soils has been based on dilute solution approximations. Here a sensitivity analysis compares predicted liquid and vapor pressure in variably saturated porous media found using both the dilute approximations and a more general formulation that is valid for salt concentrations from zero to saturation. Sodium chloride (NaCl) was selected as a representative salt of environmental importance. Salt-mineral interactions are not included in the analysis. The dilute approximations neglect the salt-related changes in specific volume, which translate into nonnegligible pressure effects (i.e., error >1%) under dry conditions, being more pronounced for finer media. The analysis shows that for silt textures, the dilute approximation to the vapor pressure constitutive relation is acceptable for water contents $\theta > 5\%$, for sand $\theta > 1\%$, and for loam $\theta > 2\%$. When computing gradients of vapor pressure resulting from gradients in salt concentration, volume correction is necessary for silt for $\theta < 10\%$. Gradients in vapor pressure with changes in water content require volume correction, except under dilute conditions (i.e., <0.5 molal). For concentrated solutions in silt, salt effect errors are not acceptable for prediction of liquid pressure, nor are the effects on gradients negligible. Errors for sand and loam are only marginally better, with acceptable errors generally occurring only for ionic strengths of less than 1 molal. An example of use of the constitutive relations to plot results from experiments is provided to illustrate how the theory may be used to determine which thermodynamic corrections must be incorporated into analyses of the experimental results. Here the volumetric effects of the salt on vapor depression were negligible, though volumetric effects may be nonnegligible for computation of gradients of both vapor and liquid pressures. The method of analysis of nonideal effects developed herein is general, and the resulting corrections to the dilute approximation may be easily implemented in numerical codes.

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1. Introduction

[2] It is important to understand the behavior of flow of saline fluids in nonisothermal, unsaturated porous media. Understanding the effects of salt in such systems is required in soil science (e.g., arid soils [Weisbrod *et al.*, 2000]), in the design of hazardous waste storage (e.g., the Hanford site), and in drying science (e.g., manufacturing and processing of materials). As early as 1909 [Müntz and Gaudechon, 1909], it was noted that water accumulated near salt crystals in soil, and it has long been known that water vapor pressure is reduced above both curved liquid-gas interfaces and above saline fluids [cf. Edlefsen and

Anderson, 1943]. It is also known that addition of salt will alter the specific volume of water [cf. Heyrovská, 1996]. However, to date, understanding of the effects of salinity on water movement in soils has been based on dilute solution assumptions that neglect the effects of changes in specific volume corresponding to changes in salt concentration.

[3] Very general relationships describing salt effects on water vapor pressure and liquid pressure for variably saturated soils have been derived from first principles for isothermal soils where the local equilibrium assumption is valid [Burns *et al.*, 2006]. For simplicity, only isothermal conditions are considered here; but it is noted that the extension of the theory to anisothermal systems only requires that all computations of pressures and any other appropriate variables occur at a range of temperatures, allowing determination of an empirical relationship describing the temperature dependence. This is a common strategy for modeling anisothermal conditions, where the implicit assumption is that concentration and temperature are independent [cf. Nassar and Horton, 1989; Bear and Gilman, 1995; Olivella *et al.*, 1996].

[4] We now provide an application of this theory. It is of interest to understand when the “standard theory” (defined

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rigorously by *Burns et al.* [2006]), which is based broadly on the dilute solution assumption, is insufficient. The two goals of this paper are: (1) to show the information required and procedure for application of the theory and (2) to identify the conditions for which it may be necessary to use this more complex general formulation. An example computation is performed for a range of soil textures with sodium chloride (NaCl), to illustrate the effects of different soils on the constitutive relations. Predictions are also compared with the experimental results of *Scotter* [1974].

2. Related Literature

[5] Thermodynamic relationships describing vapor pressure reduction have been derived for the curved interface and the salt effect separately [cf. *Edlefsen and Anderson*, 1943]. However, to the authors' knowledge, no general derivation from first principles of the synergistic effects of salt and the curved interface had been accomplished prior to *Burns et al.* [2006]. Similar thermodynamic constitutive relationships with varying amounts of detail have been defined for various purposes [*Olivella et al.*, 1996; *Bear and Gilman*, 1995; *Nassar and Horton*, 1989]. *Olivella et al.* [1996] use a very similar functional form to that which we employ (equation (1) below) with the exception of the use of a constant integrand (allowing evaluation of the integral) in their model CODE_BRIGHT. To show when the constant integrand approximation is valid, it is necessary to compute the value of the integral in equation (1) and to compare the magnitude of the terms in the equation. This is accomplished in this manuscript for sodium chloride.

[6] *Bear and Gilman* [1995] state that for their problem, the effects of a curved interface is negligible, and so write down a functional form of the vapor pressure relationship using Raoult's law and the Clausius-Clapeyron equation. The assumption that the interface curvature is negligible is shown here to be valid under some conditions for sodium chloride, and is therefore likely true for other salts of interests. *Bear and Gilman's* resulting equation is similar to the one derived here (assuming a negligible volume correction term) in that it takes a reference vapor pressure and multiplies it by correction terms. Their salt correction term uses the mole fraction of water in the liquid as an approximation for the activity which is generally assumed to be valid for dilute solutions. *Bear and Gilman* also have a temperature correction term that includes the latent heat of vaporization, while *Olivella et al.* [1996] and *Nassar and Horton* [1989] both compensate for temperature with empirical relations, but separate out the latent heats and other energy transfers for inclusion in energy conservation equations.

[7] *Nassar and Horton* [1989] find that the total relative humidity is equal to the relative humidity due to the matric potential multiplied by the osmotic relative humidity. Functional forms of these humidities are taken from the literature. The osmotic term has the expected exponential form, but *Nassar and Horton* also use an exponential approximation for the osmotic relative humidity which differs from the results utilized herein.

[8] Finally, there has been much work on describing the flow of water in the presence of salt in porous media [cf. *Low*, 1955; *Qayyum and Kemper*, 1962; *Letey et al.*, 1969; *Kelly and Selker*, 2001]. Little of this work is analogous to the thermodynamically derived equations of state examined

herein. The partial exception to this is *Low* [1955], who used thermodynamic principles to postulate a total pressure gradient (i.e., "usual" pressure + osmotic pressure) for a dilute single-phase solution and for a single-phase solution for which the salt concentration does not affect the constant partial molar volume of the water. Because *Low's* system includes only a single fluid phase, no accounting for the air-water interface occurs, so a direct comparison to the new theory presented here is impossible. However, *Low's* assumptions of dilute solution or constant molar volume of the water are analogous to the assumptions analyzed below.

3. Constitutive Relationships

[9] The constitutive relations for saline solutions in unsaturated porous media were derived by *Burns et al.* [2006] for vapor and liquid pressures of saline solutions with salt concentrations from zero to saturation. *Burns et al.* consider an isothermal system for which the local equilibrium assumption applies and for which a single dissolved salt species is present in water in a porous medium that is well connected to the atmosphere. These conditions are summarized in the following assumptions [*Burns et al.*, 2006].

[10] Assumption 1: The total system is closed to mass transfer. This assumption is consistent for the case where diffusion or other mass flows are slow relative to the time it takes to come to thermodynamic equilibrium locally (i.e., the local equilibrium assumption).

[11] Assumption 2: The liquid-gas interface is thin and may be well approximated by a surface.

[12] Assumption 3: The solid phase of the porous media does not deform (or the deformation is very small). It is only necessary that this condition hold on the timescale dictated by chemical equilibrium (i.e., for the quasi-static process), ensuring that the relationships developed also hold for "slowly" deforming porous media.

[13] Assumption 4: Equilibrium between the phases is reached much faster than changes driven by external forcing (i.e., the local equilibrium assumption is valid).

[14] Assumption 5: The system is adiabatically connected to an isothermal heat reservoir, but is otherwise closed.

[15] Assumption 6: The mixture in each phase may be well described as a mixture of water (w), dry air (a), and pure salt (h).

[16] Assumption 7: The salt (h) is either a single salt species or may be well represented with effective parameters (e.g., affinity) such that all salt chemical potentials and mole numbers are well defined as single-valued variables.

[17] Assumption 8: The gas (G) is made up of air (aG; read as air in gas) and water vapor (wG; water in gas).

[18] Assumption 9: The liquid (L) is made up of water (wL) and salt (hL). Explicitly, the air is considered to be negligibly reactive with the liquid (i.e., negligible when considering the thermodynamics of electrolyte solutions).

[19] Assumption 10: All phase changes occur under isothermal conditions.

[20] Assumption 11: The gas phase behaves like an ideal gas.

[21] Assumption 12: The volume of the liquid (V^L) is a function of moles of water in the liquid (N^{wL}) and moles of salt in the liquid (N^{hL}). Further, if any two of the values $\{V^L, N^{wL}, N^{hL}\}$ are known, then the third variable may be

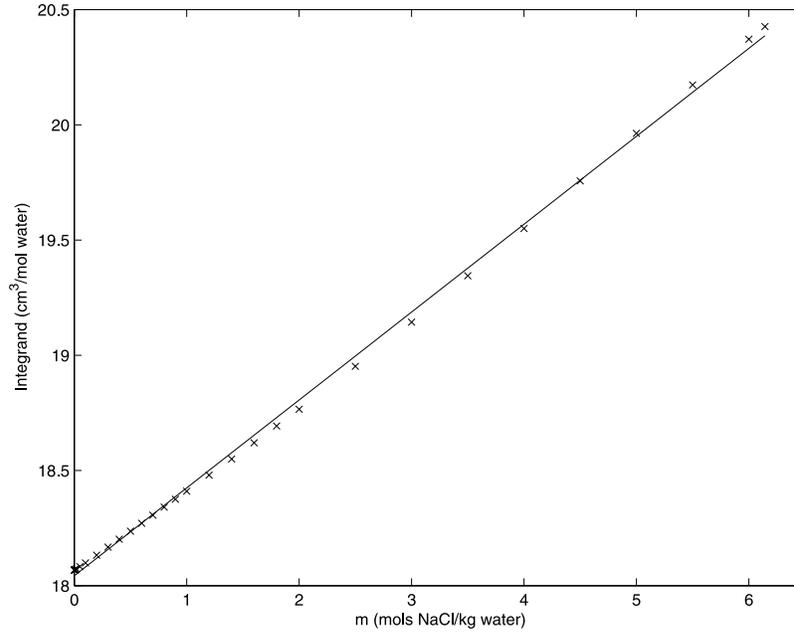


Figure 1. Integrand of the volume correction term as a function of NaCl(aq). The linear fit is to the values computed using the relations of *Heyrovská* [1996].

computed (e.g., if the number of moles of salt and water in an aqueous solution are known, then the volume of the solution is known).

[22] Assumption 13: The gas phase inside the porous media is connected with a sufficiently large gas volume (e.g., the atmosphere).

[23] Assumption 14: The surface tension at the liquid-gas interface (σ^{LG}) is a function of salt content and temperature only (i.e., it is a microscopic, subpore-scale property), and $\frac{dA^{LG}}{dV^L}$ (i.e., the change in interfacial surface area with a change in liquid volume) is only a function of saturation. This latter function arises naturally in the derivation of the constitutive relations, and in general, this function is hysteretic.

[24] The procedure to generalize the relationships to multiple salts and anisothermal conditions are described by *Burns et al.* [2006]. We restrict the present analysis to a single salt to enhance clarity. The resulting constitutive relations derived by *Burns et al.* [2006] are

$$P^{wG} = P_{0\infty}^{wG} a^{wL} \exp\left(\frac{V_0^L}{N_0^{wL} RT} (P_0^L - P_{0\infty}^L)\right) \cdot \exp\left(\frac{1}{RT} \left[\int_0^{N^{hl}} \frac{V^L}{N^{wL}} dP^L \right]_{N^{wL}}\right) \quad (1)$$

$$P^L = \frac{\sigma_0^{LG}}{\sigma_0^{LG}} \tilde{P}^L, \quad (2)$$

where

$$\tilde{P}^L \equiv -\sigma_0^{LG} \frac{dA^{LG}}{dV^L},$$

where the notation pressure (P), activity (a), volume (V), number of moles (N), the ideal gas constant (R), temperature (T), area (A), and surface tension (σ) are used,

with superscripts to indicate which subsystem or constituent is being considered. Lowercase letters describe the constituent (water (w) or salt (h)), and the capital letters describe the phase (liquid (L) or gas (G) (see Notation section)).

[25] Liquid volume changes with NaCl salt concentration (Figure 1); thus equation (2) implies that the liquid pressure will be affected by changes in liquid volume (possibly associated with changes in salt concentration), and by changes in surface tension. Defining the unit pore volume: $V^{pore} \equiv 1$ (units to be chosen on the basis of available empirical relationships), the liquid saturation may be defined as

$$S^L \equiv \frac{V^L}{V^{pore}}. \quad (3)$$

\tilde{P}^L , which represents the pressure corresponding to an equivalent saturation of salt-free water $\tilde{P}^L \equiv P^L(S^L)$, is a function of water geometry only (specifically, the change in liquid-gas interfacial area with a change in liquid volume), and S^L is a function of both water and salt contents [*Burns et al.*, 2006]. Hence \tilde{P}^L may be determined from the pressure-saturation curves for salt-free water. Changes to liquid pressure resulting from changes in surface tension are accounted for separately in equation (2).

[26] The constitutive relations (1) and (2) are used to couple differential equations of flow, providing a constraint on the mass and momentum conservation equations for water flow. Flow will be driven by the gradients of the liquid and vapor pressures (∇P^L and ∇P^{wG}). It is useful to employ the general derivative, $\equiv d/d \cdot$, where the “dot” may be replaced with any primary variable. In order to compute the derivatives, it is first necessary to choose two variables that completely describe the system via a set of constitutive relations. Molality and salt-free water saturation (m and S_0^L) are chosen here because constitutive relations in

terms of these variables are readily available in the literature. The resulting general derivative of equation (1) is

$$\frac{dP^{wG}}{d\cdot} = \left(\frac{\partial P^{wG}}{\partial m} \right) \frac{dm}{d\cdot} + \left(\frac{\partial P^{wG}}{\partial S_0^L} \right) \frac{dS_0^L}{d\cdot}, \quad (4)$$

with

$$\frac{\partial P^{wG}}{\partial m} = P^{wG} \left(\frac{\partial(\ln a^{wL})}{\partial m} + \frac{\partial}{\partial m} \left(\frac{1}{RT} \int_C^B \frac{V^L}{N^{wL}} dP^L \right) \right) \quad (5a)$$

$$\begin{aligned} \frac{\partial P^{wG}}{\partial S_0^L} &= P^{wG} \left(\frac{\partial}{\partial S_0^L} \left(\frac{V_0^L}{N_0^{wL} RT} (P_0^L - P_{0\infty}^L) \right) \right. \\ &\quad \left. + \frac{\partial}{\partial S_0^L} \left(\frac{1}{RT} \int_C^B \frac{V^L}{N^{wL}} dP^L \right) \right). \end{aligned} \quad (5b)$$

[27] The general derivative of equation (2) is

$$\frac{dP^L}{d\cdot} = \left(\frac{\partial P^L}{\partial m} \right) \frac{dm}{d\cdot} + \left(\frac{\partial P^L}{\partial S_0^L} \right) \frac{dS_0^L}{d\cdot} \quad (6)$$

with

$$\frac{\partial P^L}{\partial m} = \frac{1}{\sigma_0^{LG}} \left(\tilde{P}^L \frac{\partial \sigma^{LG}}{\partial m} + \sigma^{LG} \frac{\partial \tilde{P}^L}{\partial m} \right) \quad (7a)$$

$$\frac{\partial P^L}{\partial S_0^L} = \frac{\sigma^{LG}}{\sigma_0^{LG}} \frac{\partial \tilde{P}^L}{\partial S_0^L}. \quad (7b)$$

Equations (7a) and (7b) are the corrections to the coefficient of hydraulic conductivity that occur in Darcy's law if the law is written in terms of a gradient in salt and water concentrations as opposed to pressure. The use of these corrections will allow estimation of the coefficients that arise naturally in process thermodynamics [cf. Luikov, 1975].

4. Approximations to the Constitutive Relations

[28] Solution of the flow and transport equations requires the adoption of constitutive relations. The relations presented here have a broad range of validity with which the dilute approximation may be evaluated.

[29] "Valid" approximations are taken to be those which have a negligible (determined by the purpose of the study, measurement accuracy, computational accuracy, etc.) effect on prediction. We will consider approximations arising from neglecting one or more terms in equations (1), (2), (5a), (5b), (7a), and (7b). This could be accomplished in one of two ways: by showing that one or more terms dominate the equation in the region (i.e., state space) of interest or by showing that the error introduced by the approximation is small. In this work we consider that terms are negligible if they are more than two orders of magnitude smaller than those to which they are added. As an example of "domination," it is convenient to consider a slightly different form of equation (1). Taking the natural log of both sides of the equation, equation (1) may be rewritten

$$RT \ln \left(\frac{P^{wG}}{P_{0\infty}^{wG}} \right) = RT \ln a^{wL} + \frac{V_0^L}{N_0^{wL}} (P_0^L - P_{0\infty}^L) + \int_C^B \frac{V^L}{N^{wL}} dP^L. \quad (8)$$

The dilute solution approximation to (8) is given by setting $a^{wL} = X^{wL}$ (i.e., the mole fraction of water in the liquid) and $\frac{V^L}{N^{wL}} = \frac{V_0^L}{N_0^{wL}}$, which is a constant, allowing evaluation of the integral (complete details provided by Burns [2004]). Hereafter, the integral in equation (8) will be referred to as the volume correction term, and the zero-salt liquid pressure term will be called the dilute approximation term (since the dilute approximation effectively results in the last two terms collapsing to $\frac{V_0^L}{N_0^{wL}} (P^L - P_{0\infty}^L)$). The sum of these two terms is the curved interface correction term with the volume correction term only accounting for changes in curvature associated with the addition of salt. The activity term is self explanatory, and the term on the left-hand side of the equality is the desired resulting vapor depression term for which the constitutive relation has been developed. The corresponding terms in (1) will also be designated by these names. A natural extension of the dilute solution approximation to equation (8) is given by replacing the mole fraction of water in the liquid with the corresponding activity, but still assuming that the integrand is constant [Burns, 2004]:

$$RT \ln \left(\frac{P^{wG}}{P_{0\infty}^{wG}} \right) = RT \ln a^{wL} + \frac{V_0^L}{N_0^{wL}} (P^L - P_{0\infty}^L). \quad (9)$$

[30] A very similar constitutive relation is found in work by Olivella *et al.* [1996]. Equation (9) is precise if the volume correction term is negligible, or if the specific volume is constant. However, Figure 1 shows that the specific volume will change over the range of possible salt concentrations. To evaluate the validity of (9), the volume correction term is assumed to be negligible when

$$\left| \frac{\int_C^B \frac{V^L}{N^{wL}} dP^L}{RT \ln a^{wL} + \frac{V_0^L}{N_0^{wL}} (P_0^L - P_{0\infty}^L)} \right| \leq 0.01 = 1\%. \quad (10)$$

[31] Additionally, since it is known that both terms in the denominator are ≤ 0 , if either term can be shown to be 100 times the volume correction term, then the dilute approximation is also valid. On the other hand, in order to show that error is small, it is necessary to define the measure of error. Here error will be a relative error, and will be defined as

$$error = \left| \frac{[exact_result] - [approximation]}{[exact_result]} \right|. \quad (11)$$

[32] Using the vapor pressure as the example again, but this time solving for P^{wG} yields

$$error = \left| \frac{P_{eqn.8}^{wG} - P_{eqn.9}^{wG}}{P_{eqn.8}^{wG}} \right| = \left| 1 - \exp \left(\frac{-1}{RT} \int_C^B \frac{V^L}{N^{wL}} dP^L \right) \right|, \quad (12)$$

which is assumed to be negligible when $<1\%$.

5. Example: NaCl at 25°C

[33] The following is largely restricted to analysis of the volume correction term. To see the magnitude of other terms, refer to Burns [2004]. Empirical relationships be-

tween concentration, volume, and surface tension which are necessary to facilitate computation are first presented.

5.1. Computation of Salt Effects in Porous Media

[34] *Heyrovska* [1996] provides a suitable conversion between volume and salt concentration for NaCl at 25°C. *Heyrovska's* empirical relations are

$$\bar{V}^L = 1002.86 + m(26.8 - 10.55\alpha) \text{ for } m \leq 2 \quad (13)$$

$$\bar{V}^L = 1002.38 + 24.74\alpha m \text{ for } m > 2, \quad (14)$$

where $\alpha \leq 1$ is the experimentally determined degree of dissociation, with α a function of the molality (m). α accounts for the incomplete dissociation of NaCl into ions in a solvent. \bar{V}^L is the molal volume of liquid (cm^3 of liquid per kg of water). *Heyrovska* recommends that $m \cong 2$ be used as the dividing point for use of the two equations. For many purposes it may be sufficient to approximate the entire range as a line (Figure 1), but for the purposes of evaluating volumetric effects on liquid pressure, this is not done here. However, it is desired that the volume function used here be continuous, so the intersection of the two curves (at $m \cong 0.1506$) is used as the transition point rather than *Heyrovska's* recommendation of $m \cong 2$. This shift in transition point still allows an excellent fit since plots of equations (13) and (14) show that the difference between the two equations is very small between $m \cong 0.1506$ and $m \cong 2$.

[35] Examination of the integrand in equation (8) reveals that the desired integrand is the volume of liquid per mole of water. Simple multiplication of \bar{V}^L by the molar weight of water ($M^{\text{H}_2\text{O}} = .018015 \text{ kg/mol H}_2\text{O}$) gives the integrand as a function of m only. Since it does not matter which units of salt concentration are used, the integral may be written

$$\int_C^B \frac{V^L}{N^{\text{wL}}} dP^L = \int_0^m M^{\text{H}_2\text{O}} \bar{V}^L(m) d\left(\frac{\sigma^{\text{LG}}(m)}{\sigma_0^{\text{LG}}}\right) \tilde{P}^L(S^L(m)). \quad (15)$$

[36] For consistency of units, $V^{\text{pore}} \equiv 1 \text{ cm}^3$ is chosen. With this choice of V^{pore} , S^L is given by

$$S^L(m) = \frac{N^{\text{wL}} M^{\text{H}_2\text{O}} \bar{V}^L(m)}{V^{\text{pore}}} \quad (16)$$

for this path of integration (i.e., fixed N^{wL}). To get $S^L(S_0^L, m)$ in general, recognize that $\bar{V}^L(m)$ is only a function of m , and N^{wL} is a one-to-one function of only S_0^L . This implies that $N^{\text{wL}} = S_0^L V^{\text{pore}} / (M^{\text{H}_2\text{O}} \bar{V}_0^L)$ where \bar{V}_0^L is the zero salt molal volume. Substituting back into (16) gives the more general form

$$S^L(S_0^L, m) = \frac{S_0^L \bar{V}^L(m)}{\bar{V}_0^L}. \quad (17)$$

[37] A good fit to the surface tension function at 25°C is given by [*Burns*, 2004]

$$\sigma^{\text{LG}}(m) = \sigma_0^{\text{LG}} + 1.7m = 72 + 1.7m \quad (18)$$

with units of dynes/cm.

Table 1. van Genuchten Parameters^a

| Parameter | Silt | Loam | Sand |
|-----------------------------------|-------|-------|-------|
| $\bar{\alpha}$, cm^{-1} | 0.016 | 0.036 | 0.145 |
| N | 1.37 | 1.56 | 2.68 |

^a*Carsel and Parrish* [1988].

[38] For this example, the nonhysteretic van Genuchten pressure-saturation relationship is used with parameter values taken from *Carsel and Parrish* [1988] for sand, silt, and loam (Table 1), though any functional forms of the constitutive relations may be used. As will be seen, functional forms accurate at low water saturations should be used for determining if salt effects are negligible. Head was converted to pressure by multiplication by the density of salt-free water and the gravitational constant yielding

$$\tilde{P}^L(S^L(m)) = \frac{-\rho_0 g \left((S^L)^{\frac{N}{1-N}} - 1 \right)^{\frac{1}{N}}}{\bar{\alpha}}. \quad (19)$$

[39] Equations (17) through (19) provide a complete description of the differential in equation (15) in terms of m . There are two choices for computation of (15): either fit a function of m to α so that the change of variables may be completed, or plot equation (2) directly (for fixed water content) and fit a function of m to it. After evaluation of both options for NaCl for all three soil types examined, equation (2) was found to be approximately linear for most water contents (though the slope and y intercept vary as a function of water content [*Burns*, 2004]), so the latter option was used. In order to compute P^L for use in evaluating the integral (i.e., fixed water content, variable salt), first N^{wL} is computed using equation (16) for a given fixed pure water saturation (e.g., zero salt); then this fixed value of N^{wL} is used in equation (16) to calculate saturation as a function of salt concentration. Equations (2) and (18) are used to compute the liquid pressure as a function of salt for fixed water content. For fixed water content, if water pressure may be written as a linear function of m , then

$$P^L(m) = bm + c \Rightarrow dP^L(m) = bdm, \quad (20)$$

where $b = b(S_0^L)$ which is a constant in the integral being evaluated. Since $b(S_0^L)$ is not a function of m , equation (15) may be reduced to

$$\int_C^B \frac{V^L}{N^{\text{wL}}} dP^L = b(S_0^L) \int_0^m M^{\text{H}_2\text{O}} \bar{V}^L(m) dm. \quad (21)$$

A plot of the integrand of equation (21) shows that a linear fit is a reasonable first approximation (Figure 1), allowing evaluation of the integral

$$\int_C^B \frac{V^L}{N^{\text{wL}}} dP^L = b(S_0^L) (0.1908m^2 + 18.04m), \quad (22)$$

completing the required relations.

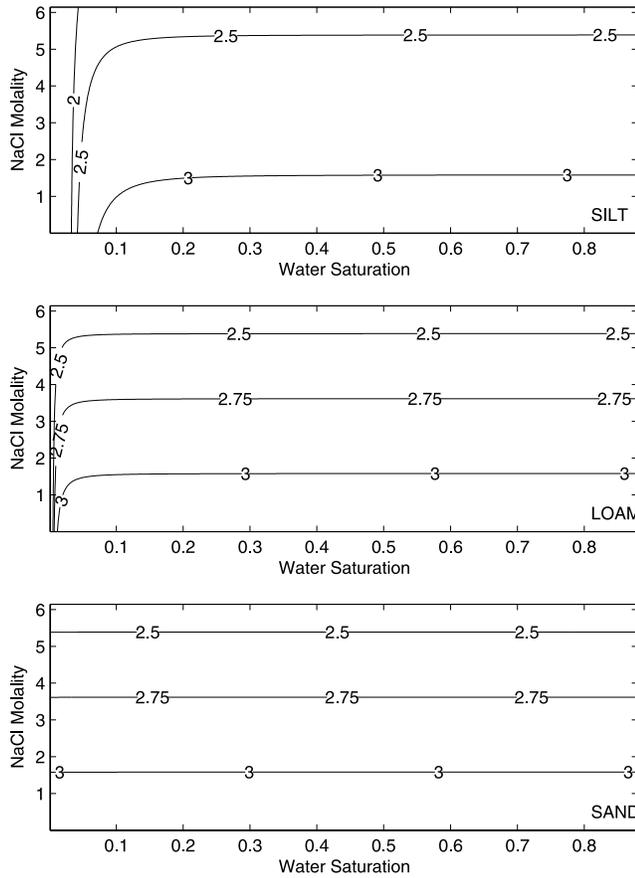


Figure 2. Plots of vapor pressure (equation (1)) as a function of water and salt content for (top) silt, (middle) loam, and (bottom) sand. Units are in kPa.

5.2. Evaluation of Approximations to the Constitutive Relations

[40] In order to determine when approximations to equations (1), (2), (5a), (5b), (7a), and (7b) are valid, the various correction terms are evaluated by using (10) and (11). Substitution of (22) into (8) gives an equation that is valid for NaCl solutions at 25°C with salt concentration from zero to saturation:

$$RT \ln \left(\frac{P^{wG}}{P_{0\infty}^{wG}} \right) = RT \ln a^{wL} + \frac{V_0^L}{N_0^{wL}} (P_0^L - P_{0\infty}^L) + b(S_0^L) \times (0.1908m^2 + 18.04m). \quad (23)$$

[41] The activity is computed as a function of m using relationships from Heyrovská's paper. Using the usual parameterization of pressure, $P_{0\infty}^L = 0$, and using pure water density at 25°C, gives

$$RT \ln \left(\frac{P^{wG}}{P_{0\infty}^{wG}} \right) = RT \ln a^{wL}(m) + \frac{M^{H_2O}}{\rho_0^{H_2O}} P^L(S_0^L) + b(S_0^L) \cdot (0.1908m^2 + 18.04m), \quad (24)$$

where

$$P^L(S_0^L) = \frac{\sigma^{LG}(m=0)}{\sigma_0^{LG}} \tilde{P}^L(S^L(0), m=0) = \tilde{P}^L(S_0^L).$$

[42] *Bear and Gilman* [1995] note that vapor depression resulting from interface curvature is often negligible compared to depression resulting from salt concentration. However, under drier conditions in finer textured media, interface curvature effects are not negligible (Figure 2). Considering the ratios of combinations of the terms on the right-hand side of equation (24) it is possible to see which terms dominate for different salt concentrations and water contents (e.g., Figure 3). The regions with relative error values below 0.01 in Figures 3c–3f indicate where the approximation given by neglecting the term in the numerator in favor of the term(s) in the denominator is valid. Comparison of Figures 3c, 3d, and 3f shows where various terms dominate the volume correction term, and Figure 3e shows that while the activity often dominates, the dilute approximation term is often nonnegligible. The plots for loam and sand are not shown, but in general, interface curvature effects are much smaller for these coarser textured soils.

[43] Note that the error (Figure 3b) is computed using equation (11) above, and that the denominator goes to zero; so even for small deviations from the linear fit, the error must go to infinity. It can be shown that even at high water contents, where the linear approximation of the pressure function may be poor, the pressure is still a well-behaved function of salt concentration and not too far from linear [Burns, 2004]. Since the activity term commonly dominates in this region, even a doubling or tripling of the slope to some conservative value shows that the departure from linearity is of small importance. For this reason, the high error in Figure 3b is of little concern. The conclusion that may be drawn from Figure 3 is that the volume correction term is negligible except under very dry conditions. Further, the effects are more substantial for finer textured soils.

[44] The algorithm used to calculate and plot Figure 3 may be used for any porous media for which the appropriate van Genuchten parameters are known [Burns, 2004]. Other constitutive functions [e.g., *Brooks and Corey*, 1964] are as easily employed, and may be needed if the fit is not good. This is especially true for poor fit in the dry region where nonnegligible effects due to the volume correction term may occur.

[45] Except under very dilute conditions, each of the salt corrections to the liquid pressure is important (Figure 4), with the effects being more pronounced in finer soils [Burns, 2004]. Interestingly, the error is smaller where both corrections are neglected, since the correction to surface tension tends to increase the magnitude of the pressure, while the volume correction tends to lower the magnitude of pressure.

[46] Equation (5a) may be thought of as the efficiency with which a gradient in salt is converted into a gradient in vapor pressure. In order to compute equation (5a), it is necessary to take the derivative of the activity. For this order of magnitude analysis, it is sufficient to assume the activity is linear with respect to molality [Burns, 2004]. With this assumption, it can be seen that the volume correction term in (5a) is largely dominated by the activity term, but that drier, finer soils are more strongly affected by the volume correction term (Figure 5). In the wetter region (Figure 5d), a constant value of -0.124 is a good approximation to equation (5a), and that neglecting

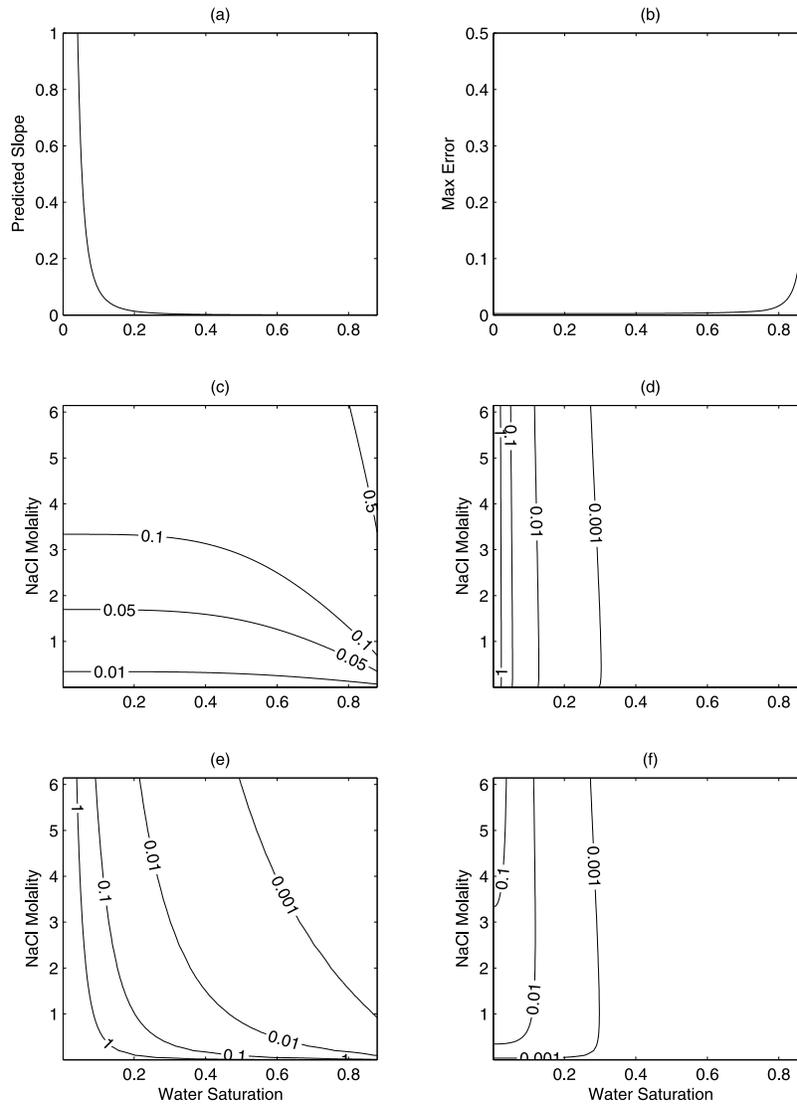


Figure 3. Plots comparing the various terms in the vapor pressure constitutive relation for silt. (a) Slope of the linear approximation ($b(S_0^L)$) to the pressure function. (b) Error (equation (11)) between the linear fit and the computed pressure. (c) Absolute value of the ratio of the volume correction term to the dilute approximation term for equation (8). (d) Absolute value of the ratio of the volume correction term to the activity term for equation (8). (e) Absolute value of the ratio of the dilute approximation term to the activity term for equation (8). (f) Plot of equation (10): absolute value of the ratio of the volume correction term to the sum of the dilute approximation and activity terms for equation (8). The contours in Figures 3c through 3f represent the magnitude of relative error.

only the volume correction terms in (5a) (in both the differential and the vapor pressure) yields only marginally better results (Figure 5c). The domain over which this is true is even larger for loam and sand. In fact, the plot for sand is indistinguishable from a constant on the scale of the plots shown here.

[47] Equation (5b) may be thought of as the efficiency with which a gradient in liquid water content is converted into a gradient in vapor pressure. Solution of this equation shows that neglecting the salt effects on specific volume is only acceptable for dilute solutions (Figure 6). The silt again showed the strongest influence, and under very dry conditions (i.e., the indistinguishable contours near zero saturation) the magnitudes and signs of the differential terms in

(5b) are such that they effectively cancel, resulting in a very rapid decrease to zero.

[48] Equation (7a) may be thought of as the efficiency with which a gradient in salt concentration is converted into a gradient in liquid pressure. Analysis of equation (7a) for silt (the results for loam and sand are very similar to silt) shows that the differential in terms of pressure (\tilde{P}^L) are almost always dominated by the differential term for surface tension (Figures 7a and 7b). It is still necessary to account for the volumetric effect in \tilde{P}^L , except in the dilute case (Figure 7c). A very good approximation to equation (7a) is

$$\frac{\partial P^L}{\partial m} = \frac{\tilde{P}^L}{\sigma_0^{LG}} \frac{\partial \sigma^{LG}}{\partial m} = \frac{1.7}{72} \tilde{P}^L (S^L(S_0^L, m)), \quad (25)$$

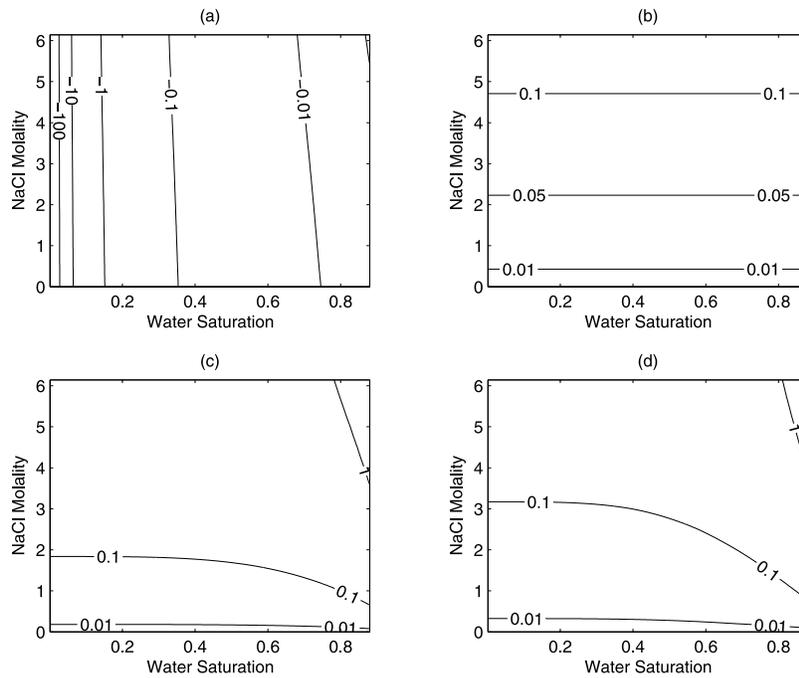


Figure 4. Plots comparing the various terms in the liquid pressure constitutive relation for silt. (a) Plot of liquid pressure (equation (2)) in units of MPa. Figures 4b–4d are of the error (equation (11)) induced by neglecting one or more terms in equation (2): (b) Only the surface tension correction term ($\sigma^{LG}/\sigma_0^{LG}$) is neglected; (c) only the volume correction to the saturation is neglected; and (d) both corrections are neglected (i.e., using the pressure relationship for only water content). The contours in Figures 4b–4d represent the magnitude of relative error.

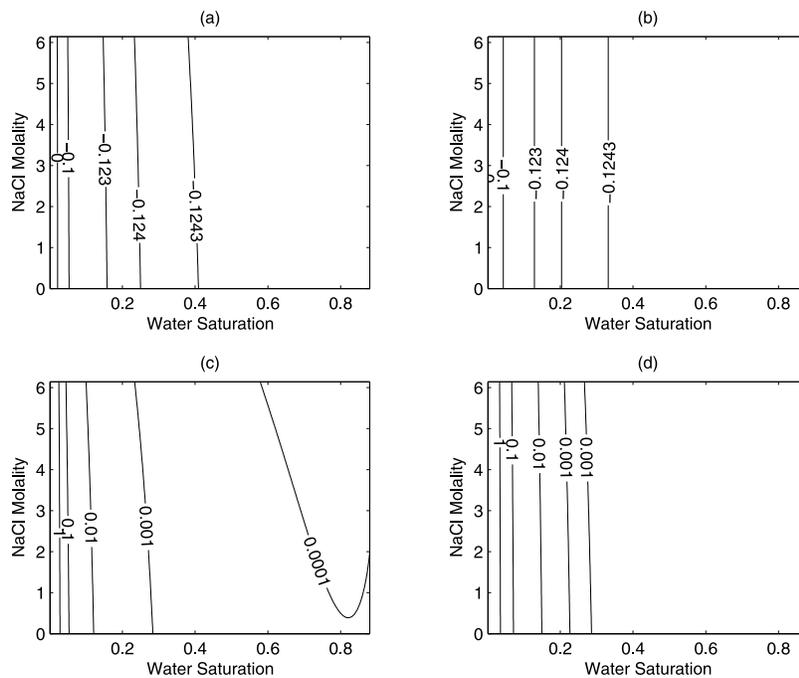


Figure 5. Plots comparing terms related to the vapor pressure gradient resulting from salt gradients for silt. (a) Plot of equation (5a). (b) Plot of equation (5a) but neglecting the volume correction terms. (c) Error (equation (11)) induced by neglecting volume correction terms. (d) Error induced by approximating equation (5a) with the constant -0.124 . The contours in Figures 5a and 5b represent the values of the differential on the left-hand side of equation (5a), and the contours in Figures 5c and 5d represent the magnitude of relative error.

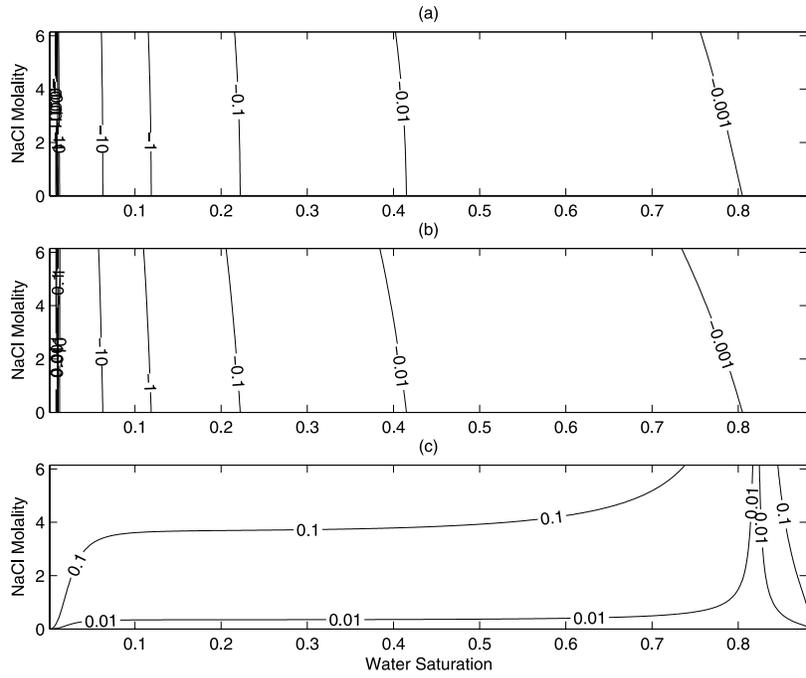


Figure 6. Plots comparing terms related to the vapor pressure gradient resulting from water content gradients for silt. (a) Plot of the differential on the left-hand side of equation (5b) (shown as contours). (b) Plot of the same differential in equation (5b) but neglecting the volume correction terms in both the vapor pressure and the differential. (c) Plot with contours representing relative error (equation (11)) resulting from the approximation described in Figure 6b.

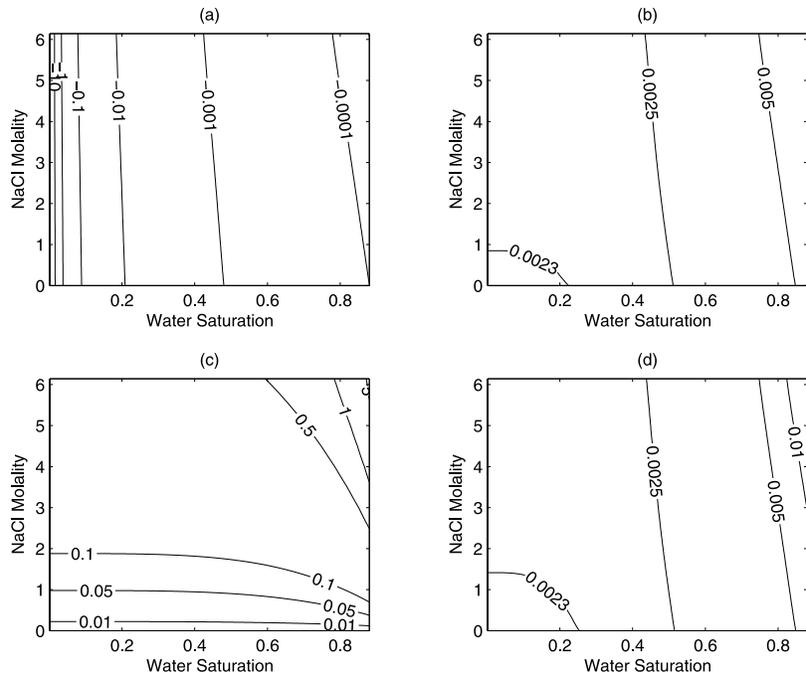


Figure 7. Plots comparing terms related to the liquid pressure gradient resulting from salt gradients for silt. (a) Plot of the left-hand side of equation (7a) (shown as contours). (b) Plot with contours showing the ratio of the magnitudes of the pressure differential term to the surface tension differential term. (c) Plot with contours showing the magnitude of relative error (equation (11)) induced by assuming that \tilde{P}^L is not a function of salt content (i.e., there is no correction of saturation for salt content). (d) Plot with contours of the relative error induced by assuming that the \tilde{P}^L derivative term is negligible compared to the surface tension derivative term (but still allowing \tilde{P}^L to be a function of m).

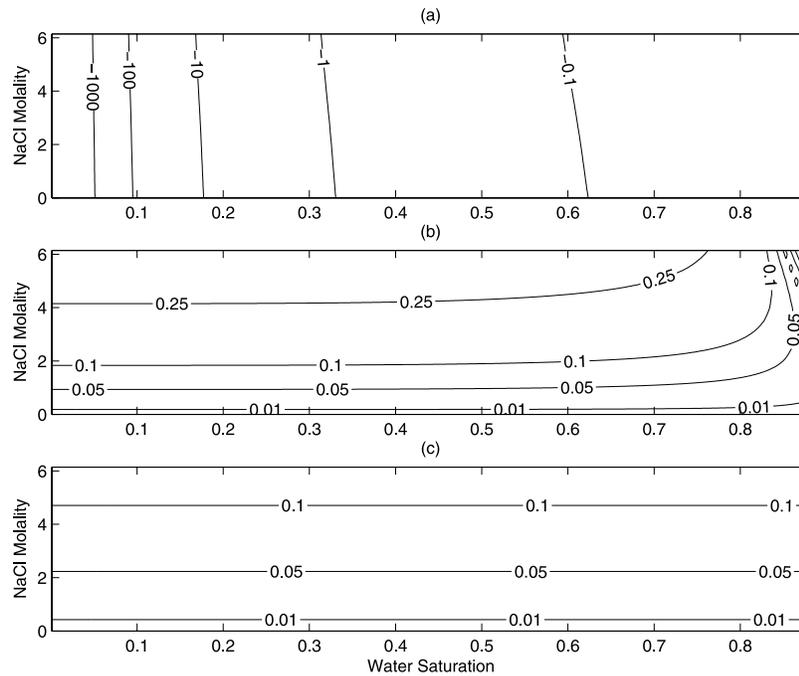


Figure 8. Plots comparing terms related to the liquid pressure gradient resulting from water content gradients for silt. (a) Plot of the left-hand side of equation (7b) (shown as contours). (b) Plot with contours of the relative error induced by neglecting the volume correction in the derivative. (c) Relative error induced by neglecting the surface tension.

where equation (18) was used (Figure 7d). This is true for loam and sand also.

[49] When considering gradients in liquid pressure resulting from gradients in water content (equation (7b)), neither the volume correction nor the surface tension may be neglected except in the dilute case for silt (Figure 8), which is true in general for loam and sand also.

[50] It is tempting to consider the magnitudes of (5a) compared to (5b) or (7a) compared to (7b), but without prior knowledge of the gradients in water and salt content to be encountered during evolution of an initial boundary value problem, this is not possible. Instead, it is noted that (5a), (5b), (7a), and (7b) provide the appropriate conversions from the dependent variables (pressures) to the primary variables (water and salt contents) for solution of the differential equations.

5.3. Application to the Data of Scotter

[51] In a series of papers by *Scotter and Raats* [1970], *Parlange* [1973], and *Scotter* [1974], the phenomenon of water condensation near salt crystals in a relatively dry porous medium is experimentally and mathematically analyzed. In the experiments, a pure phase salt (in this case NaCl) was placed against an unsaturated soil at uniform unsaturated moisture content at 25°C. Moisture and salt profiles were found to be constant (for the same initial conditions) with respect to the transformed variable $\eta = x/t^{1/2}$ (Figure 9). In these experiments water in the vapor phase moved from the dry region to the wet region, where it condensed because of vapor pressure lowering associated with the salt (solid phase salt is at $\eta = 0$) and saline water. Because of this condensation, the moisture content of the soil adjacent to the salt was sufficiently high to cause water flow back toward the dry region. Movement in the right-hand side was dominated by

vapor flow (hereafter called the dry region), and the left-hand side has combined liquid and vapor flow (hereafter called the wet region).

[52] Using the above results, the vapor pressures and water potentials for the Scotter data may be plotted [*Scotter*, 1974]. The reported gravimetric values of water and salt were converted to volumetric assuming a porosity of 0.3 and a solid density of 2.65 g/cm³. van Genuchten parameters that represent Scotter's soil are $\bar{\alpha} = 0.000329573$ and $N = 1.483$. Equation (6) of *Heyrovska* [1996] was used to compute a^{wL} using linear interpolation from the closely spaced tabulated values. Alternatively, the method of *Pitzer and Peiper* [1984] could be used to get the information computed from the Heyrovska relations. The method of Heyrovska was selected for superior full range performance at 25°C, and because the underlying physics proposed by Heyrovska appears to be more likely correct. The Pitzer theory supposes that the salts completely dissociate even at high strength, then correct for this error with an activity coefficient.

[53] Equation (24) may again be employed to perform an order of magnitude analysis and to plot vapor pressure. When predicting vapor pressure (equation (1)), the error induced by neglecting the volume correction term is small (Figure 10). The effect of the salt content and interface curvature on the vapor pressure (Figure 11) is large; though, as predicted by Figure 10, there appears to be little effect due to neglecting the volume correction term. It is likely that measurement errors are larger than errors induced by neglecting the volume correction term. In the dry region, Scotter's data showed detectible salt concentrations, resulting in the nonnegligible salt effects. In most of the wet region, high salt concentrations dominate the vapor depres-

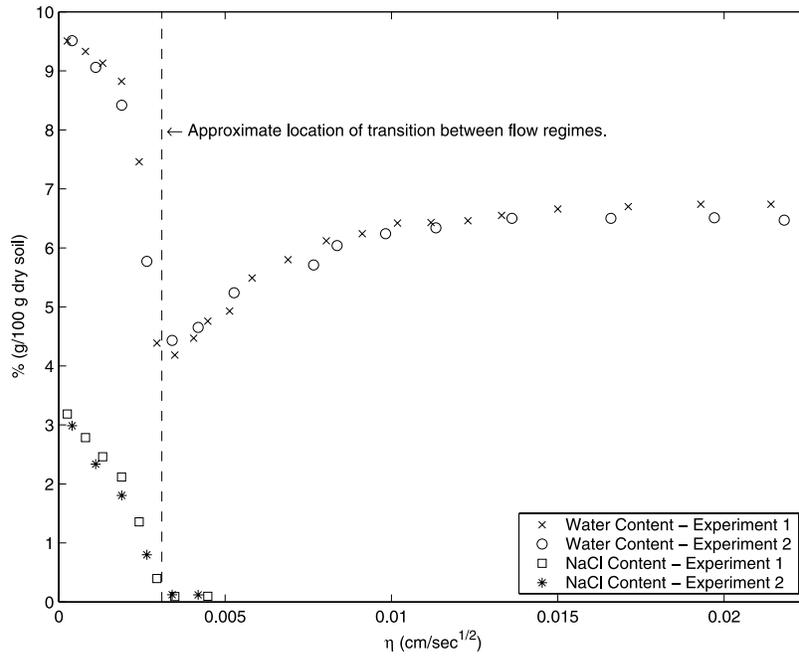


Figure 9. Gravimetric water and NaCl content from *Scotter* [1974]: $\eta = x/\sqrt{t}$ is the transformed variable used by Scotter, and the figure may be viewed as showing concentrations along the soil column for two different times (i.e., rescaling the data by a factor of \sqrt{t} will show the actual spatial distribution of the measured concentrations). This transform is helpful when investigating diffusion-like processes. Pure solid phase NaCl is at $\eta = 0$ (analogously, $x = 0$).

sion resulting in the interface curvature effects being relatively small. For comparison, the vapor pressure of pure water over a flat interface and the vapor pressure over a saturated salt solution are plotted (using data from *Apelblat and Korin* [1998]).

[54] The volume correction term is not negligible when computing equation (5a) for Scotter's soil (Figure 12). However, for most of the low salt concentration data (i.e., most of the points where this correction may be required), the gradients in salt concentration are small enough that it is

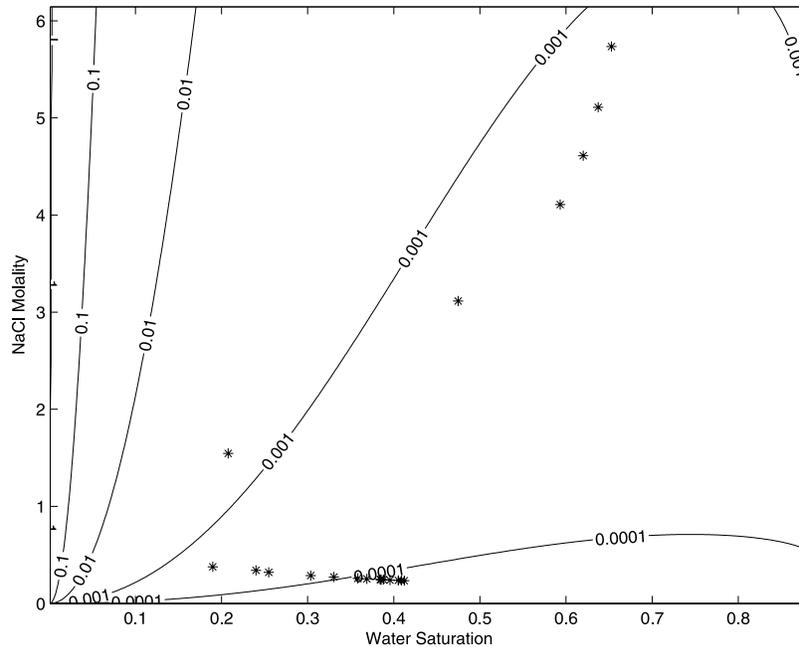


Figure 10. Scotter's data: plot of the error (equation (11)) induced by neglecting the volume correction term in equation (2) (relative error is shown by contours). The asterisks are data from experiment 1.

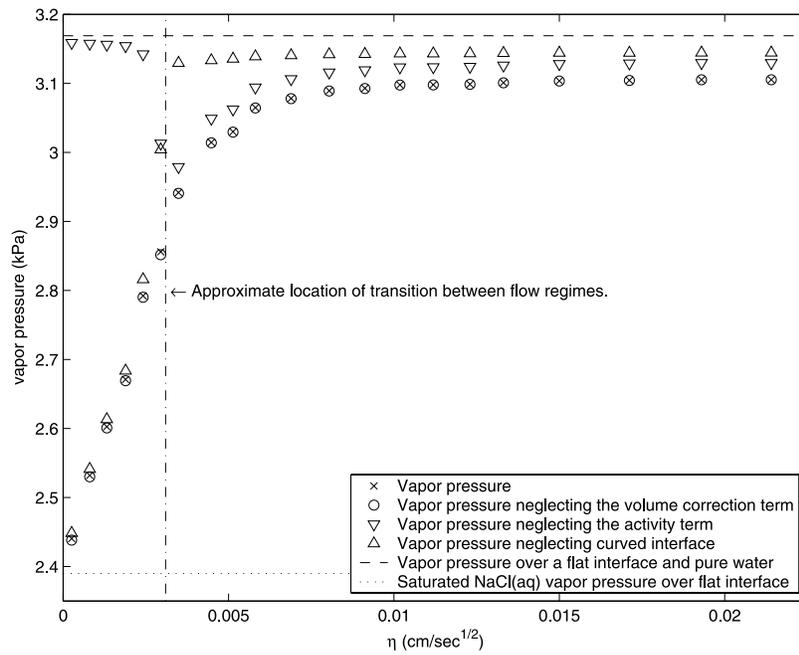


Figure 11. Comparison of the relative importance of different corrections when computing vapor pressure for Scotter’s data. Computed vapor pressure (equation (1)) from experiment 1 is shown for four cases: (1) the full equation, (2) neglecting only the volume correction term (equation (4) or, more specifically, equation (11)), (3) neglecting the activity term (activity = 1), and (4) neglecting the entire exponential term (curved interface correction).

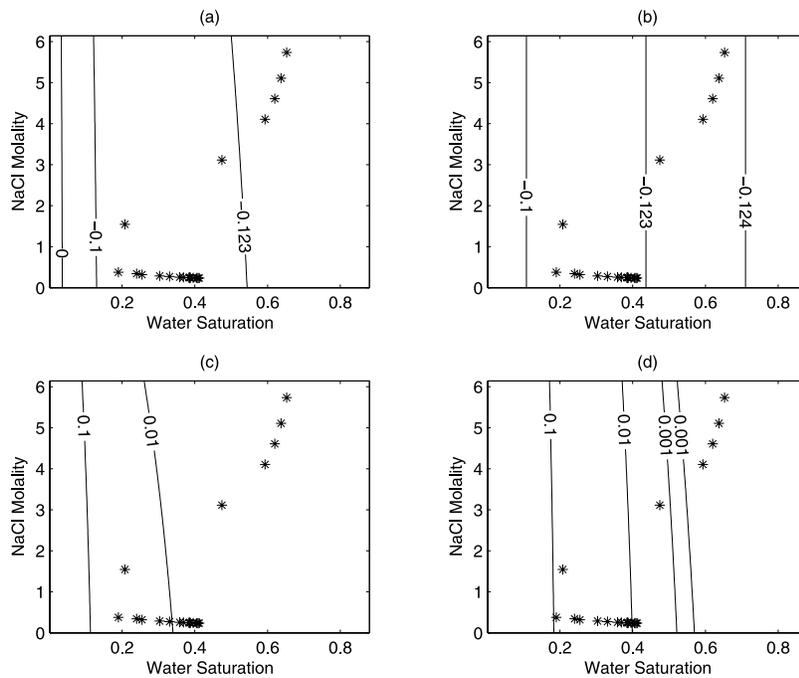


Figure 12. Plots comparing terms related to the vapor pressure gradient resulting from salt gradients for Scotter’s soil. (a) Contour plot of the differential on the left-hand side of equation (5a). (b) Contour plot of the same differential (equation (5a)) but neglecting the volume correction terms. (c) Contour plot of the relative error (equation (11)) induced by neglecting volume correction terms. (d) Contour plot of the relative error (equation (11)) induced by approximating equation (5a) with the constant -0.123 . Asterisks are data from experiment 1.

likely that there is a negligible vapor flux resulting from salt gradients in this region. This leaves only a very narrow region at the transition from dry to wet where this correction may be important. This provides a concrete example of why comparison of (5a) to (5b) (analogously, (7a) to (7b)) should not occur a priori.

[55] As expected, equation (25) is also a good approximation for equation (7a) for the Scotter data (figure not shown). Examination of Figures 6 and 8 indicates that no terms may be neglected for equations (5b) and (7b).

[56] Scotter's data provide one more important support for the previous analysis. It is natural to wonder if the use of the van Genuchten pressure-saturation relation for representing the dry end behavior is appropriate. Scotter measured the pressure-saturation relationship at a range of water contents [Scotter, 1974], and his lowest two water contents correspond to $\sim 2\%$ and $\sim 6\%$ saturation for the van Genuchten model and the previous analysis. The dominant effect controlling dry end behavior for Figure 10 is the rate of change of pressure for a small change in saturation (associated with an addition of salt). In other words, it is the slope of the pressure-saturation curve that is most important, and the behavior of the curves in Figure 10 is supported by data between 2% and 6%, and not the asymptotic behavior of the van Genuchten model. Since Figure 10 shows nonnegligible effects up to 17% saturation, the exhibited behavior is not an artifact of the selected model.

6. Conclusions

[57] The methodology developed in this manuscript is general, while the constitutive relations used (e.g., van Genuchten pressure-saturation relation) were introduced only to allow consideration of a specific case. Constitutive relations that fit real data well should be used to estimate the importance of various terms for any particular problem of interest. The application to the Scotter data set shows that while the volume correction term may not be important for computation of vapor pressure, it may still be important to account for when computing the coefficients of gradients in the primary variables (i.e., vapor and water pressure).

[58] The linear approximation to pressure as a function of NaCl salt concentration (yielding $b(S_0^L)$) provides a good, robust correction in the volume correction term for all water contents. This is true because the correction is accurate in the dry region and negligible in the wet region. As a result, the approximation scheme, given by equation (22), would provide a simple and effective first-order correction for high-strength brines for use in numerical models.

[59] For high-concentration NaCl solutions the dilute approximation may be insufficient for computation of vapor and liquid pressures. Specifically, it may be necessary to include volume corrections under drier conditions and for finer textured sediments. These conditions naturally occur in many arid environments subjected to continued high evaporative potentials. Examination of Scotter's data shows that, except under these extreme conditions, it is likely that the relationships utilized by Olivella *et al.* [1996], Bear and Gilman [1995], and Nassar and Horton [1989] may be quite useful for sodium chloride under a broad range of natural conditions. For conditions where it is suspected that the dilute approximation is insufficient, and it is desired to evaluate the necessity of including additional terms, it is

particularly critical to use a model that represents the dry end behavior of the pressure saturation curve well, since the model is very sensitive to the pressure-saturation curve slope in this region.

Notation

Variables

| | |
|---|---|
| T | absolute temperature. |
| P | pressure. |
| V | volume. |
| R | universal gas constant. |
| $\mu^{i\alpha}$ | chemical potential of the i th constituent in phase α . |
| $a^{i\alpha}$ | chemical activity of the i th constituent in phase α . |
| $N^{i\alpha}$ | number of moles of the i th constituent in phase α . |
| m | molality of salt in water. |
| $v^{iL} \equiv \frac{m}{N^{iL}}$ | specific volume of the i th constituent in the liquid phase (ratio of liquid volume to moles of water in the liquid). |
| $\sigma^{LG} = \frac{\partial U^{LG}}{\partial A^{LG}}$ | surface tension at the gas-liquid interface. |
| A^{LG} | area of the gas-liquid interface. |
| $\frac{dA^{LG}}{dV^L}$ | the gas-liquid interface area to liquid volume ratio (or the density of gas-liquid interface). |
| $\tilde{P}^L \equiv P^L(S^L)$ | equivalent liquid pressure neglecting changes in surface tension (see discussion following equation (3)). |
| S | saturation. |
| ϕ^L | volumetric liquid content (volume of liquid divided by total volume of soil, liquid, and gas in porous media). |
| $\eta = x/t^{1/2}$ | transformed variable for data analysis. |
| Differentials | |
| d | total differential. |
| α | partial differential. |
| Superscripts | |
| aG | air in gas. |
| α | arbitrary phase or subsystem.. |
| G | gas phase. |
| hL | salt in liquid. |
| L | liquid phase. |
| LG | gas-liquid interface. |
| wL | water in liquid. |
| wG | water in gas. |
| Subscripts | |
| ∞ | reference condition of flat gas-liquid interface (i.e., infinite radius of curvature). |
| 0 | reference condition corresponding to known salt content (generally zero or negligible amount of salt). |

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