

AN ABSTRACT OF THE THESIS OF

Erick R. Burns for the degree of Master of Science in Mathematics presented on May 26, 2004.

Title: Thermodynamic Correction for Salts in Variably Saturated Porous Media.

Abstract approved:

Redacted for Privacy

Ronald B. Guenther

Using thermodynamic principles, the general relationship describing the equilibrium vapor content in the gas phase above a saline liquid and across a curved liquid-gas interface is developed. Since high salt concentration also affects the intensive and extensive liquid properties, it is also necessary to account for these effects in liquid water content/liquid water pressure relationship curves so that experimentally derived curves for pure water may be useful for elevated salt concentrations. The appropriate thermodynamic relationship is derived to describe the salt effects on liquid and vapor properties. The resulting equations are valid for salt concentrations between zero and saturation, and for any temperatures that nominally occur in near-surface geologic materials. An example using the derived relationships for NaCl is included.

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May 26, 2004

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Thermodynamic Correction for
Salts in Variably Saturated Porous Media.

by
Erick R. Burns

A THESIS

submitted to

Oregon State University

in partial fulfillment
of the requirements for the
degree of

Master of Science

Presented May 26, 2004
Commencement June 2005

Master of Science thesis of Erick R. Burns presented on May 26, 2004.

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ACKNOWLEDGEMENTS

I wish to express my thanks to many individuals. First, I thank Professor Emeritus Ron Guenther. He is a rare individual with a great capacity to teach and to encourage. Since my previous academic training is in geology and engineering, it was a tortuous path that led to a M.S. in mathematics. Ron's enthusiasm for the subjects of applied mathematics and the flow of fluids in porous media provided a common ground upon which to base this work and much of the work still to be published in my Ph.D. dissertation.

Thanks are also due to Professor Maria Dragila. She, Ron, and I spent many hours discussing research topics, from which funding was finally derived. Professor Emeritus Larry Boersma was instrumental in getting us interested in problems related to the unsaturated flow of saline fluids. Professor Noam Weisbrod has provided much help over the years, and his conceptual model of flow of salts in unsaturated porous media formed the foundation upon which the research proposal was based. I thank the U.S. EPA for funding this research under a STAR (Science to Achieve Results) Fellowship. Maria and Ron both deserve additional thanks for their contributions towards my PhD research, but the details shall have to wait until the acknowledgements section of that dissertation.

Professors John Selker and Jean-Yves Parlange have been instrumental in the research summarized in this thesis. The nucleus of this thesis (and the subsequent paper to be submitted) was written during a one-month visit to Cornell University to work with

Yves. It has been my great pleasure to work with both of these scientists/engineers, and they and Ron Guenther fully deserve co-authorship of this work.

Professors Enrique Thomann (minor advisor) and Don Solmon (second committee member in major) have both been a great encouragement to me. Both are enthusiastic about mathematics and its use, and both have helped me understand some aspect of applied mathematics that has aided in the production of this thesis.

Thanks also to Brian Wood. Not only has he been the graduate school representative, but his research is half a step away from my research, so he has been a wonderful surprise addition to both the M.S. and Ph.D. committees. He has been both a resource and a sounding board for ideas that dance along the line between mixture theory and averaging theory.

I have been told that it is rare that a graduate student ends up working with each of their committee members and other faculty on campus as much as I have. I think this is unfortunate because my research has only been made better by conversations with all of the above people (plus a few to be mentioned in the Ph.D. acknowledgements). I feel blessed by God (to whom I also owe thanks) to have so many people that I enjoy both personally and scientifically involved with my graduate studies.

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DEDICATION

For Mandy ...my biggest supporter.

Introduction

It is important to understand the behavior of the flow of saline fluids in non-isothermal, unsaturated porous media. Understanding the effects of salt in such systems is required in soil science, in the design of hazardous waste storage, and in drying science (e.g., manufacturing and processing of materials). It has long been known that vapor density is reduced above both curved interfaces and above saline fluids. Relationships describing this vapor pressure reduction have been derived for the curved interface and the salt effect separately (see for example Edlefsen and Anderson, 1943), but to the authors' knowledge, no general derivation from first principles of the synergistic effects of salt and the curved interface has been accomplished prior to this work. However, relationships have been defined for various purposes (Olivella et al. 1996; Bear and Gilman 1995; and Nassar and Horton 1989), but the detail and method of determination of these relationships has been dictated by the level of detail necessary to accomplish specific tasks. A brief comparison of the results of this paper to those listed above is accomplished in the "Discussion" section below.

The goal of this work is to define a general analytic relationship that aids in the conceptual understanding of the underlying physics, as well as allowing the use of numerical approximation for computation. An example of such a numerical approximation for NaCl is shown below, as well as an example of use of this approximation to real data collected during laboratory experiments.

Derivation of Constitutive Relationships

Preliminaries and Assumptions

In this section, the equilibrium relation between a saline solution and the overlying air water vapor mixture is derived for a curved gas-liquid interface. First, the general relations are developed; then, the often used dilute solution approximation is derived. Finally, derivation of a method to compute non-dilute salt concentration effects is completed.

During the derivation, several assumptions will be used. These assumptions are not overly restrictive, so the results are quite general. The assumptions are stated explicitly in an attempt to remove ambiguity over the applicability of the results. As a generalization, the assumptions may be grouped naturally into three sets.

Assumptions 1 through 5 give sufficient (though not necessary) conditions to use equilibrium thermodynamics.

Assumption 1: The total system is closed to mass transfer.

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

Assumption 3: The total system is bounded by rigid walls (i.e., the total system, composed of one or more fluids, is constant volume).

Assumption 4: Equilibrium between the phases is reached much faster than changes driven by external forcing.

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

The equations resulting from application of the first five assumptions are very general. In fact they are so general that it is necessary to define the system of interest further before computations may be made. Assumptions 6 through 12 describe some general conditions that hold for saline fluids in an isothermal two-phase system.

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

Assumption 7: The salt (h) is either a single salt species or may be well-represented with effective parameters such that all salt chemical potentials (e.g., μ^{hL}) and mole numbers (e.g., N^{hL}) are well-defined as single-valued variables.

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

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).

Assumption 10: All phase changes occur under isothermal conditions. This condition may be relaxed later, but provides clarity during the derivation.

Assumption 11: The gas phase behaves like an ideal gas.

Assumption 12: There exists a unique single-valued function $V^L = V^L(N^{wL}, N^{hL})$ such that if any two of the values (V^L, N^{wL}, N^{hL}) are known, then the third variable may be computed.

Assumptions 6 through 12 narrow the scope of our relations further, and some very nice results may be derived. Lastly, assumptions 13 and 14 narrow the scope of the relations to a porous media. It is noted that while assumption 12 is grouped above, it is not used until porous media are considered.

Assumption 13: Assume that the gas phase inside the porous media is connected with

$$\text{a sufficiently large gas volume such that } \left| \int_{\infty}^P \frac{V^L}{N^{wL}} dP^L \right| \gg \left| \int_{\infty}^P \frac{V^L}{N^{wL}} dP^G \right|.$$

Assumption 14: Assume that σ^{LG} is a function of salt content and temperature only,

$$\text{and } \frac{dA^{LG}}{dV^L} \text{ is only a function of saturation.}$$

Admittedly, assumptions 13 and 14 appear somewhat cryptic at this point, but during the course of derivation, the relations arise naturally. They are listed at this point for the sake of completeness. In the following derivations, the assumptions are implemented sequentially, so that it is easy to see what limitations exist for use of the resulting equations.

Derivations

Consider the super-system in the schematic diagram, Figure 1. The system is composed of the liquid (L), the gas (G), and the liquid-gas interface (LG). This super-system may be well approximated by two adjacent homogeneous sub-systems (i.e., a liquid phase and a gas phase) with a thin transition zone between the phases. In order to accurately describe the system thermodynamics it is necessary to account for the liquid-gas interface explicitly. If assumptions 1 through 5 are satisfied, then the tools provided by standard reversible thermodynamics may be used to provide a precise formulation of the energy relations for each phase. For a reversible process in a homogeneous system, the differential form of the conservation of energy equation is given by the Gibbs relation (Callen, 1960):

$$(1) \quad dU = TdH - PdV + \sum_i \mu^i dN^i,$$

where the index i includes every chemical constituent in the homogeneous mixture, and the symbols are defined in the “Notation” section of the appendices.

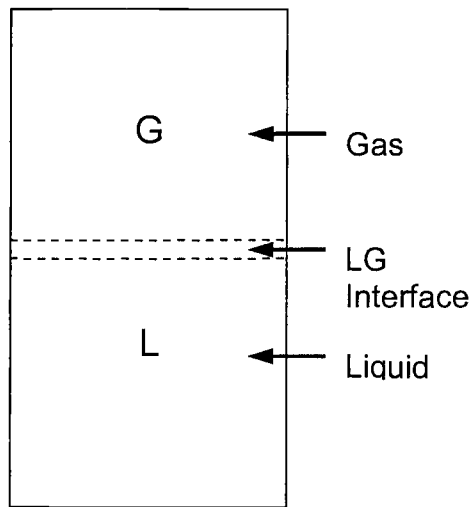


Figure 1: Schematic representation of a system composed of both a liquid and a gas.

Another well-known fact that may be used is that under the above conditions, the Gibbs-Duhem relation also holds (Callen, 1960):

$$(2) \quad 0 = HdT - VdP + \sum_i N^i d\mu^i.$$

Equations (1) and (2) are the standard starting place for the use of equilibrium thermodynamics. Equation (1) relates the differentials of the extensive variables. Equation (2) relates the differentials of the intensive variables. Defining surface

tension in the usual way (i.e. $\sigma^{LG} = \frac{\partial U^{LG}}{\partial A^{LG}}$), and writing the appropriate versions of equation (1) for each phase and the interface yields:

$$(3a) \quad dU^L = T^L dH^L - P^L dV^L + \sum_i \mu^{iL} dN^{iL} ,$$

$$(3b) \quad dU^G = T^G dH^G - P^G dV^G + \sum_i \mu^{iG} dN^{iG} , \text{ and}$$

$$(3c) \quad dU^{LG} = T^{LG} dH^{LG} - \sigma^{LG} dA^{LG} + \sum_i \mu^{iLG} dN^{iLG} .$$

Here, it is worthwhile to note that the sign convention for the pressure and surface tension terms varies from author to author and discipline to discipline. Care must be taken to use a consistent sign convention throughout application of the thermodynamic results. The corresponding Gibbs-Duhem relations are:

$$(4a) \quad 0 = H^L dT^L - V^L dP^L + \sum_i N^{iL} d\mu^{iL} ,$$

$$(4b) \quad 0 = H^G dT^G - V^G dP^G + \sum_i N^{iG} d\mu^{iG} , \text{ and}$$

$$(4c) \quad 0 = H^{LG} dT^{LG} - A^{LG} d\sigma^{LG} + \sum_i N^{iLG} d\mu^{iLG} .$$

Since the eventual goal is to use conservation equations to simplify the relations, it is convenient to note here that:

$$(5) \quad U^{sys} = U^L + U^G + U^{LG} ,$$

$$(6) \quad H^{sys} = H^L + H^G + H^{LG},$$

$$(7) \quad V^{sys} = V^L + V^G + V^{LG}, \text{ and}$$

$$(8) \quad N^{i,sys} = N^{iL} + N^{iG} + N^{iLG} \text{ for all } i.$$

Recall that assumptions 1 through 5 are sufficient conditions to ensure equations (1) through (8) describe the system in question, but they are not necessary. In fact, the assumptions above are more restrictive than necessary, so re-iterating the assumptions in mathematical form gives additional restrictions on the set of equations.

Assumption 1 ensures equation (8) is equal to a constant, which implies:

$$(9) \quad dN^{iL} + dN^{iG} + dN^{iLG} = 0 \text{ for all } i.$$

Assumption 2 allowed the use of surface tension in equations (3c) and (4c), and it also implies that the volume of the interface is negligibly small. Equation (7) becomes:

$$(10) \quad V^{sys} = V^L + V^G.$$

Assumption 3 ensures equations (7) and (10) are equal to constants. This implies:

$$(11) \quad dV^L + dV^G = 0.$$

Assumption 4 implies that thermal and chemical equilibrium exists between the phases, giving:

$$(12) \quad T^L = T^G = T^{LG} \equiv T, \text{ and}$$

$$(13) \quad \mu^{iL} = \mu^{iG} = \mu^{iLG} \equiv \mu^i \text{ for all } i.$$

Assumption 5 implies that the only energy flux into or out of the system is heat flux.

The heat flux is described by the imperfect differential, δQ . From Callen (1960),

$\delta Q = TdH$. Combining this with equation (12) gives:

$$(14) \quad dU^{sys} = TdH^{sys}.$$

Adding equations (3a), (3b), and (3c), and using relations described by equations (9)

and (11) through (14) yields the commonly accepted form of the mechanical

equilibrium condition across an interface:

$$(15) \quad P^G - P^L = \sigma^{LG} \frac{dA^{LG}}{dV^L}.$$

As a quick check of the validity of equation (15), Laplace's Equation may be derived.

For a meniscus with zero contact angle in a capillary tube, it is known that

$A^{LG} = \frac{1}{2} 4\pi r^2$ and $V^L = \frac{1}{2} \frac{4}{3} \pi r^3$ (r = radius of tube) from which it follows immediately

that:

$$\frac{dA^{LG}}{dV^L} = \frac{2}{r}, \text{ which results in Laplace's Equation: } P^G - P^L = \sigma^{LG} \frac{2}{r}.$$

Since the Gibbs-Duhem relations relate the differentials of the intensive variables, the conservation conditions do not lead to immediate simplification. Instead, it is necessary to make additional assumptions that adequately describe the real physical system of interest. For this reason, assumptions 6 through 12 are used to describe exactly what is assumed to be true for a saline liquid.

Assumption 6 implies:

$$(16) \quad \sum_i N^{i\alpha} = N^{w\alpha} + N^{a\alpha} + N^{h\alpha} \equiv N^{\alpha} \text{ for all } \alpha .$$

Assumption 7 is used in this derivation to greatly simplify notation and to show the utility of the results. The theory developed here extends naturally to multiple salts (e.g., $N_1^{hL}, N_2^{hL}, N_3^{hL}, \dots$), but appropriate definitions of chemical affinities must be made (c.f., DeHoff, 1993).

Assumptions 8 and 9 give:

$$(17) \quad N^{hG} = 0 , \text{ and}$$

$$(18) \quad N^{aL} \cong 0 .$$

Assumptions 8 and 9 are consistent with the notion that the change in chemical potential of air in water (and salt in air) between any two thermodynamic states has a negligible impact on the system. In a system where pH is important, it would become

necessary to further subdivide the air into constituents that affect equilibrium values of pH, though this is not considered here.

Assumption 10 is used to simplify the relations, and to preclude the need for defining entropy. It is beyond the scope of this paper to show sufficient conditions for this assumption to be valid, but instead, it is noted that isothermal conditions are expected under many laboratory conditions. Also, during the drying of porous media, isothermal conditions have been documented to persist for extended periods of time (c.f., Luikov, 1975). This is true because the process of evaporation at a constant atmospheric pressure implies that the process is occurring at the saturation temperature. Assumption 10 implies:

$$(19) \quad dT = 0 .$$

Assumption 11 allows the use of the ideal gas law and Dalton's law of partial pressures. This assumption is deemed valid for low gas pressures (e.g., atmospheric pressure). By assumption 8, Dalton's Law gives:

$$(20) \quad P^G = P^{wG} + P^{aG} .$$

Dividing equation (4b) by the total number of moles in the gas (N^G), then substituting in equations (16), (17), (19), and (20), and solving for the chemical potential of water yields:

$$(21) \quad d\mu^{wG} = \frac{1}{X^{wG}} \left(\frac{V^G}{N^G} dP^G - X^{aG} d\mu^{aG} \right), \text{ where } X^{iG} = \frac{N^{iG}}{N^G} \text{ is the mole fraction.}$$

Using the ideal gas law as it applies to the total and partial pressures yields the following relation:

$$(22) \quad X^{iG} P^G = \frac{N^{iG}}{N^G} P^G = \frac{N^{iG} RT}{V^G} = P^{iG} \text{ for all } i.$$

Equation (22) allows equation (21) to be written:

$$(23) \quad d\mu^{wG} = \frac{1}{P^{wG}} (RT dP^G - P^{aG} d\mu^{aG}).$$

For gases at low pressure, the following relation holds:

$$(24) \quad \mu^{iG} = \mu_0^{iG} + RT \ln \left(\frac{P^{iG}}{P_o^{iG}} \right) \text{ for all } i.$$

It is more convenient here to write equation (24) in its differential form:

$$(25) \quad d\mu^{iG} = RT d(\ln P^{iG}) = RT \frac{dP^{iG}}{P^{iG}} \text{ for all } i.$$

Substituting equation (25) for the air constituent into equation (23), and using equation (20) yields:

$$(26) \quad d\mu^{wG} = \frac{RT}{P^{wG}} (dP^G - dP^{aG}) = RT \frac{dP^{wG}}{P^{wG}}.$$

The result of this derivation is not surprising since it is the expected result of just writing down equation (25) for the water vapor. What has been shown, however, is that the chemical potential of the water vapor is independent of the air pressure (and vice versa) when total gas pressures are sufficiently low such that the ideal gas law and Dalton's law are obeyed.

Applying equations (18) and (19) to equation (4a) yields:

$$(27) \quad d\mu^{wL} = \frac{V^L}{N^{wL}} dP^L - \frac{X^{hL}}{X^{wL}} d\mu^{hL}.$$

By definition, the appropriate version of equation (25) for aqueous solutions is:

$$(28) \quad d\mu^{iL} = RT d(\ln a^{iL}), \text{ where } a^{iL} \text{ is the activity of constituent } i \text{ for all } i.$$

Now, all of the groundwork has been laid to derive some constitutive relations. This is accomplished by using equation (13) for the water constituent. This yields the following relation:

$$(29) \quad \int_{\mu_0^{wL}}^{\mu^{wL}} d\mu^{wL} = \mu^{wL} - \mu_0^{wL} = \mu^{wG} - \mu_0^{wG} = \int_{\mu_0^{wG}}^{\mu^{wG}} d\mu^{wG}.$$

Note that it is critical that the limits of integration correspond to the same equilibrium states, and that the integration path between the states must also be such that equilibrium holds at all points along the path (also known as a quasi-static process).

In a more general sense, the integrals should be thought of as from one state to another. The choice of integration limits shown here is possible because the integrand may be written as functions of the variable of integration. In this case, it is the constant function = 1, and this condition is trivially satisfied.

Using equations (26) through (29), the form of the equation to be used to derive constitutive relations can be written:

$$(30) \quad \int RT \frac{dP^{wG}}{P^{wG}} = \int \left(\frac{V^L}{N^{wL}} dP^L - \frac{X^{hL}}{X^{wL}} RT d(\ln a^{hL}) \right),$$

where the limits of integration are from some reference state to some final state. Now, by imposing physical constraints, equation (30) may be used to develop constitutive relations. In the following sub-sections, this is accomplished for several physical constraints, starting with the simplest forms. First, the psychometric equation is derived, followed by the dilute approximation for saline fluids. Since the thickness of the interface is small with respect to the curvature, thermodynamic relations derived for flat interfaces may be extended to the curved interface case (Guggenheim, 1977). For this reason, the thermodynamic relation for non-dilute salt content over a flat interface is derived. This may then be extended to the general case of brine strength saline solutions in porous media.

Vapor pressure for zero-salt condition with a curved interface:

If there is no salt in the liquid, then the second term on the right hand side of equation (30) is identically zero. If there is no salt, all of the volume of the liquid is made up of water molecules. In this case, the integrand of the liquid pressure integral is effectively the reciprocal of the density (it is exactly the reciprocal of the *molar* density) of pure water. Assuming the liquid is virtually incompressible, the integrand is essentially a constant. Noting that we are considering isothermal conditions, equation (30) becomes:

$$(31) \quad RT \int \frac{dP^{wG}}{P^{wG}} = \int \frac{V^L}{N^{wL}} dP^L = \int \frac{V_0^L}{N_0^{wL}} dP^L = \frac{V_0^L}{N_0^{wL}} \int dP^L.$$

Now, it is apparent that the limits of integration are just the initial and final pressures of water vapor and water, respectively. Evaluating the integral gives the well-known psychometric equation:

$$(32) \quad P^L = P_{0\infty}^L + \frac{N_0^{wL} RT}{V_0^L} \ln \left(\frac{P^{wG}}{P_{0\infty}^{wG}} \right), \text{ or } P^{wG} = P_{0\infty}^{wG} \exp \left(\frac{V_0^L}{N_0^{wL} RT} (P^L - P_{0\infty}^L) \right).$$

Vapor pressure for dilute solution approximation with a curved interface:

Now, assume there is some amount of salt in the solution. If the solution is sufficiently dilute, the density change of the solution will be negligible; so again, the integrand of the liquid pressure term is essentially constant, and it necessarily must be

the inverse of the pure water molar density. The left hand side of equation (30) is unchanged, so the immediate result is:

$$(33) \quad RT \int \frac{dP^{wG}}{P^{wG}} = \frac{V_0^L}{N_0^{wL}} \int dP^L - \int \frac{X^{hL}}{X^{wL}} RT d(\ln a^{hL}).$$

For dilute strength solutions, $a^{hL} = X^{hL}$; and it is helpful to observe that:

$$(34) \quad X^{wL} + X^{hL} = 1 \Rightarrow dX^{wL} = -dX^{hL}.$$

Substituting these facts into equation (33) yields:

$$(35) \quad RT \int \frac{dP^{wG}}{P^{wG}} = \frac{V_0^L}{N_0^{wL}} \int dP^L + RT \int \frac{dX^{wL}}{X^{wL}},$$

where again the limits of integration become obvious. Noting that $a_0^{wL} = X_0^{wL} = 1$,

(35) may be evaluated to give:

$$(36) \quad P^L = P_{0\infty}^L + \frac{N_0^{wL} RT}{V_0^L} \ln \left(\frac{P^{wG}}{X^{wL} P_{0\infty}^{wG}} \right) \quad \text{or} \quad P^{wG} = P_{0\infty}^{wG} X^{wL} \exp \left(\frac{V_0^L}{N_0^{wL} RT} (P^L - P_{0\infty}^L) \right).$$

By the second relation in (36), it is apparent that increased salt concentration has the effect of lowering the vapor pressure. This is a well-documented fact, and Bear and Gilman (1995) correctly note that, under some circumstances, the salt activity term (or

mole fraction in this case) may dominate the vapor depression resulting in a negligible effect of interface curvature.

According to Guggenheim (1977, pp. 50-52), as long as the thickness of the liquid-gas interface is much smaller than the radius of curvature (assumption 2), “formulae strictly derived for plane interfaces may be applied to curved interfaces with an accuracy sufficient for experimental purposes.” Therefore, an alternative formulation of the activity for dilute systems ($X^{wL} = P_{\infty}^{wG} / P_{0\infty}^{wG}$) may be used yielding an alternative form of equations (36):

$$(37) \quad P^L = P_{0\infty}^L + \frac{N_0^{wL} RT}{V_0^L} \ln \left(\frac{P^{wG}}{\left(\frac{P_{\infty}^{wG}}{P_{0\infty}^{wG}} \right) P_{0\infty}^{wG}} \right), \text{ or}$$

$$P^{wG} = P_{0\infty}^{wG} \left(\frac{P_{\infty}^{wG}}{P_{0\infty}^{wG}} \right) \exp \left(\frac{V_0^L}{N_0^{wL} RT} (P^L - P_{0\infty}^L) \right).$$

Now, it becomes clear that the approximation is computed by taking the reference condition, and correcting for salt and for interface curvature. The reason that these corrections may occur independently is that the corrections are only weakly coupled for dilute concentrations.

One notes that $P_{0\infty}^L \cong P^G$, and since it is more convenient to measure the gas pressure, it becomes instructive to see under what conditions this approximation is valid.

Defining the specific volume ($v_0^{wL} = V_0^L / N_0^{wL}$), the first relation in equation (37) may be written:

$$(38) \quad P^L - P_{0\infty}^L = \frac{RT}{v_0^{wL}} \ln \left(\frac{P^{wG}}{P_{\infty}^{wG}} \right),$$

or equivalently,

$$(39) \quad \frac{P^{wG}}{P_{\infty}^{wG}} = \exp \left(\frac{(P^L - P_{0\infty}^L) v_0^{wL}}{RT} \right) = \exp \left(\frac{(P^L - P^G) v_0^{wL}}{RT} \right) \exp \left(\frac{(P^{wG} - P_{0\infty}^{wG}) v_0^{wL}}{RT} \right),$$

where the facts that $P^G = P_{0\infty}^G + P^{wG} - P_{0\infty}^{wG}$ and $P_{0\infty}^G = P_{0\infty}^L$ have been used.

Equivalently, (39) may be written:

$$(40) \quad P^L - P^G = \frac{RT}{v_0^{wL}} \ln \left(\frac{P^{wG}}{P_{\infty}^{wG}} \right) - (P^{wG} - P_{0\infty}^{wG}) = \frac{v_0^{wG}}{v_0^{wL}} P^{wG} \ln \left(\frac{P^{wG}}{P_{\infty}^{wG}} \right) - (P^{wG} - P_{0\infty}^{wG}).$$

For a curved interface, it is known that for the vapor pressure $0 < P^{wG} \leq P_{\infty}^{wG}$. For this condition, it is a mathematical fact that:

$$(41) \quad \left| \ln \left(\frac{P^{wG}}{P_{\infty}^{wG}} \right) \right| \geq \left| \left(\frac{P^{wG}}{P_{\infty}^{wG}} - 1 \right) \right|.$$

This is true, because the two functions intersect only at the point $P^{wG} / P_{\infty}^{wG} = 1$, and the natural log function is concave down. Equation (41) implies that:

$$(42) \quad \left| \frac{RT}{v_0^{wL}} \ln \left(\frac{P^{wG}}{P_{\infty}^{wG}} \right) \right| \geq \left| \frac{v^{wG} P^{wG}}{v_0^{wL} P_{\infty}^{wG}} \frac{(P^{wG} - P_{\infty}^{wG})}{(P^{wG} - P_{0\infty}^{wG})} (P^{wG} - P_{0\infty}^{wG}) \right| \gg |(P^{wG} - P_{0\infty}^{wG})|$$

because $P^{wG} / P_{\infty}^{wG} \sim 1$, $\left| \frac{(P^{wG} - P_{\infty}^{wG})}{(P^{wG} - P_{0\infty}^{wG})} \right| \sim 1$, and $v^{wG} \gg v_0^{wL}$. This implies that the last

term in equation (40) is dominated by the natural log term. So, to a very good approximation, (37) may be rewritten:

$$(43) \quad P^L = P^G + \frac{N_0^{wL} RT}{V_0^L} \ln \left(\frac{P^{wG}}{\left(\frac{P_{\infty}^{wG}}{P_{0\infty}^{wG}} \right) P_{0\infty}^{wG}} \right), \text{ or}$$

$$P^{wG} = P_{0\infty}^{wG} \left(\frac{P_{\infty}^{wG}}{P_{0\infty}^{wG}} \right) \exp \left(\frac{V_0^L}{N_0^{wL} RT} (P^L - P^G) \right).$$

When desired, this same general procedure may be followed to substitute P^G for $P_{0\infty}^L$ in other relationships developed in this document. Considering the case above, it becomes instructive to examine the case where there is little or no curvature (i.e., the pressure term in equation (30) is negligible), but the salt effect may be considerable.

Vapor pressure for non-dilute solution with negligible interface curvature:

Using equations (27), (28), and (34), it is possible to write:

$$(44) \quad RT \int \frac{dP^{wG}}{P^{wG}} = RT \int d(\ln a^{wL}) = -RT \int \frac{X^{hL}}{1 - X^{hL}} d(\ln a^{hL}).$$

The result of equation (44) is that vapor pressure may be expressed in terms of the activity of water (second integral) or in terms of the mole fraction of salt plus the activity of the salt (last integral). Clearly, the activity of a constituent is a function of its concentration, which in this case is uniquely defined by the mole fraction. It remains to define this relationship to evaluate the last integral. Since the activity of water in the presence of an electrolyte is a commonly measured value, it will often be easier to use this value for computation. Using the appropriate limits, equation (44) becomes:

$$(45) \quad P^{wG} = P_{0\infty}^{wG} a^{wL}(X^{wL}) = P_{0\infty}^{wG} \exp\left(-\int \frac{X^{hL}}{1-X^{hL}} d(\ln(a^{hL}(X^{hL})))\right).$$

Here it becomes apparent how chemists measure the water activity in the presence of a salt. They simply measure vapor pressures at two different salt concentrations. It is also obvious by equation (34) that either one of the activities and the integrand of the integral above may be written in terms of either mole fraction.

Vapor pressure for non-dilute solution with non-negligible interface curvature in an unsaturated porous media:

In order to determine a constitutive relationship for this more general case, it becomes necessary to account for the effects of salt concentration on the integrand of the liquid pressure integral in equation (30). To do this, it must be understood how a non-negligible change in salt concentration (intensive property) affects the volume (extensive property) and the density (intensive property) of the liquid, plus any other

relevant changes to the physics of the problem. For this reason, the response to changes in volume, density, and other relevant parameters must be known for both the integrand and the variable of integration. This allows the appropriate choice of integration limits. For this exercise, the physics imposed by porous media geometry are used.

It is reasonable to suppose that for a homogenous water-salt mixture that the specific volume (analogously, density) is uniquely defined by the salt to water ratio (Motivation for the approach to be taken is developed here, but these statements will be made precise below). In a porous media, it is also reasonable to suppose that when the volume of liquid per volume of porous media is known, then the relationship between liquid volume and liquid pressure is well-defined (e.g., pressure-saturation curves). If the above two conditions are satisfied, then the moles of water and the moles of salt in a fixed volume (larger than the representative elementary volume) may act as state variables. It is known that integration over state variables is path-independent. For this reason, any convenient integration path may be selected.

Invoking the proposition of Guggenheim (stated above immediately before equation (37)), equation (30) is immediately reduced to:

$$(46) \quad RT \ln \left(\frac{P^{wG}}{a^{wL} P_{0\infty}^{wG}} \right) = \int_{0\infty}^B \frac{V^L}{N^{wL}} dP^L \quad \text{where } B \text{ is the final state.}$$

Notice here that if the integrand is sufficiently close to constant, then the integrand may be replaced by the zero salt value and moved outside the integral as before. The integral is then trivial to solve. However, for the case of NaCl at 25 C, Heyrovska (1996) documents the fact that between zero and saturation (6.144 m [molal]), the integrand changes by about 15%. This implies that there exist cases where high salt concentrations may result in non-negligible effects.

In general, the integration must occur from an initial state A to a final state B.

Invoking the fact that integration is path-independent, it is convenient to integrate along the path ACB (see Figure 2). Notice that path AC is a constant salt content path, and the path CB is a constant water content path. Since A for equation (46) is the zero salt, flat interface condition (i.e., 0∞), the integrand is again the zero salt case, which may be assumed to be constant. Equation (46) may be rewritten as:

$$(47) \quad RT \ln \left(\frac{P^{wG}}{P_{0\infty}^{wG}} \right) = RT \ln a^{wL} + \frac{V_0^L}{N_0^{wL}} (P_0^L - P_{0\infty}^L) + \int_C^B \frac{V^L}{N^{wL}} dP^L.$$

Hereafter, the integral in equation (47) will be referred to as the **volume correction term**, and the zero-salt liquid pressure term will be called the **dilute approximation term** (since only considering this term is the dilute approximation). 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 is being developed. This constitutive relation provides the vapor pressure used to compute

vapor flow (diffusion) resulting from vapor pressure gradients, and by use of the ideal gas law, may also be used to compute mass density of water in the gas phase.

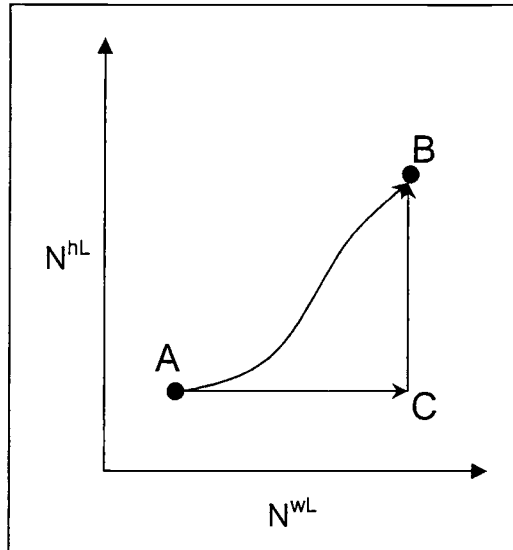


Figure 2: Diagram showing the change in state between two arbitrary states A and B, and another path AC followed by CB.

When considering the volume correction term, notice that it is a function of only liquid variables. Further, it is observed that the liquid is a function of only salt content (N^{hL}), water content (N^{wL}), liquid volume (V^L), and liquid pressure (P^L). Volume and pressure are already intimately related (classical thermodynamics gives $P^L = \frac{\partial U^L}{\partial V^L}$), and water content is a constant for this term. This implies that if a one-to-one relationship between salt content and volume or pressure can be developed, then the integral may be written as a function of salt content only, and the limits of integration are obviously from zero to the final salt concentration. This provides the motivation for computations in subsequent sections.

Liquid pressure correction for high strength salt solutions

In order to evaluate the volume correction term, it is necessary to estimate the effects of salt on the liquid pressure. It is known that surface tension is affected by salt concentration (see Figure 4), and the condition of mechanical equilibrium (Equation 15) shows that for relatively constant gas pressure, that the liquid pressure must necessarily be a function of salt concentration. Taking the differential of the mechanical equilibrium equation yields:

$$(48) \quad dP^G - dP^L = d\left(\sigma^{LG} \frac{dA^{LG}}{dV^L}\right).$$

Recall that assumption 13 is precisely:

$$(49) \quad \left| \int_{\infty}^B \frac{V^L}{N^{wL}} dP^L \right| \gg \left| \int_{\infty}^B \frac{V^L}{N^{wL}} dP^G \right|.$$

This assumption is just a formalization of the notion that gas pressure changes negligibly in a porous media compared to the liquid pressure. To ensure the assumption is satisfied, it is sufficient to consider the system shown in Figure 3 where there is a unit volume of porous media in a closed container with a gas-filled head-space. If there was no head-space, then since it has been assumed that air is insoluble in water, any air in the system would be trapped air and the incompressibility of water would require the gas pressure to fluctuate strongly. If the head space is sufficiently large, then changes in air pressure will be small compared to changes in water

pressure. Since the partial pressure of water vapor is small compared to the pressure of the total gas, changes in vapor pressure do not cause a violation of the condition (49). In a natural system, it is not necessary to assume that the system is closed. It is sufficient that that vapor pressure at the soil surface is near equilibrium with the porous media, and there is no significant gas pressure built up within the porous media. Since it is beyond the scope of this paper to describe all conditions under which this assumption is valid, this condition shall just be stated here, and it is noted that this assumption is valid for a wide range of natural conditions occurring within soils and sediments. For the derivations in this paper, application of assumption 13 coupled with equation (48), allows use of the following for evaluation of integrals:

$$(50) \quad dP^L \cong -d\left(\sigma^{LG} \frac{dA^{LG}}{dV^L}\right).$$

To use this relation, apply assumption 14. When considering the validity of this assumption, it is convenient to note that surface tension is a microscopic property that can be shown to vary with temperature and salt concentration (see Figure 4 for the NaCl example). Also, the ratio of the change in liquid-gas surface area to a change in liquid volume is clearly a function of liquid saturation. If assumption 14 is valid, then it is possible to account for the effects of salt, temperature, and saturation explicitly. In practice, it is only necessary that these functions are weakly coupled. This result should be experimentally verified for the salts of interest.

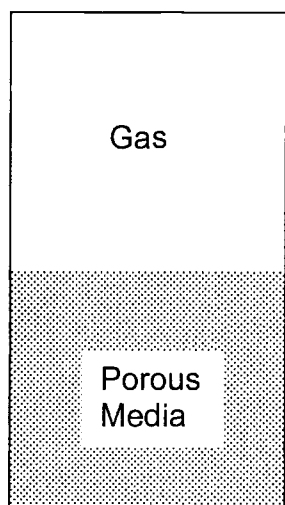


Figure 3: Schematic representation of a partially saturated porous media overlain by a gas filled space

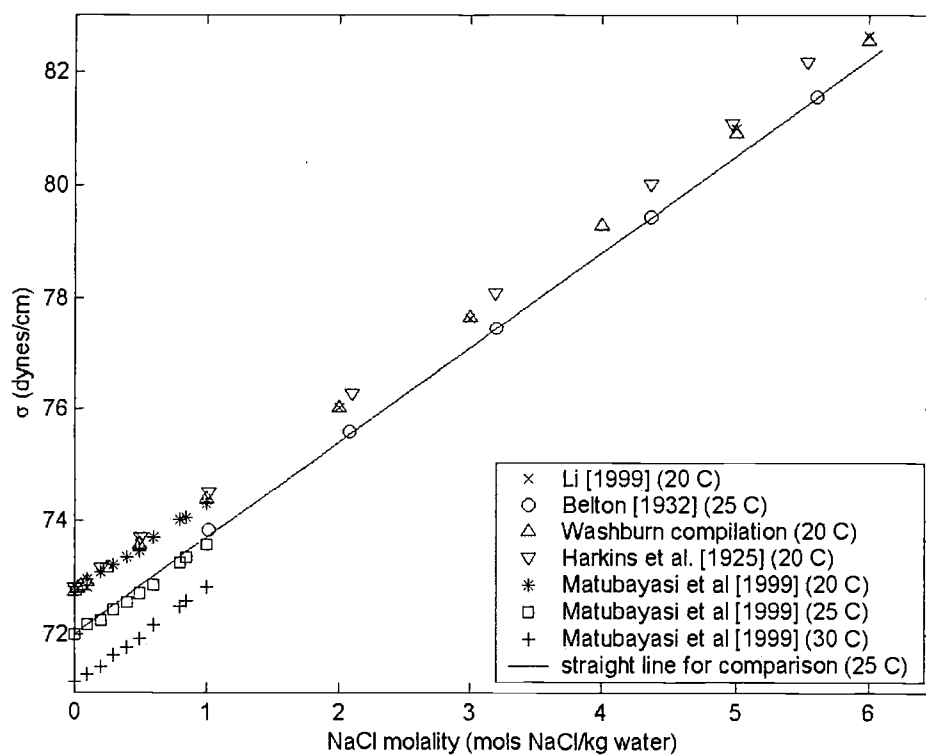


Figure 4: Surface tension as a function of NaCl(aq).

Applying assumption 14, and considering the case of constant temperature and zero or negligible salt concentration, it is known that P^L is a hysteretic function of saturation.

This can be written:

$$(51) \quad P^L(S_0^L) = -\sigma_0^{LG} \frac{dA^{LG}}{dV^L}(S_0^L).$$

Notice that for porous media, equation (51) is simply the water content/pressure relationship that is often experimentally determined. Define $\tilde{P}^L \equiv P^L(S_0^L)$. It is clear that the functional form of \tilde{P}^L depends only on geometric constraints. If the salt does not strongly affect contact angles for a given liquid content, then the relation in equation (51) is independent of salt concentration except for its effects on the volume of the liquid. This implies that $\tilde{P}^L = P^L(S^L)$. Notice that \tilde{P}^L is not a true pressure, but rather, it represents the pressure corresponding to an equivalent saturation of fresh water. Changes to liquid pressure resulting from changes in surface tension are accounted for separately. Since the relation in Equation (51) will be experimentally determined, it is convenient to write Equation (50) as:

$$(52) \quad P^L(T, N^{hL}, S^L) = \frac{\sigma^{LG}(T, N^{hL})}{\sigma_0^{LG}} \tilde{P}^L(S^L) = -\frac{\sigma^{LG}(T, N^{hL})}{\sigma_0^{LG}} \left(\sigma_0^{LG} \frac{dA^{LG}}{dV^L}(S^L) \right).$$

Notice that the decomposition above makes clear the assumption that the pressure-saturation curve is not strongly coupled with the surface tension, and the surface

tension is not affected by curvature of the interface. Again, such a decoupling should be experimentally verified.

Noting that the integrand in the volume correction term in equation (47) is in fact an intensive variable and that pressure is an intensive variable, it is recognized that total pore volume of the porous media is arbitrary for this derivation. So, define $V^{pore} \equiv 1$ (units to be chosen based on available empirical relationships). The saturation may be defined as:

$$(53) \quad S^L \equiv \frac{V^L}{V^{pore}}.$$

Since V^{pore} is a constant, this relation allows the application of assumption 12 to the saturation. Since it is possible to write V^L as a function of salt concentration, it is also possible to do the same for saturation, and in general: $S^L = S^L(N^{wL}, N^{hL})$. As a result, for isothermal conditions it is possible to write the constant water content volume correction term in terms of the function of the single variable, salt concentration.

$$(54) \quad \int_c \frac{V^L}{N^{wL}} dP^L = \int_b^{N^{hL}} \frac{S^L(N^{hL}) V^{pore}}{N^{wL}} d\left(\frac{\sigma^{LG}(N^{hL})}{\sigma_0^{LG}} \tilde{P}^L(S^L(N^{hL})) \right),$$

where the appropriate limits of integration are obviously from zero salt to the desired final salt concentration. In order to clarify the meaning of all of the terms in equation (54), an example calculation is accomplished below for NaCl.

Now, recognizing that equation (52) is a constitutive relation for P^L , leads to the conclusion that equation (47) may be written as the constitutive relation for P^{wG} .

Suppressing the functional dependence of the variables, the constitutive relations may be summarized as follows:

$$(55a) \quad P^{wG} = P_{0\infty}^{wG} a^{wL} \exp\left(\frac{V_0^L}{N_0^{wL} RT} (P_0^L - P_{0\infty}^L)\right) \exp\left(\frac{1}{RT} \int^{V^{wL}} \frac{S^L V^{pore}}{N^{wL}} d\left(\frac{\sigma_0^{LG}}{\sigma_0^{LG}} \tilde{P}^L\right)\right), \text{ and}$$

$$(55b) \quad P^L = \frac{\sigma_0^{LG}}{\sigma_0^{LG}} \tilde{P}^L \quad \text{where:} \quad \tilde{P}^L = -\sigma_0^{LG} \frac{dA^{LG}}{dV^L}.$$

Notice that since \tilde{P}^L is the equivalent pressure (equivalent to pure water) as a function of liquid saturation, it is an implicit function of salt content because saturation may be a function of salt concentration.

Derivatives

The constitutive relations (55a) and (55b) are used to couple differential equations of flow, and in particular, they provide a constraint on the mass and momentum conservation equations for water flow. For such governing equations, not only the liquid and vapor pressures are important, but so are the gradients of the liquid and vapor pressures (∇P^L and ∇P^{wG} respectively). During analysis of governing equations, it is desirable to show when certain approximations are valid. Just because certain terms in equations (55a) and (55b) may be shown to be negligible, this is no guarantee that the derivatives of these terms are also negligible. For this reason,

analysis of the effect of approximations on the derivatives is also required. To provide a general treatment, the general derivative, $\equiv d/d\cdot$, for fixed temperature is considered. The “dot” may be replaced with any primary variable of interest.

Differential of water vapor pressure

The general derivative of equation (55a) is:

$$(56) \quad \frac{dP^{wG}}{d\cdot} = \frac{d}{d\cdot} \left(P_{0\infty}^{wG} a^{wL} \exp\left(\frac{V_0^L}{N_0^{wL} RT} (P_0^L - P_{0\infty}^L)\right) \exp\left(\frac{1}{RT} \int_{\infty}^P \frac{V^L}{N^{wL}} dP^L\right) \right),$$

where the notation of equation (47) is used for simplicity. Notice that $P_{0\infty}^{wG}$ is a constant, a^{wL} is only a function of salt concentration (i.e., salt density), the dilute approximation term is only a function of S_0^L (water saturation), and the volume correction term is a function of both salt concentration and S_0^L . For convenience when applying the following to the NaCl example, the measure of salt concentration shall be in terms of molality (moles of salt per kg of pure water), and the variable is defined as m . Equation (56) may be rewritten:

$$(57) \quad \frac{dP^{wG}}{d\cdot} = \left(\frac{\partial P^{wG}}{\partial m} \right) \frac{dm}{d\cdot} + \left(\frac{\partial P^{wG}}{\partial S_0^L} \right) \frac{dS_0^L}{d\cdot},$$

with

$$(58a) \quad \frac{\partial P^{wG}}{\partial m} = P_{0\infty}^{wG} \exp\left(\frac{V_0^L}{N_0^{wL} RT} (P_0^L - P_{0\infty}^L)\right) \left(\frac{\partial \left(a^{wL} \exp\left(\frac{1}{RT} \int^B \frac{V^L}{N^{wL}} dP^L\right) \right)}{\partial m} \right), \text{ and}$$

$$(58b) \quad \frac{\partial P^{wG}}{\partial S_0^L} = P_{0\infty}^{wG} a^{wL} \left(\frac{\partial \left(\exp\left(\frac{V_0^L}{N_0^{wL} RT} (P_0^L - P_{0\infty}^L)\right) \exp\left(\frac{1}{RT} \int^B \frac{V^L}{N^{wL}} dP^L\right) \right)}{\partial S_0^L} \right).$$

Recognizing that $a^{wL} = \exp(\ln(a^{wL}))$ and differentiating (58a) and (58b) yields:

$$(59a) \quad \frac{\partial P^{wG}}{\partial m} = P^{wG} \left(\frac{\partial(\ln a^{wL})}{\partial m} + \frac{\partial}{\partial m} \left(\frac{1}{RT} \int^B \frac{V^L}{N^{wL}} dP^L \right) \right), \text{ and}$$

$$(59b) \quad \frac{\partial P^{wG}}{\partial S_0^L} = P^{wG} \left(\frac{\partial}{\partial S_0^L} \left(\frac{V_0^L}{N_0^{wL} RT} (P_0^L - P_{0\infty}^L) \right) + \frac{\partial}{\partial S_0^L} \left(\frac{1}{RT} \int^B \frac{V^L}{N^{wL}} dP^L \right) \right).$$

Differential of liquid pressure

The general derivative of equation (55b) is:

$$(60) \quad \frac{dP^L}{d\cdot} = \frac{d}{d\cdot} \left(\frac{\sigma^{LG}}{\sigma_0^{LG}} \tilde{P}^L \right).$$

Recall that \tilde{P}^L is a function of liquid saturation which is a function of salt concentration. In Equation (55a), this term is only in the fixed water content integral.

In general, water content can also vary, implying \tilde{P}^L is a function of both m and S_0^L .

Equation (60) may be written:

$$(61) \quad \frac{dP^L}{d\cdot} = \left(\frac{\partial P^L}{\partial m} \right) \frac{dm}{d\cdot} + \left(\frac{\partial P^L}{\partial S_0^L} \right) \frac{dS_0^L}{d\cdot},$$

with

$$(62a) \quad \frac{\partial P^L}{\partial m} = \frac{1}{\sigma_0^{LG}} \left(\tilde{P}^L \frac{\partial \sigma^{LG}}{\partial m} + \sigma^{LG} \frac{\partial \tilde{P}^L}{\partial m} \right), \text{ and}$$

$$(62b) \quad \frac{\partial P^L}{\partial S_0^L} = \frac{\sigma^{LG}}{\sigma_0^{LG}} \frac{\partial \tilde{P}^L}{\partial S_0^L}.$$

It is noted here that equations (62a) and (62b) are the corrections to the coefficient of 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 Darcy's Law and these corrections will allow estimation of the coefficients that arise naturally in non-equilibrium or process thermodynamics.

Approximations to the Constitutive Relations

The ultimate goal of developing the constitutive relations above is the solution of coupled systems of partial differential equations describing flow and transport of saline solutions in porous media. In order to solve the systems of equations, it is

advantageous to make reasonable approximations. In order to rigorously show that approximations to the above constitutive relations are valid, it is necessary to show that there is a negligible impact due to neglecting one or more terms in equations (55a), (55b), (59a), (59b), (62a), and (62b). In principle, this can be accomplished in one of two ways: 1) it may be shown that one or more terms dominate the equation in the region (i.e., state space) of interest, or 2) it may be shown that the error introduced by the approximation is small. In general, “domination” or “small” are qualitative terms, but for the discussions herein, two orders of magnitude difference shall be considered sufficient. The example below will be an order of magnitude analysis of the relevant terms.

As an example of “domination”, it is convenient to consider the approximation of equation (47) by:

$$(63) \quad RT \ln \left(\frac{P^{wG}}{P_{0\infty}^{wG}} \right) = RT \ln a^{wL} + \frac{V_0^L}{N_0^{wL}} (P_0^L - P_{0\infty}^L).$$

Equation (63) is essentially an extension of the dilute solution approximation (equations shown in (36)) to the non-dilute case by using the activity of water. This can be seen by recognizing that if the volume correction term is negligible, then $P^L \cong P_0^L$, and (63) becomes:

$$(64) \quad RT \ln \left(\frac{P^{wG}}{P_{0\infty}^{wG}} \right) = RT \ln a^{wL} + \frac{V_0^L}{N_0^{wL}} (P^L - P_{0\infty}^L).$$

This is a very natural extension, and a very similar constitutive relation is found in Olivella et al. (1996). Since knowledge of the vapor depression (left-hand side of (64)) is desired, the mathematically precise statement of the volume correction term being negligible is:

$$(65) \quad \frac{\left| \int_c^B \frac{V^L}{N^{wL}} dP^L \right|}{\left| RT \ln a^{wL} + \frac{V_0^L}{N_0^{wL}} (P_0^L - P_{0\infty}^L) \right|} \leq 0.01.$$

Additionally, since it is known that both terms in the denominator are $\neq 0$, if either term can be shown to dominate the volume correction term, then the dilute approximation is also valid.

In order to show that error is small, it is necessary to define the measure of the error.

Here error will be a relative error, and will be defined as:

$$(66) \quad error = \left| \frac{[exact_eqn] - [approximation]}{[exact_eqn]} \right|.$$

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

$$(67) \quad error = \left| \frac{P_{eqn.47}^{wG} - P_{eqn.64}^{wG}}{P_{eqn.47}^{wG}} \right| = \left| 1 - \exp \left(\frac{-1}{RT} \int_c^B \frac{V^L}{N^{wL}} dP^L \right) \right| \leq 0.01,$$

where the inequality is the condition to show the error in neglecting the volume correction term is negligible. With the above notions of error and domination of terms, it is now possible to do some computations for an example where brine strength NaCl solutions are considered.

Example: NaCl at 25C

As will be seen below, a substantial amount of experiments must be performed on the basic physical properties of the salt of interest. Since such information is readily available for NaCl, this salt is used in the example below. While there are a large number of plots developed below, in general, the results show that the volume correction term of equation (47) (or equivalent) is important only for low saturations and is of increasing importance for finer textured soils.

Computation of brine strength salt effects in porous media

Heyrovska (1996) provides a suitable conversion between volume and salt concentration for NaCl at 25C, though some manipulation is necessary to get consistent units. Heyrovska's empirical equations 13 and 14 (equation numbers are from Heyrovska's paper) are:

$$(68) \quad \bar{V}^L = 1002.86 + m(26.8 - 10.55\alpha), \text{ and}$$

$$(69) \quad \bar{V}^L = 1002.38 + 24.74\alpha m,$$

where $\alpha \leq 1$ is the experimentally determined degree of dissociation. α is a function of the molality (m), and it 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). The reason that there are two equations is that due to the functional form of α , the van't Hoff factor is minimum at $m \cong 2$. Heyrovská recommends that this be used as the dividing point for use of the two equations. Equation (68) holds to the left of the minimum and equation (69) to the right.

For engineering purposes, it may be sufficient to approximate the entire range as a line (see Figure 5), 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 Heyrovská's $m \cong 2$. A plot of the data (not shown) indicates that most of the departure from equation (69) occurs below the intersection, so the formulation here still substantially captures the variation of volume with molality.

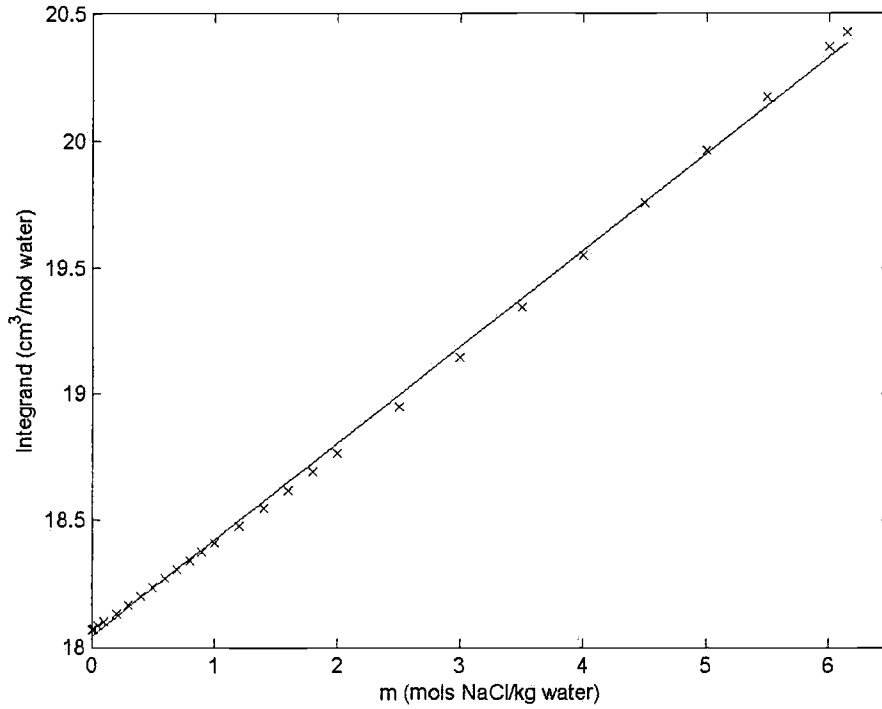


Figure 5: Integrand of the volume correction term as a function of NaCl(aq).

Examination of the integrand in equation (47) (equivalently (55a)) 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:

$$(70) \quad \int_c^b \frac{V^L}{N^{\text{wL}}} dP^L = \int_0^m M^{\text{H}_2\text{O}} \bar{V}^L(m) d\left(\frac{\sigma^{\text{LG}}(m)}{\sigma_0^{\text{LG}}} \tilde{P}^L(S^L(m)) \right).$$

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:

$$(71a) \quad S^L(m) = \frac{N^{wL} M^{H_2O} \bar{V}^L(m)}{V^{pore}}, \text{ for this path of integration (i.e., fixed } N^{wL} \text{).}$$

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 $N^{wL} = S_0^L V^{pore} / (M^{H_2O} \bar{V}_0^L)$ where \bar{V}_0^L is the zero salt molal volume. Substituting back into (71a) gives the more general form:

$$(71b) \quad S^L(S_0^L, m) = \frac{S_0^L \bar{V}^L(m)}{\bar{V}_0^L}.$$

Examination of Figure 4 shows that a good fit to the surface tension function is given by:

$$(72) \quad \sigma^{LG}(m) = \sigma_0^{LG} + 1.7m = 72 + 1.7m \text{ with units of dynes/cm.}$$

For the purposes of this example, the non-hysteretic van Genuchten pressure-saturation relationship is used (as written in Carsel and Parrish (1988)) with parameter values taken from Carsel and Parrish for sand, silt, and loam. The values used are shown in Table 1, and were chosen to represent a wide range of values that may be encountered in natural porous media. The van Genuchten head was converted to pressure by multiplication by the density of fresh water and the gravitational constant yielding:

$$(73) \quad \tilde{P}^L(S^L(m)) = \frac{-\rho_0 g \left((S^L)^{\frac{N}{1-N}} - 1 \right)^{\frac{1}{N}}}{\bar{\alpha}}.$$

Table 1: van Genuchten parameters (Carsel and Parrish (1988))

PARAMETER	SILT	LOAM	SAND
$\bar{\alpha}$	0.016	0.036	0.145
N	1.37	1.56	2.68

Equations (71) through (73) provide a complete description of the differential in equation (70) in terms of m . Now, there are two choices: either fit a function of m to α so that the change of variables may be completed, or plot equation (55b) directly and fit a function of m to it. After evaluation of both options for NaCl, equation (55b) was found to be approximately linear for most fixed water contents, so this option was used. To plot equation (55b), for a given zero-salt saturation, N^{wL} may be calculated using equation (71a). Then this fixed value of N^{wL} is used in equation (71a) to calculate saturation as a function of salt concentration. As an example, see Figure 6 for three different water contents. There is nothing special about these three values other than they have y-intercepts that allow them all to be plotted on the same graph. In general, for all three sediment types, the plots are approximately linear, and the slopes vary from one water-content to another. As will be seen later, the linear approximation is good for a wide range of water contents.

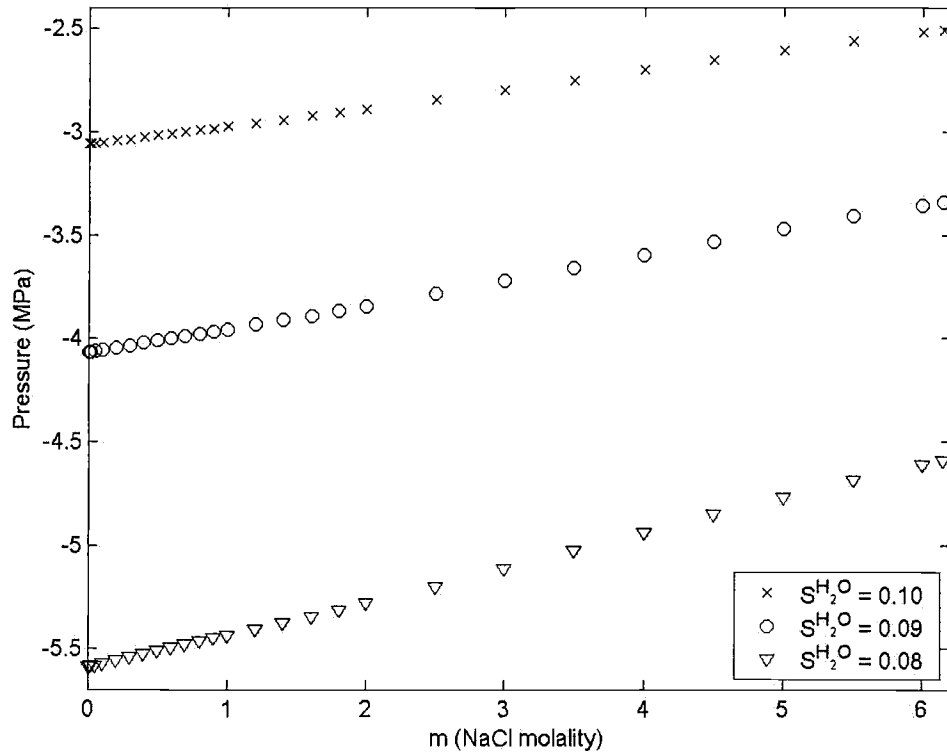


Figure 6: Liquid pressure as a function of molality for a silt for three different fixed water contents.

For fixed water content, if water pressure may be written as a linear function of m , then:

$$(74) \quad P^L(m) = bm + c \Rightarrow dP^L(m) = bdm,$$

where b is clearly a function of water content ($b = b(S_0^L)$). It is also worth noting that in general, $b(S_0^L)$ is a hysteretic function, and is in fact the sole source of hysteresis in equation (55b). Since $b(S_0^L)$ is not a function of m , equation (70) may be reduced to:

$$(75) \quad \int_c^B \frac{V^L}{N^{wL}} dP^L = b(S_o^L) \int_0^m M^{H_2O} \overline{V^L}(m) dm.$$

A plot of the integrand of equation (75) shows that a linear fit is a reasonable first approximation (see Figure 5). Rather than using Heyrovska's equations, if a linear fit to the integrand is utilized, the integral is trivial to evaluate, yielding:

$$(76) \quad \int_c^B \frac{V^L}{N^{wL}} dP^L = b(S_o^L) (0.1908m^2 + 18.04m).$$

Now, all required relations have been developed to allow an order-of-magnitude analysis of the constitutive relations.

Evaluation of approximations to the constitutive relations

In order to determine when approximations to equations (55a), (55b), (59a), (59b), (62a), and (62b) are valid and may be used, it is necessary to learn when the effect of various terms are negligible. To do this, equations of the form shown in (65) and (66) are used. Now that a complete set of relations have been developed for NaCl, this may be accomplished.

Using the approximation given by equation (76), it is trivial to evaluate both the vapor pressure (equation (55a)) and any desired approximations. The relations described by equation (65) and (67) may then be used to evaluate the relative contribution of various terms or the error induced by any approximations. Plots of the vapor pressure

for the three example soil textures (Table 1) are shown in Figure 7. It is instructive to consider the relative magnitude of the appropriate terms from equation (47):

$$(77) \quad RT \ln \left(\frac{P^{wG}}{P_{0\infty}^{wG}} \right) = RT \ln a^{wL} + \frac{V_0^L}{N_0^{wL}} (P_0^L - P_{0\infty}^L) + b(S_0^L)(0.1908m^2 + 18.04m).$$

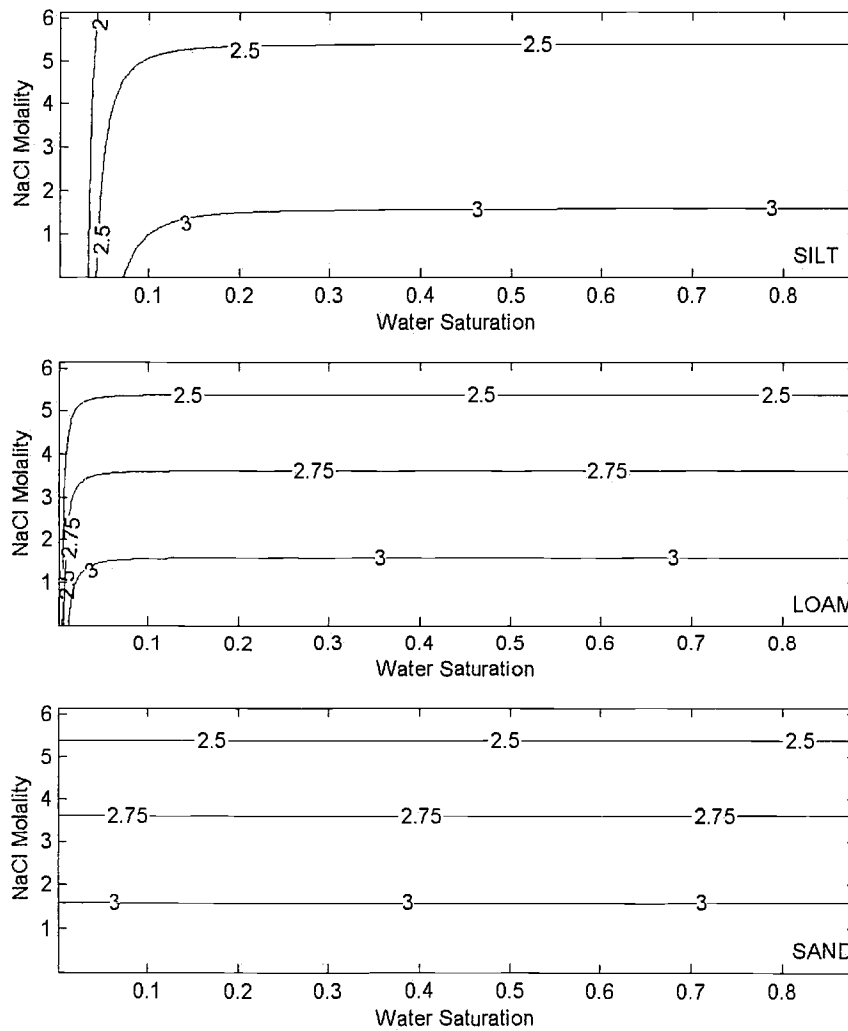


Figure 7: Plots of vapor pressure (equation (55a)) for silt (top), loam (middle), and sand (bottom). Units are in kPa.

The activity is computed using relationships from Heyrovská's paper where the input parameters are tabulated values of m and α as a function of m . The density of the tabulated values is sufficient for computations here, and when necessary, a simple linear interpolation is used. Using the usual parameterization of the dilute approximation term for computation, $P_{0\infty}^L = 0$ and using pure water density at 25 C, gives:

$$(78) \quad RT \ln \left(\frac{P^{wG}}{P_{0\infty}^{wG}} \right) = RT \ln a^{wL}(m) + \frac{M^{H_2O}}{\rho_0^{H_2O}} P^L(S_0^L) + b(S_0^L) (0.1908m^2 + 18.04m),$$

where

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

For the specific functional forms given in (78), Figures 8a through 8c show plots of relative magnitudes of terms and the predicted values of $b(S_0^L)$ for silt, loam, and sand, respectively. The ratio given in the worked example (equation (65)) is shown in plot (f) of each figure, and plots (c) through (e) show ratios of various other terms. The relative maximum error between the computed pressure (equation (55b)) and the linear approximation (equation (74)) is shown in plot (b).

It is worthwhile to note that the plots are only for $0 < S_0^L \leq 0.88$. This is because the addition of salt necessarily implies that liquid saturation increases (because specific

volume of the liquid increases). The maximum pure water content that will result in a liquid saturation of the maximum acceptable value 1 may be calculated as:

$$(79) \quad (S_0^L)_{\max} = \frac{\bar{V}_0^L}{\bar{V}_{\text{saturated}=6.144\text{ m}}^L} \cong 0.884.$$

By considering ratios of all possible combinations of the terms on the right hand side of equation (78), it is possible to see which terms dominate for different salt concentrations and water contents. The region with values below 0.01 on contour plots (c) through (f) of each Figure 8 describes where the approximation given by neglecting the term in the numerator in favor of the term(s) in the denominator is valid with error under 1%. As previously stated, since both the dilute approximation term and the activity term are always non-positive, there is never an instance when the effects cancel. Comparison of plots (c), (d), and (f) shows where each term dominates the volume correction term; and plot (e) shows that while the activity often dominates, the dilute approximation term is often non-negligible.

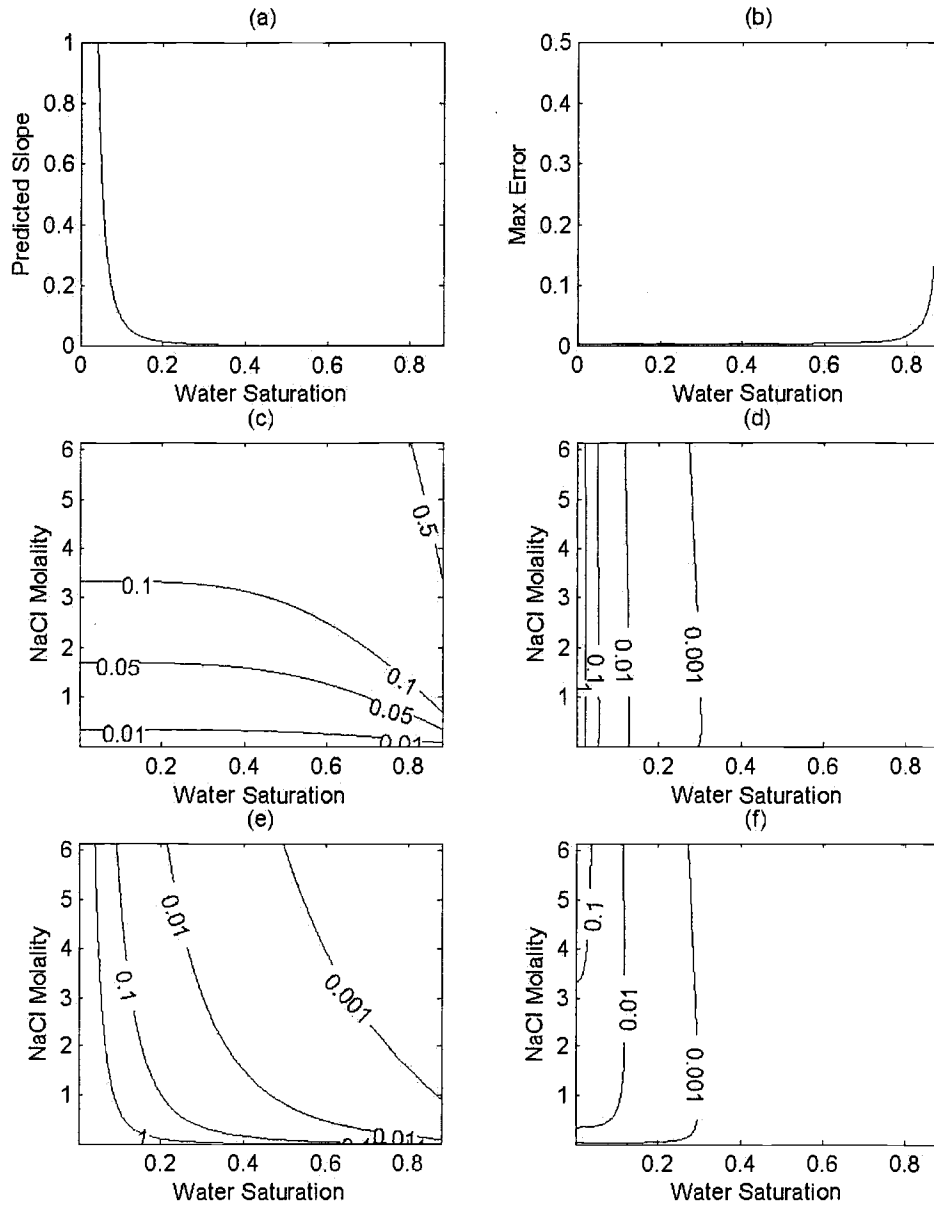


Figure 8a: Plots for silt: (a) The slope of the linear approximation ($b(S_o^L)$) to the pressure function. (b) The error (eqn (66)) between the linear fit and the computed pressure. (c) The absolute value of the ratio of the volume correction term to the dilute approximation term for equation (47). (d) The absolute value of the ratio of the volume correction term to the activity term for equation (47). (e) The absolute value of the ratio of the dilute approximation term to the activity term for equation (47). (f) Plot of equation (65): The absolute value of the ratio of the volume correction term to the sum of the dilute approximation and activity terms for equation (47).

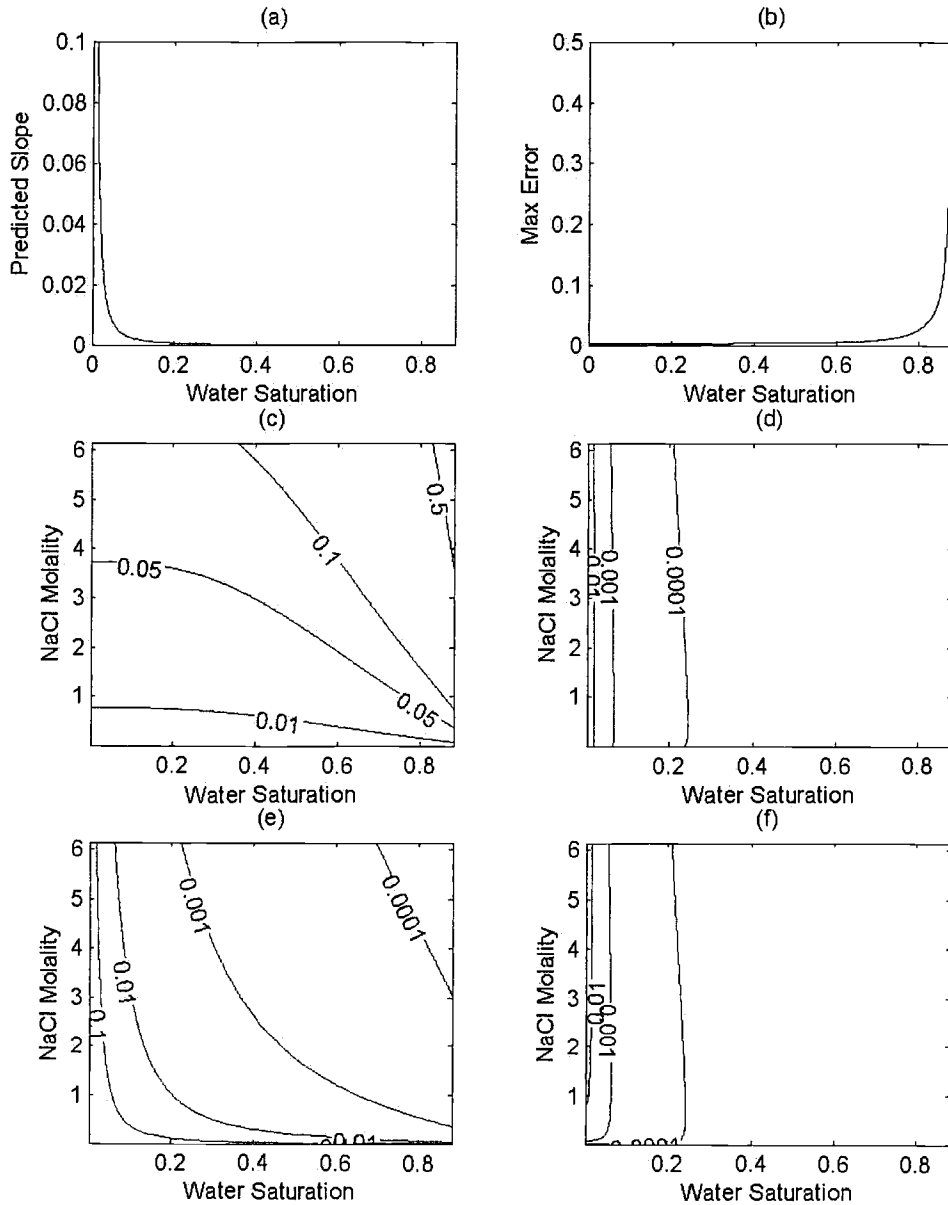


Figure 8b: Plots for **loam**: (a) The slope of the linear approximation ($b(S_o^L)$) to the pressure function. (b) The error (eqn (66)) between the linear fit and the computed pressure. (c) The absolute value of the ratio of the volume correction term to the dilute approximation term for equation (47). (d) The absolute value of the ratio of the volume correction term to the activity term for equation (47). (e) The absolute value of the ratio of the dilute approximation term to the activity term for equation (47). (f) Plot of equation (65): The absolute value of the ratio of the volume correction term to the sum of the dilute approximation and activity terms for equation (47).

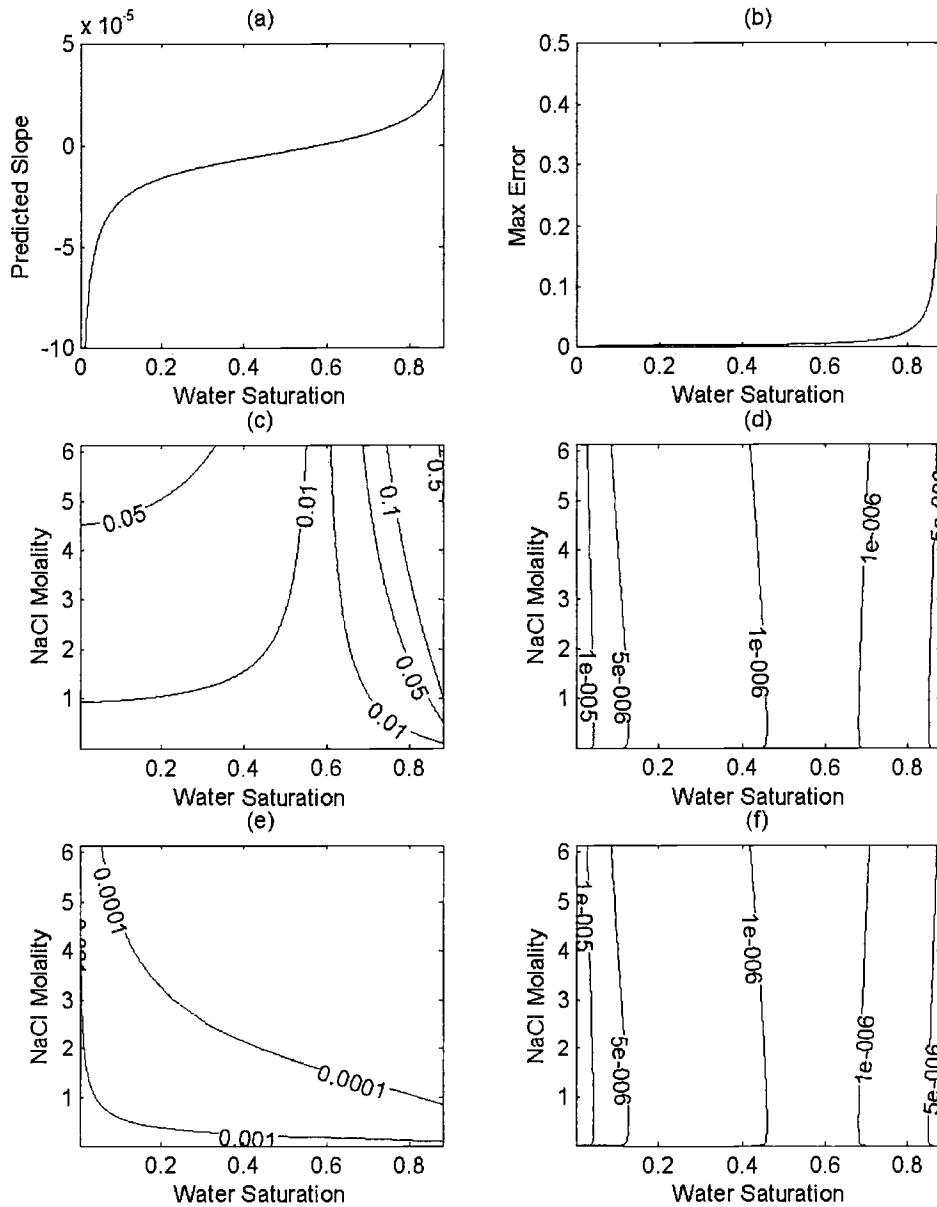


Figure 8c: Plots for **sand**: (a) The slope of the linear approximation ($b(S_o^L)$) to the pressure function. (b) The error (eqn (66)) between the linear fit and the computed pressure. (c) The absolute value of the ratio of the volume correction term to the dilute approximation term for equation (47). (d) The absolute value of the ratio of the volume correction term to the activity term for equation (47). (e) The absolute value of the ratio of the dilute approximation term to the activity term for equation (47). (f) Plot of equation (65): The absolute value of the ratio of the volume correction term to the sum of the dilute approximation and activity terms for equation (47).

Note that the error (plot (b) of each Figure 8) is computed per equation (66) above, and that the denominator goes to zero. This implies that even for small departures 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 suspect, the pressure is still a well-behaved function of salt concentration and not too far from linear (see Figure 9 for an example). 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 plot (b) of each Figure 8 is of little concern for this analysis.

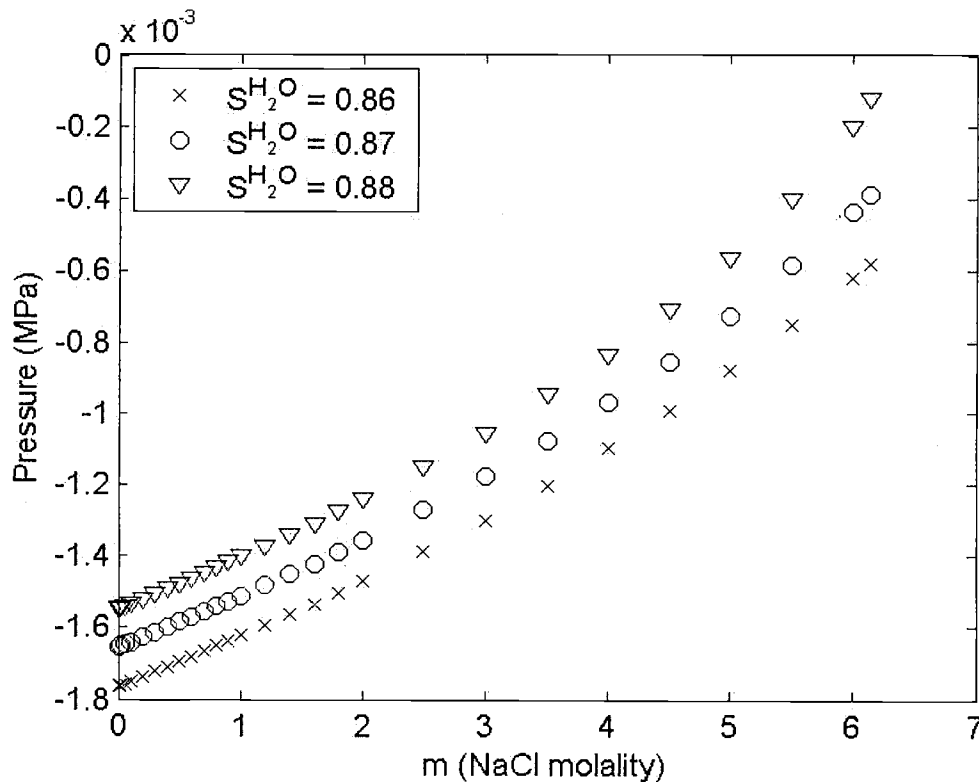


Figure 9: Liquid pressure as a function of molality for a loam at three fixed water contents. Notice this plot is at high saturation where the error function shown in Figure 8b(b) indicates the pressure may not be well-represented as a straight line.

The conclusion that may be drawn from Figures 8a through 8c is that the volume correction term is negligible in most cases. The exception to this is that for finer textured soils under very dry conditions, this term may be non-negligible when compared to the other terms.

An example of the algorithm used to calculate and plot Figures 8a through 8c is given in Appendix 1. This algorithm may be used for any porous media for which the appropriate van Genuchten parameters are known. It may also be easily altered to call another pressure function (e.g., Brooks and Corey (1964)) if it is deemed that this alternative pressure function yields better results in the range of water contents of interest. Fit may especially be important in the dry region since this is the region where non-negligible effect due to the volume correction term may occur. The algorithm becomes unstable at non-physically realistic saturations (i.e., saturation greater than 1).

Figures 10a through 10c show the error (defined by equation (66)) in computed vapor pressure (equation (55a)) in a silt, loam, and sand, respectively, induced by neglecting various terms or corrections. For each figure, plot (a) shows the error induced by neglecting the volume correction term. This approximation appears to be quite good for all three types of soils. However, in the silt, the approximation may have appreciable errors under very dry conditions, and in general, the finer the texture of the soil, the more influence of the volume correction term. Plots (b) through (c) show the effect of neglecting various other terms. The (b) plots illustrate the well-known

fact that for most saturations, the water vapor pressure (analogously, the relative humidity) remains very high relative to that encountered above a flat interface. If salt is present in the porous media, a comparison of (b) to (c) shows that vapor pressures may be easily dominated by salt content. In the absence of salt, even though the vapor pressure lowering is relatively small, this may be the only source of vapor pressure gradients that result in vapor diffusion.

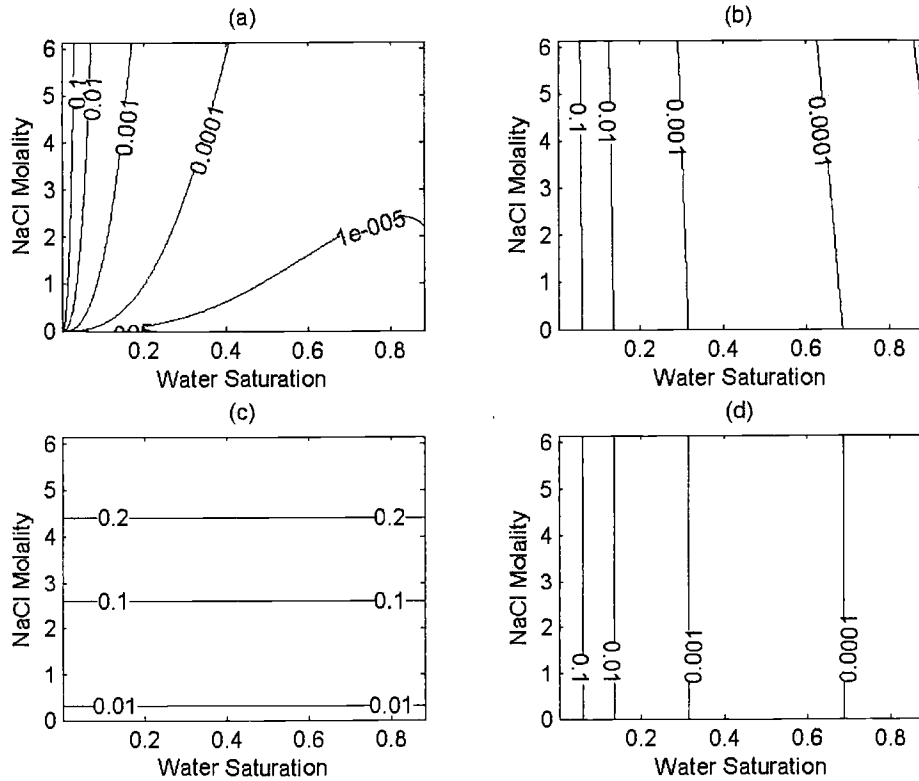


Figure 10a: Plots of the error (equation (66)) for salt induced by neglecting one or more terms in equation (55a): (a) only the volume correction term is neglected (worked example equation (67)); (b) interface curvature is neglected (both dilute approximation term and volume correction term); (c) only the activity term is neglected; and (d) only the dilute approximation is neglected.

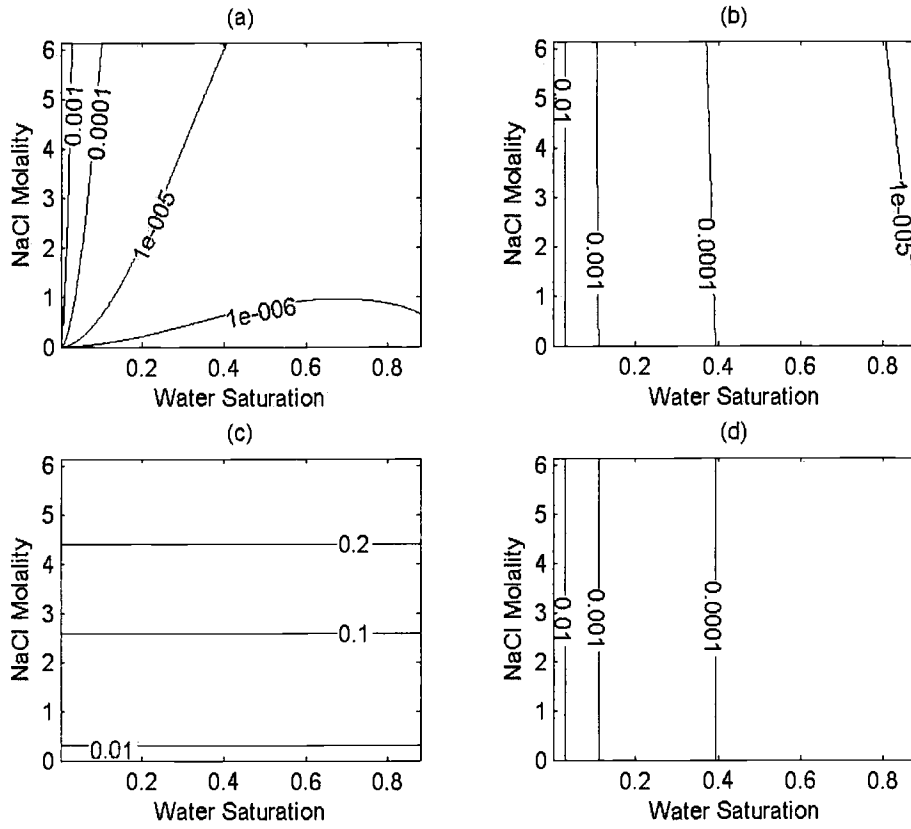


Figure 10b: Plots of the error (equation (66)) for loam induced by neglecting one or more terms in equation (55a): (a) only the volume correction term is neglected (worked example equation (67)); (b) interface curvature is neglected (both dilute approximation term and volume correction term); (c) only the activity term is neglected; and (d) only the dilute approximation is neglected.

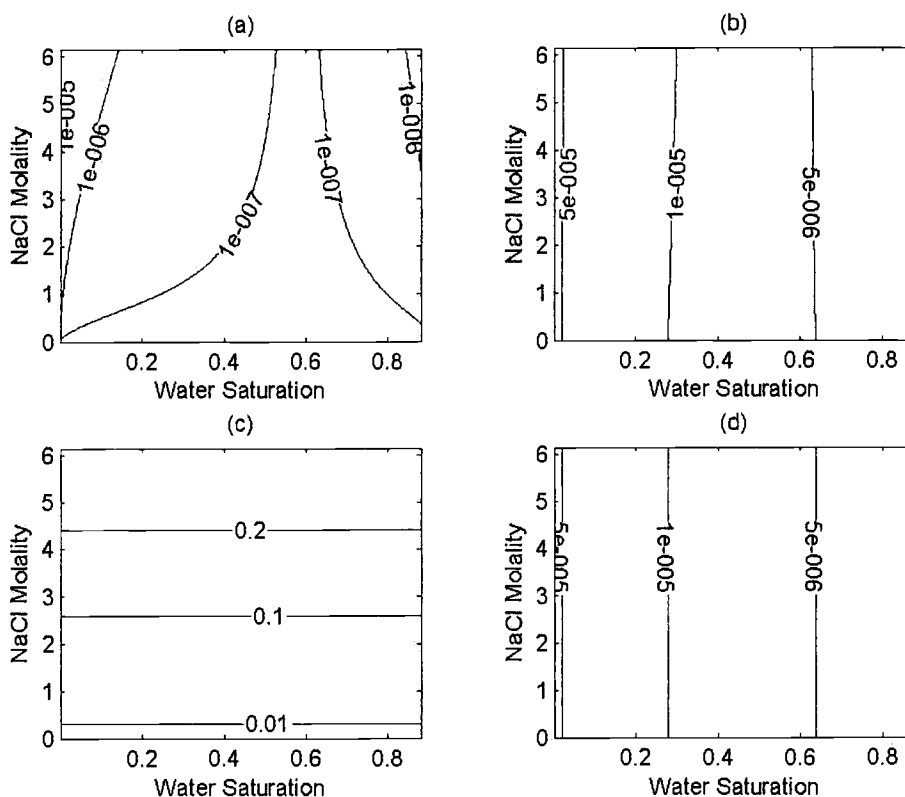


Figure 10c: Plots of the error (equation (66)) for **sand** induced by neglecting one or more terms in equation (55a): (a) only the volume correction term is neglected (worked example equation (67)); (b) interface curvature is neglected (both dilute approximation term and volume correction term); (c) only the activity term is neglected; and (d) only the dilute approximation is neglected.

Figures 11a through 11c show plots for liquid pressure (equation (55b)) in a silt, loam, and sand, respectively. Plot (a) in each figure is the liquid pressure as a function of water and salt content, and plots (b) through (d) show the error in computed liquid pressure induced by neglecting various terms or corrections. The error plots show that there may be appreciable errors induced by neglecting any corrections except under dilute conditions. Note that the error is smaller where both corrections are neglected. This is because the correction to surface tension tends to increase the magnitude of the

pressure, while the volume correction tends to lower the pressure. This implies the approximation is better if both are ignored rather than only one of the two.

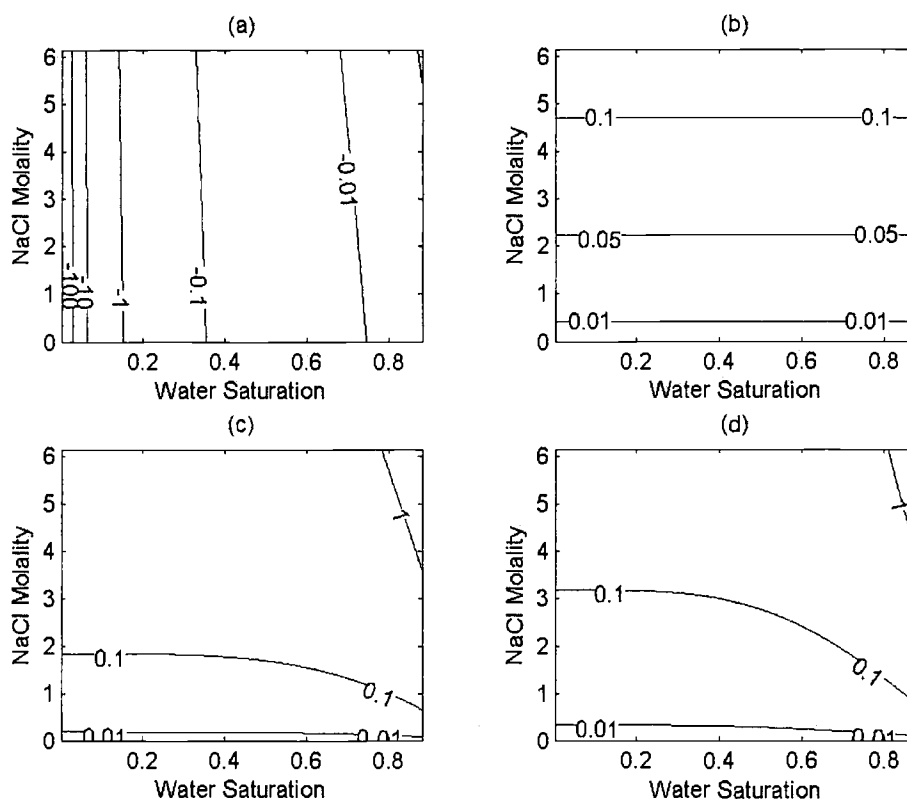


Figure 11a: Plots for silt: (a) Plot of equation (55b) in units of MPa. Plots (b) through (d) are of the error (equation (66)) induced by neglecting one or more terms in equation (55b): (b) only the surface tension correction term $(\sigma^{LG} / \sigma_0^{LG})$ is neglected; (c) only the volume correction to the saturation is neglected; and (d) both corrections are neglected (i.e., using the pressure relationship for only water content).

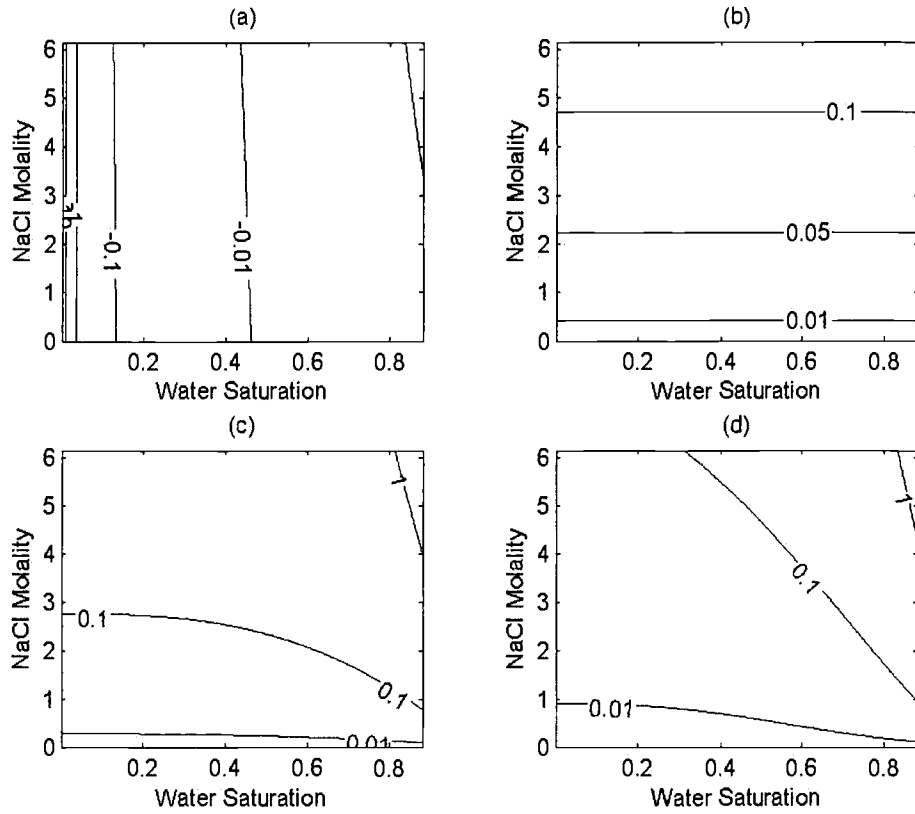


Figure 11b: Plots for **loam**: (a) Plot of equation (55b) in units of MPa. Plots (b) through (d) are of the error (equation (66)) induced by neglecting one or more terms in equation (55b): (b) only the surface tension correction term $(\sigma^{LG} / \sigma_0^{LG})$ is neglected; (c) only the volume correction to the saturation is neglected; and (d) both corrections are neglected (i.e., using the pressure relationship for only water content).

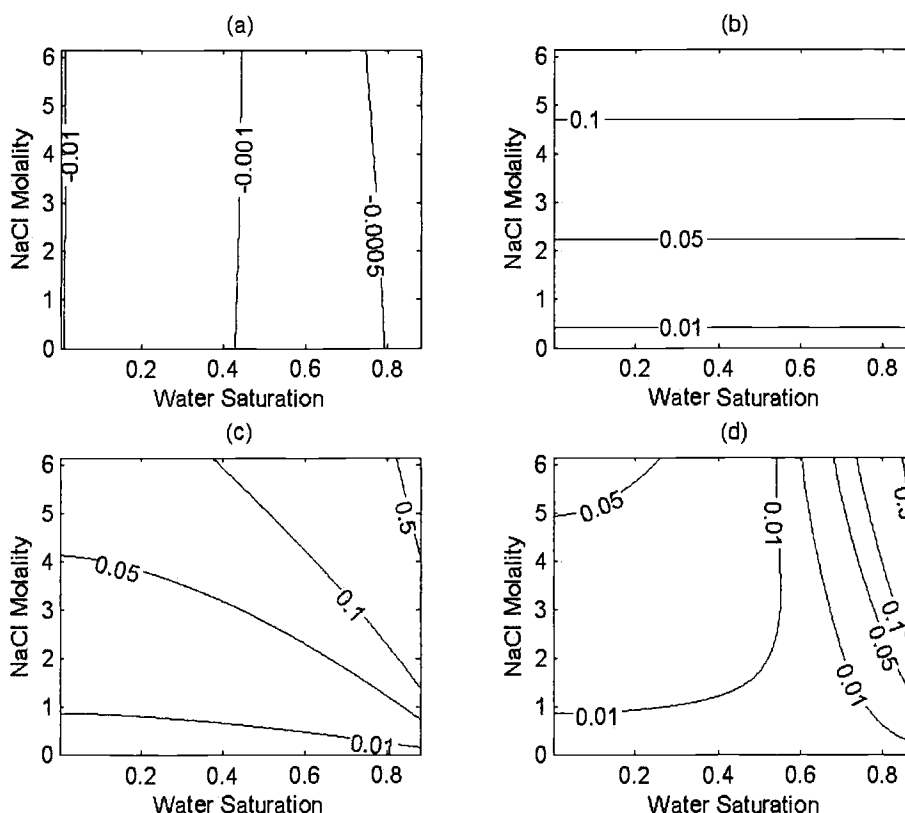


Figure 11c: Plots for **sand**: (a) Plot of equation (55b) in units of MPa. Plots (b) through (d) are of the error (equation (66)) induced by neglecting one or more terms in equation (55b): (b) only the surface tension correction term $(\sigma^{LG} / \sigma_0^{LG})$ is neglected; (c) only the volume correction to the saturation is neglected; and (d) both corrections are neglected (i.e., using the pressure relationship for only water content).

Plots for equation (59a) are shown in Figures 12a and 13a and 13b. In Figure 12a plot (a) it is shown that for an order of magnitude analysis, that a linear fit to the activity is reasonable. Plots (b) through (d) show where the differential with respect to the volume correction term is dominated by the activity term. Again, the finer the texture of soil, the larger the region where the volume correction term may cause appreciable effects, and these effects are restricted to the dryer end of the soil moisture conditions. In Figures 13a and 13b, plot (a) shows equation (59a) for silt and loam respectively.

Since the volume correction term is commonly dominated in the differential, plot (b) shows equation (59a) with the volume correction neglected in both the differential and the vapor pressure calculation. Plot (c) shows the error induced by this approximation. With plot (a) as motivation, plot (d) shows the error induced by approximating equation (59a) with the constant value -0.124 . No plots are shown for the sand because the entire surface is so close to a constant value of -0.1244 as to be rendered uninteresting.

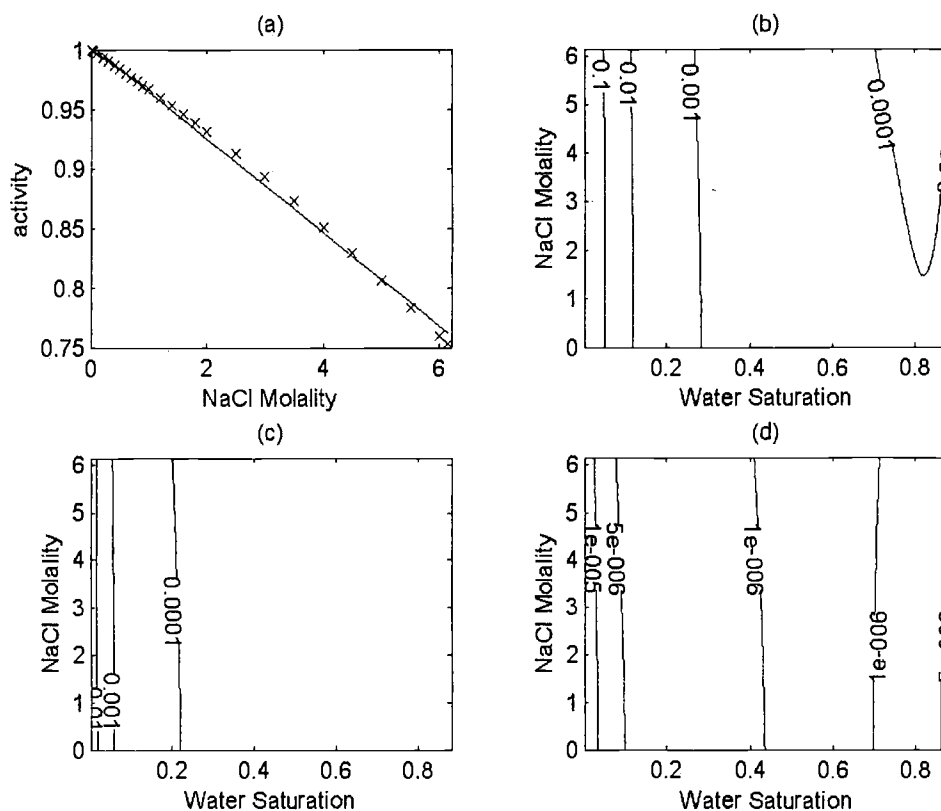


Figure 12a: (a) Linear fit to activity for order of magnitude analysis of terms in equation (59a); (b) through (d) are plots of the magnitude of the volume correction term relative to the activity term for silt, loam, and sand, respectively for equation (59a).

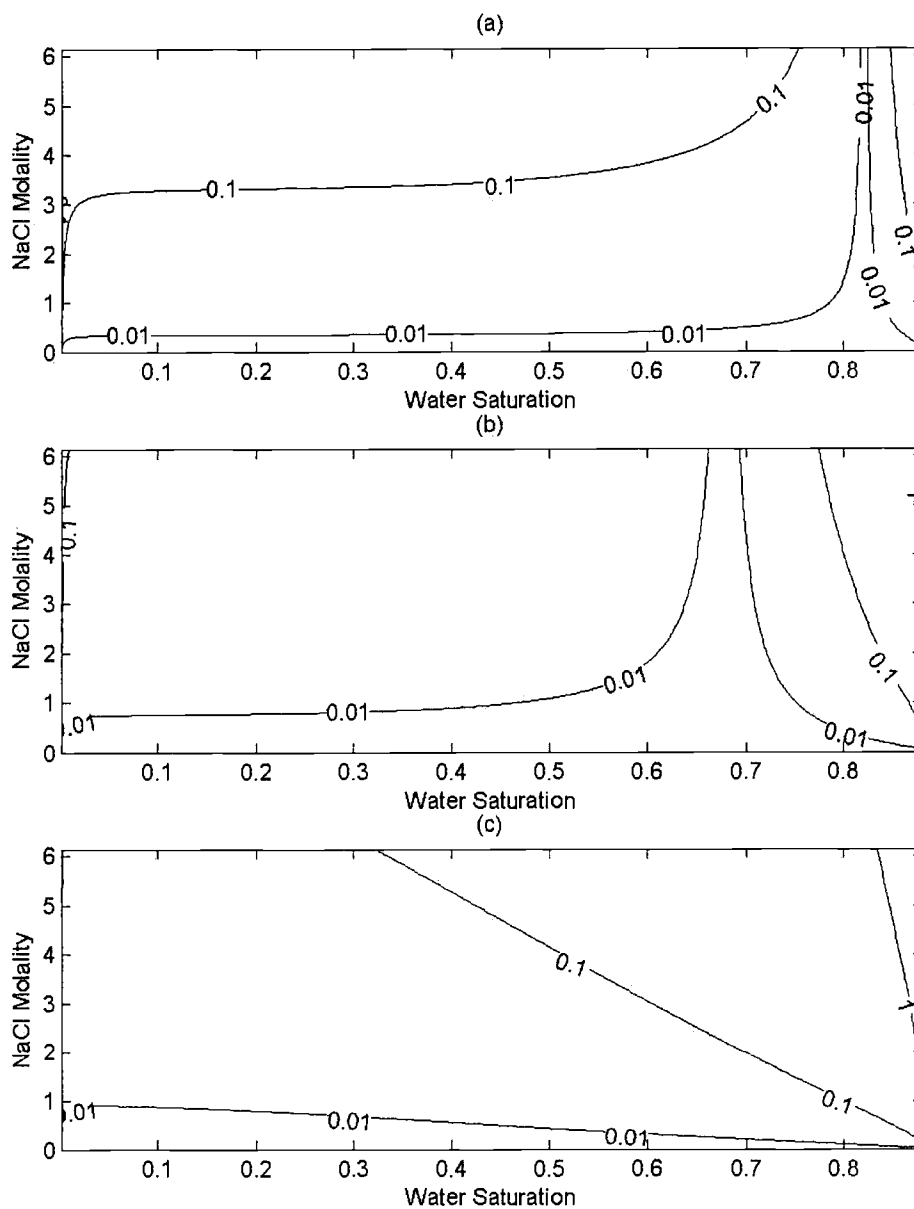


Figure 12b: (a) through (c) are plots of the magnitude of the volume correction term relative to the dilute approximation term for silt, loam, and sand, respectively for equation (59b).

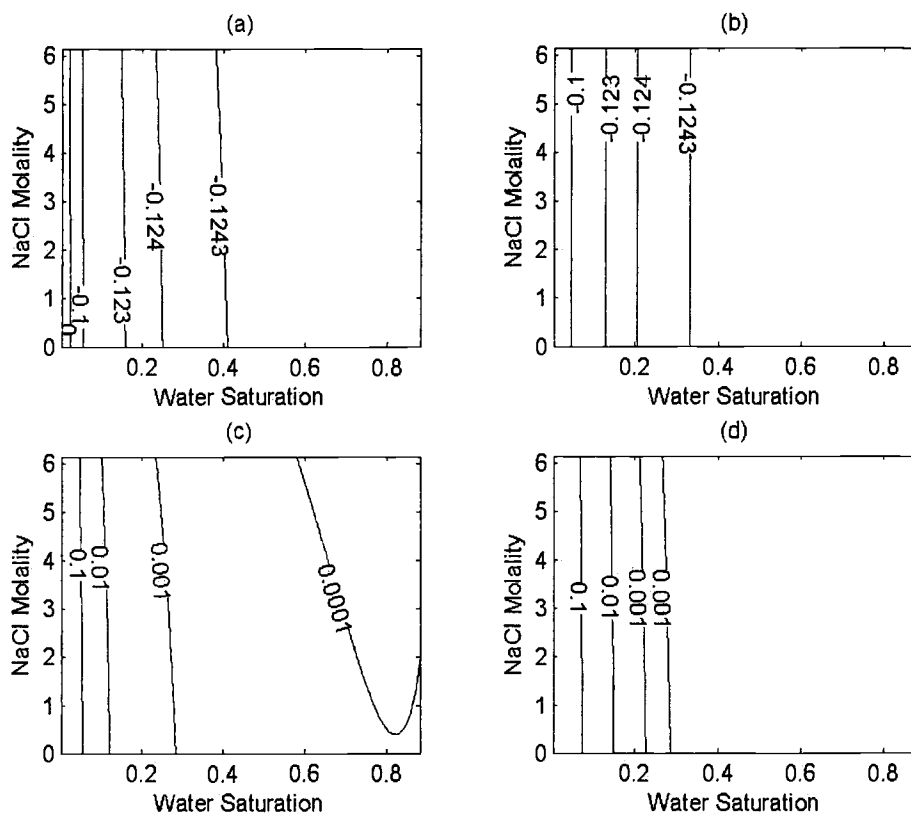


Figure 13a: Plots for silt: (a) Plot of equation (59a); (b) plot of equation (59a), but neglecting the volume correction terms; (c) error (eqn (66)) induced by neglecting volume correction terms; (d) error (eqn (66)) induced by approximating equation (59a) with the constant -0.124.

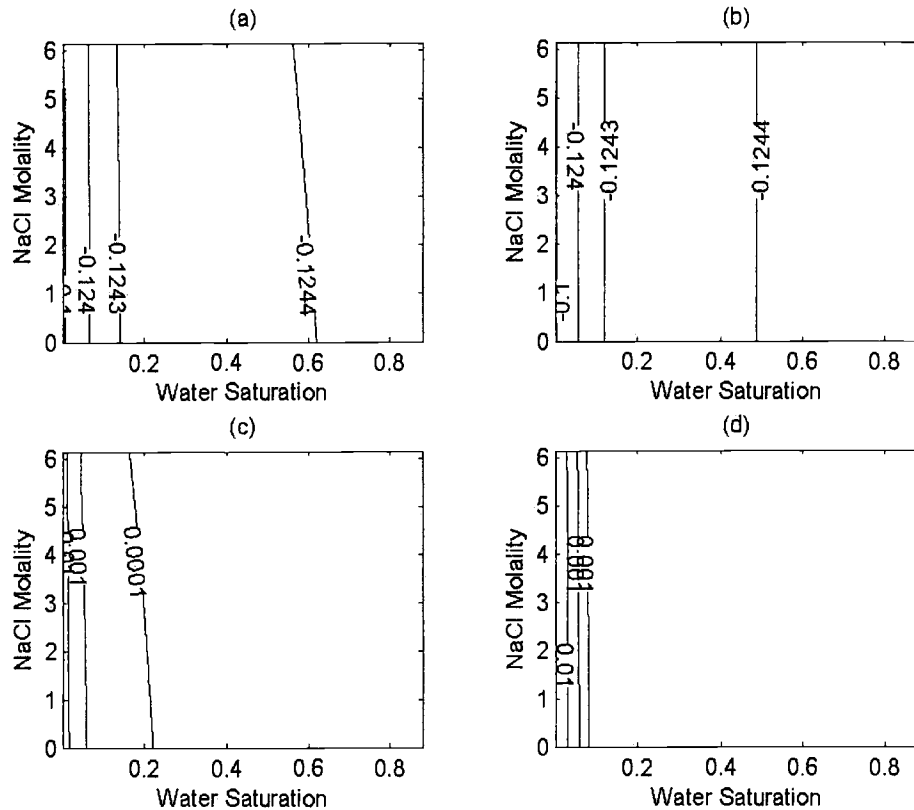


Figure 13b: Plots for **loam**: (a) Plot of equation (59a); (b) plot of equation (59a), but neglecting the volume correction terms; (c) error (eqn (66)) induced by neglecting volume correction terms; (d) error (eqn (66)) induced by approximating equation (59a) with the constant -0.124.

Figures 12b and 14a through 14c show the results for equation (59b). Figure 12b shows that only in the dilute case is it clear that the differential in the dilute approximation term dominates the differential in the volume correction term. In Figures 14a through 14c, plot (a) is of equation (59b), and plot (b) shows the effect of neglecting the volume correction term in computation of both the vapor pressure and the differential. The resulting error is shown in plot (c). In Figure 14a plot (b), it is noted that accounting for the activity results in stronger influence of salt concentration than is seen in plot (a). With this motivation, plot (d) shows the error as a result of

also neglecting the activity. At first glance, it seems that this is a superior approximation with improved performance in dryer regions, but examination of plot (d) in Figures 14b and 14c show this is merely fortuitous, and not a robust approximation.

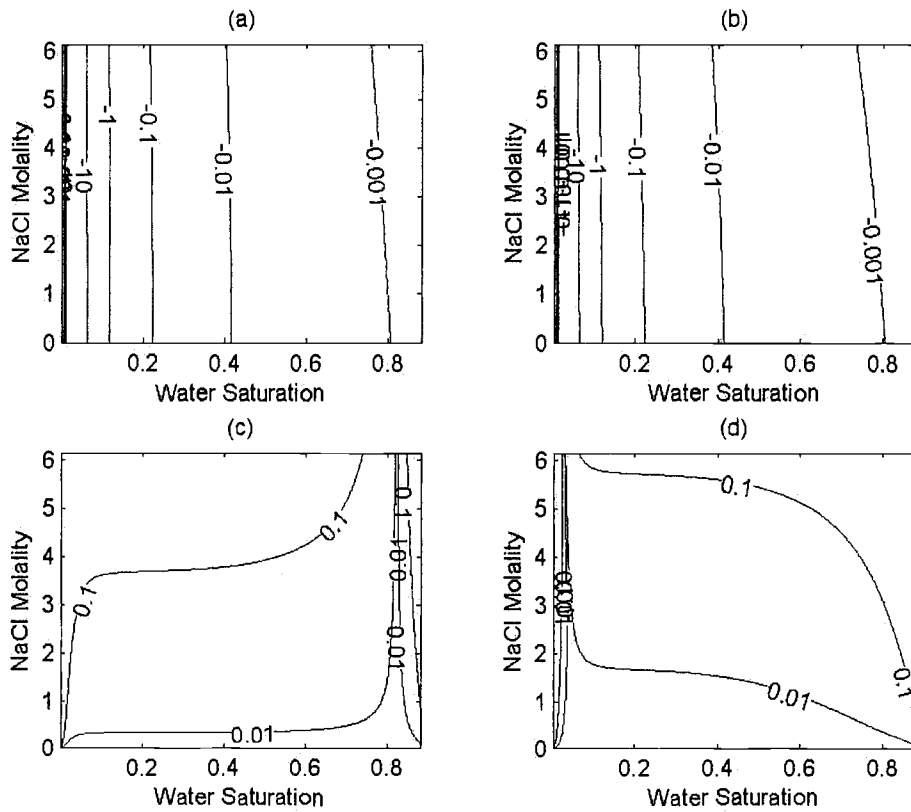


Figure 14a: Plots for silt: (a) plot of equation (59b); (b) plot of equation (59b) but neglecting the volume correction terms in both the vapor pressure and the differential; (c) error (eqn (66)) resulting from the approximation described in (b); (d) error induced by neglecting both the volume correction and activity terms.

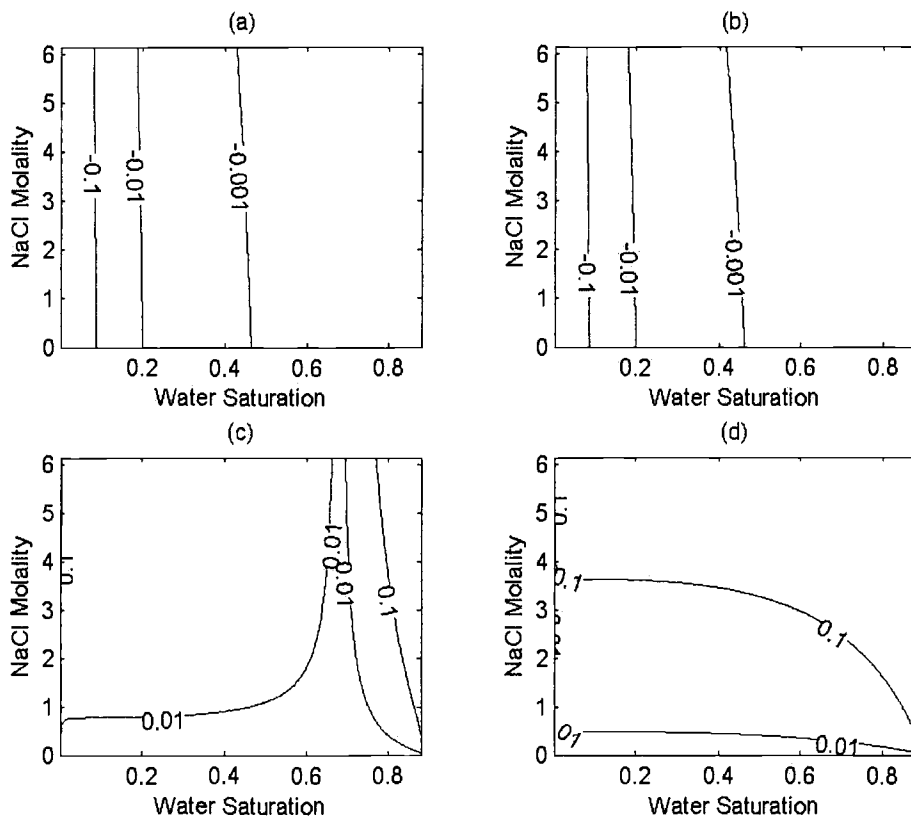


Figure 14b: Plots for **loam**: (a) plot of equation (59b); (b) plot of equation (59b) but neglecting the volume correction terms in both the vapor pressure and the differential; (c) error (eqn (66)) resulting from the approximation described in (b); (d) error induced by neglecting both the volume correction and activity terms.

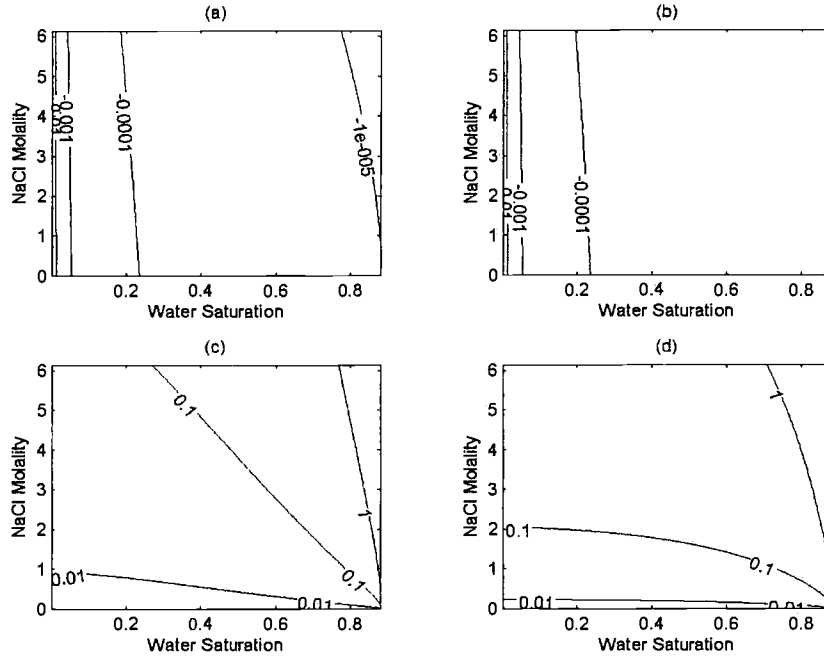


Figure 14c: Plots for **sand**: (a) plot of equation (59b); (b) plot of equation (59b) but neglecting the volume correction terms in both the vapor pressure and the differential; (c) error (eqn (66)) resulting from the approximation described in (b); (d) error induced by neglecting both the volume correction and activity terms.

Figures 15a through 15c show analysis of equation (62a) for silt, loam, and sand, respectively. Plot (b) shows equation (62a) itself, and plot (a) shows that for all three soils, the differential in terms of pressure (\tilde{P}^L) is almost always dominated by the differential term for surface tension. Plot (c) shows that it is still necessary to account for the volumetric effect in \tilde{P}^L except in the dilute case. Plot (d) indicates that failure to correct for changes in surface tension is never acceptable. Plot (e) shows that a very good approximation to equation (62a) is:

$$(80) \quad \frac{\partial P^L}{\partial m} = \frac{\tilde{P}^L}{\sigma_0^{LG}} \frac{\partial \sigma^{LG}}{\partial m} = \frac{1.7}{72} \tilde{P}^L (S^L(S_0^L, m)), \text{ where equation (72) was used.}$$

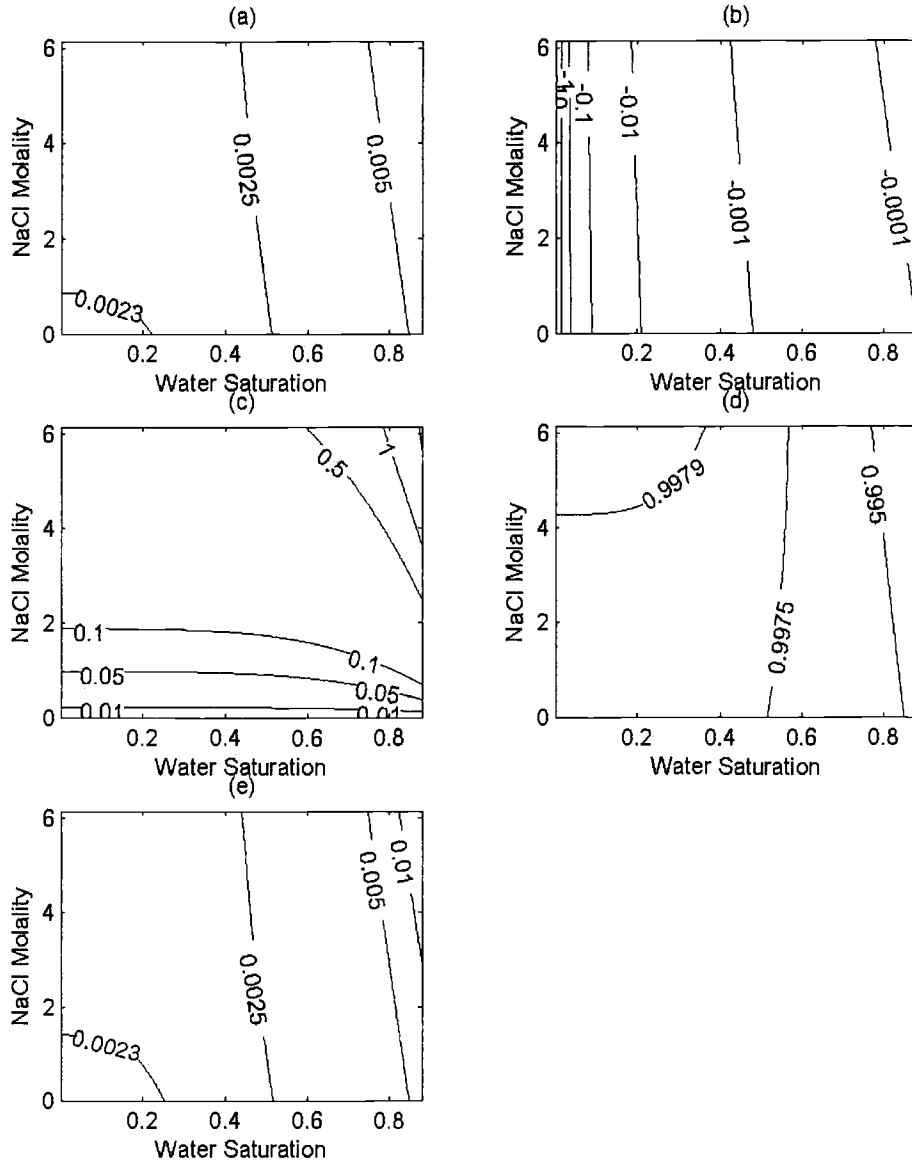


Figure 15a: Plots for equation (62a) for silt: (a) ratio of the magnitudes of the pressure differential term to the surface tension differential term; (b) plot of equation (62a); (c) error (eqn (66)) induced by assuming \tilde{P}^L is not a function of salt content (i.e., there is no correction of saturation for salt content); (d) error induced by assuming the surface tension is constant, but that saturation changes with salt content; (e) error induced by assuming 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).

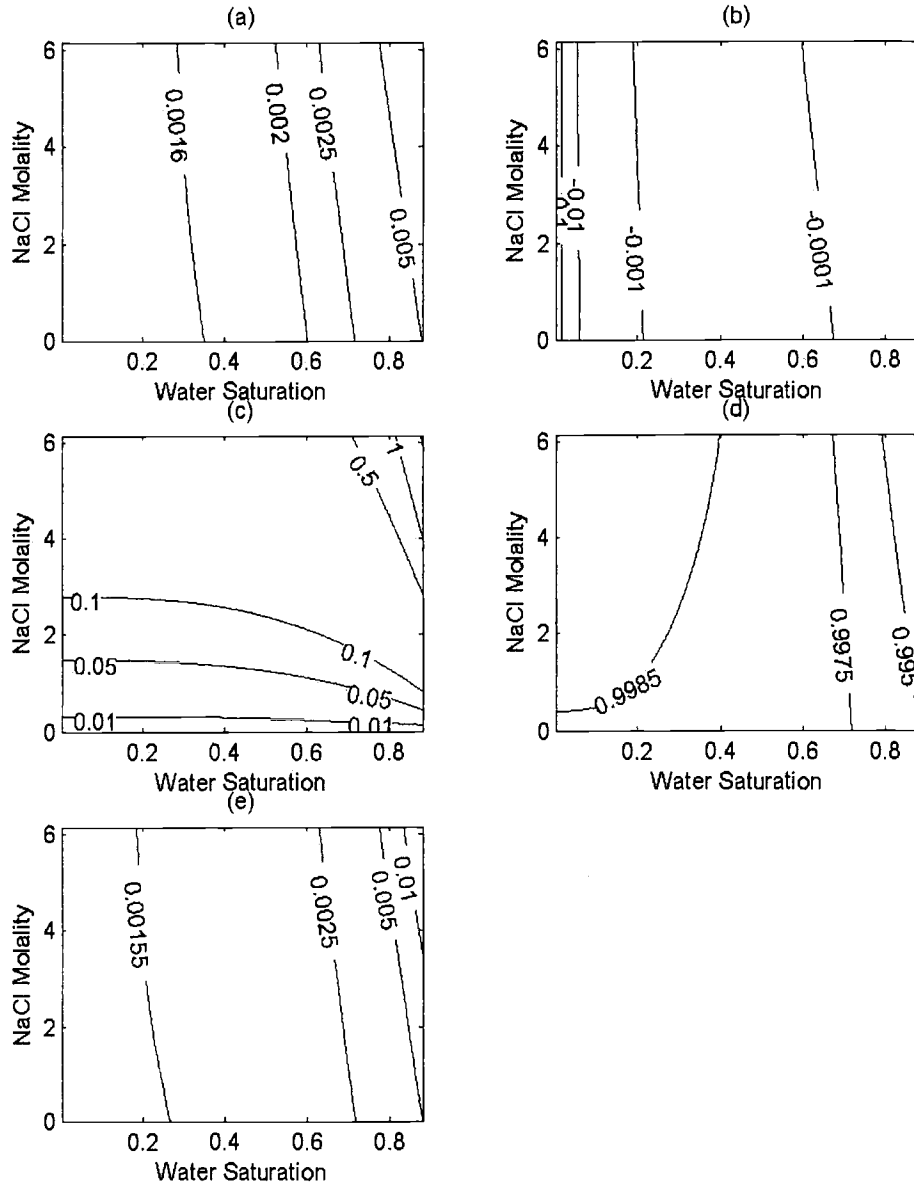


Figure 15b: Plots for equation (62a) for **loam**: (a) ratio of the magnitudes of the pressure differential term to the surface tension differential term; (b) plot of equation (62a); (c) error (eqn (66)) induced by assuming \tilde{P}^L is not a function of salt content (i.e., there is no correction of saturation for salt content); (d) error induced by assuming the surface tension is constant, but that saturation changes with salt content; (e) error induced by assuming 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).

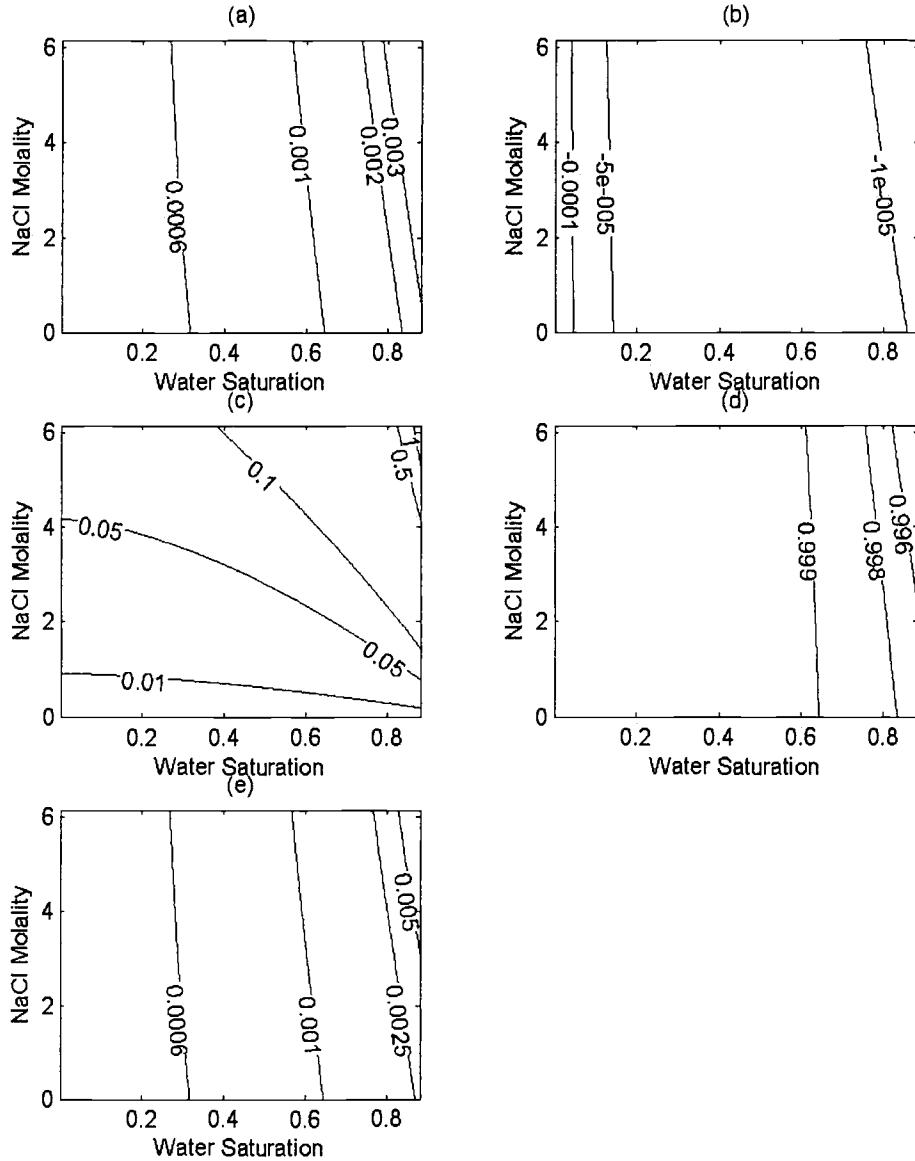


Figure 15c: Plots for equation (62a) for **sand**: (a) ratio of the magnitudes of the pressure differential term to the surface tension differential term; (b) plot of equation (62a); (c) error (eqn (66)) induced by assuming \tilde{P}^L is not a function of salt content (i.e., there is no correction of saturation for salt content); (d) error induced by assuming the surface tension is constant, but that saturation changes with salt content; (e) error induced by assuming 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).

Plots for equation (62b) are shown in Figures 16a through 16c. Clearly, these show that neither the volume correction nor the surface tension may be neglected except in the dilute case.

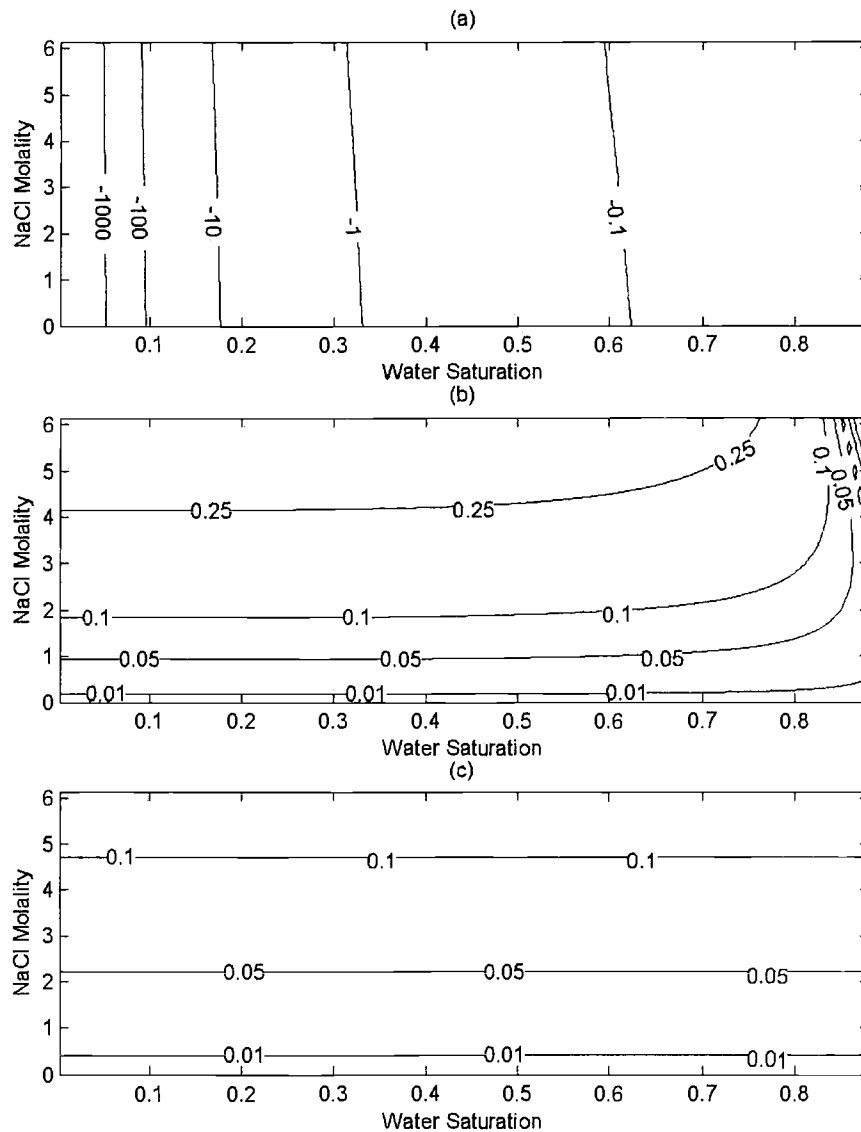


Figure 16a: Plots of equation (62b) for silt: (a) plot of the entire equation; (b) error induced by neglecting the volume correction in the derivative; (c) error induced by neglecting the surface tension.

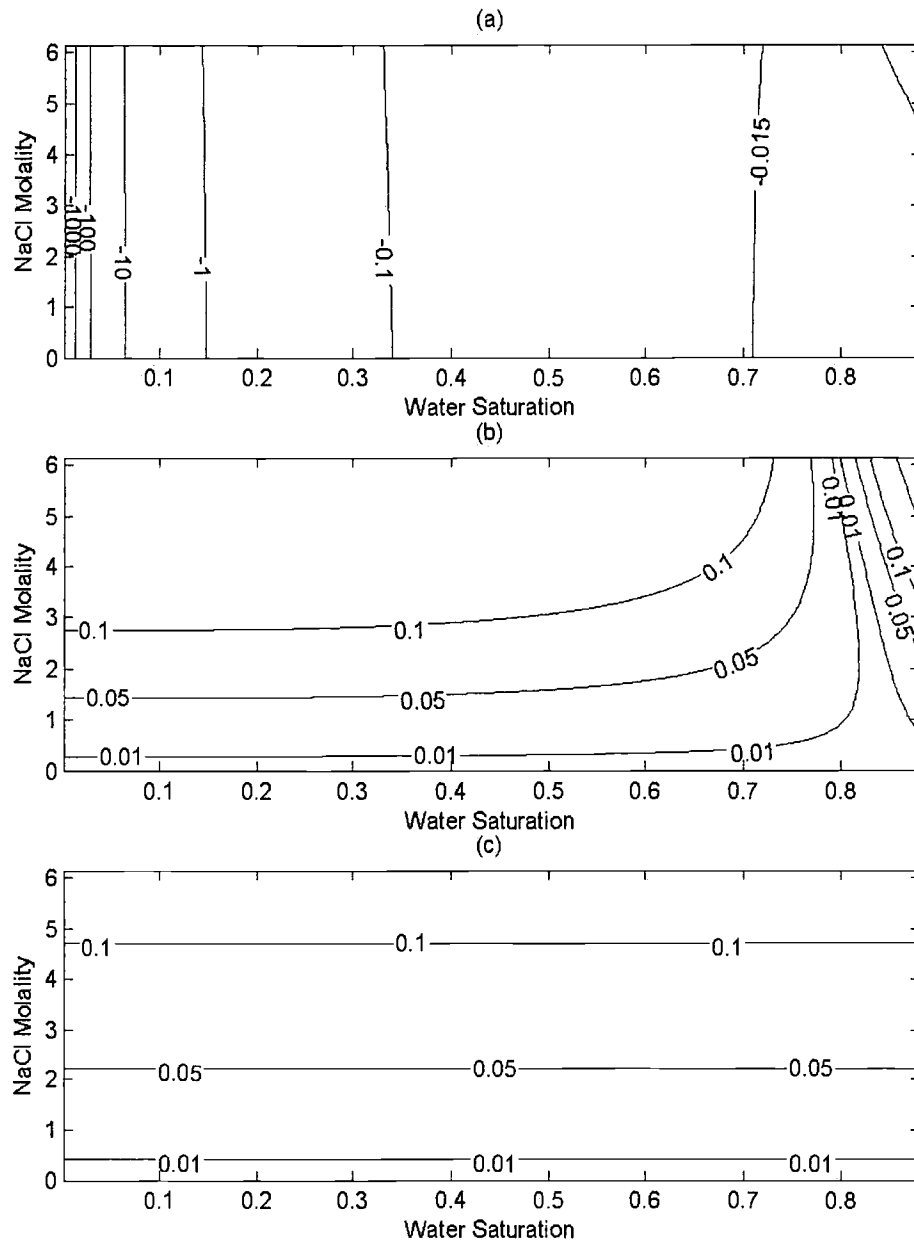


Figure 16b: Plots of equation (62b) for **loam**: (a) plot of the entire equation; (b) error induced by neglecting the volume correction in the derivative; (c) error induced by neglecting the surface tension.

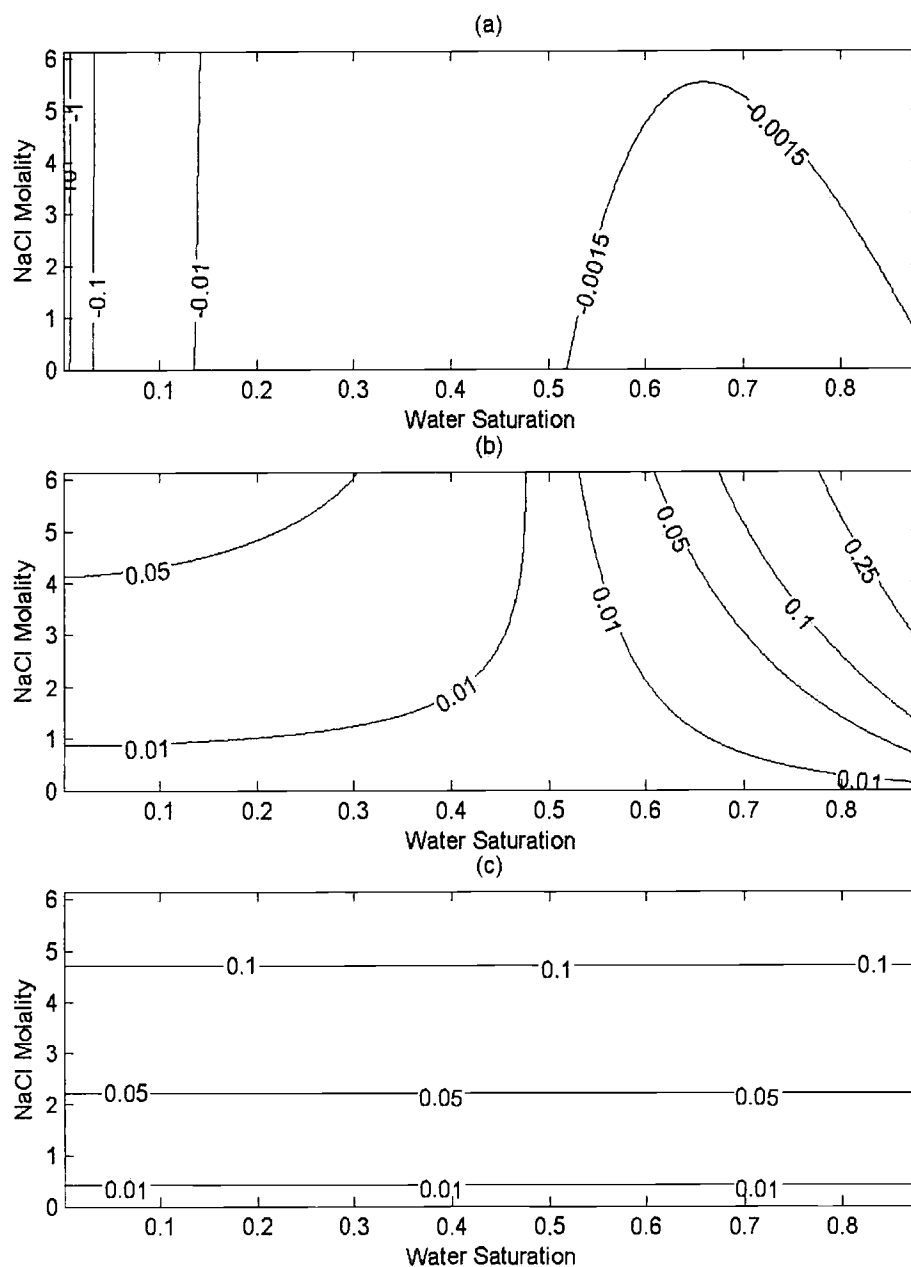


Figure 16c: Plots of equation (62b) for sand: (a) plot of the entire equation; (b) error induced by neglecting the volume correction in the derivative; (c) error induced by neglecting the surface tension.

It is tempting to consider the magnitudes of (59a) compared to (59b) or (62a) compared to (62b), but without prior knowledge of the gradients in water and salt content to be encountered during evolution of an initial boundary value problem, it is impossible to do this here. Instead, it is noted that (59a), (59b), (62a), and (62b) will provide the appropriate conversions from the dependent variables (pressures) to the primary variables (water and salt contents) for solution of the differential equations.

Application to the data of Scotter

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 media 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. It was found that the moisture and salt profiles are constant (for the same initial conditions) with respect to the transformed variable $\eta = x/t^{1/2}$. The reader is referred to the above papers for a more complete description of the experiments.

Figure 17 shows the results of two experiments (same initial conditions) conducted by Scotter (1974) in terms of the transformed variable and the gravimetric salt and water contents (g NaCl and g water per 100 g dry soil respectively). The salt is at $\eta = 0$.

The conceptual model is that water moves from the dry region (to the right of the dashed line) in the vapor phase to the wet region (to the left of the dashed line) where

it condenses due to vapor pressure lowering associated with the salt and saline water. Once the water condenses, the moisture content is sufficiently high to allow water flow back towards the dry region. It is sufficient to think of the right-hand side as the vapor flow region (hereafter called the dry region), and the left-hand side as the combined liquid-vapor flow region (hereafter called the wet region).

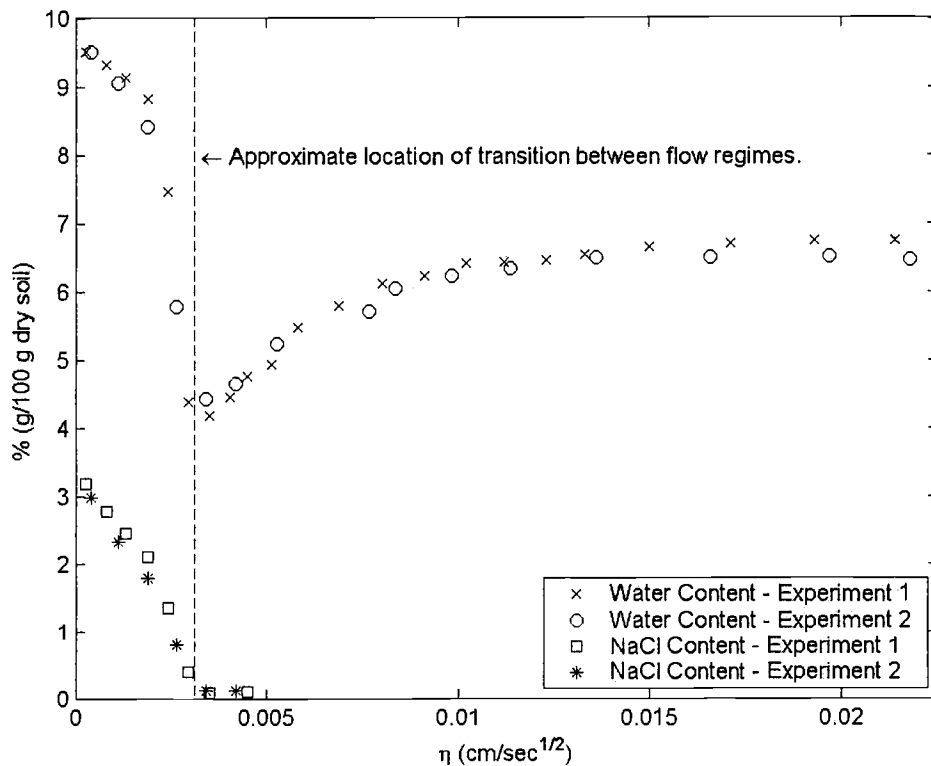


Figure 17: Gravimetric water and NaCl content from Scotter (1974). Pure phase NaCl is at $\eta = 0$.

Using the theory developed above, it is now possible to plot the vapor pressures and water potentials for the Scotter data. Since Scotter measured gravimetric values of water and salt, it is necessary to compute liquid volumes, water volumes, molal salt

concentrations, etc. in order to plot the desired results. Figure 18 shows Scotter's measured values for water content versus soil water pressure for fresh water (assumed here to be zero or negligible salt), along with a fit to the data of the van Genuchten relationship (van Genuchten, 1980). The fit of the model is sufficient for the purposes of this example, and the values of the van Genuchten parameters used are $\bar{\alpha} = 0.000329573$ and $N = 1.483$. This relationship is the required functional form for equation (73) above.

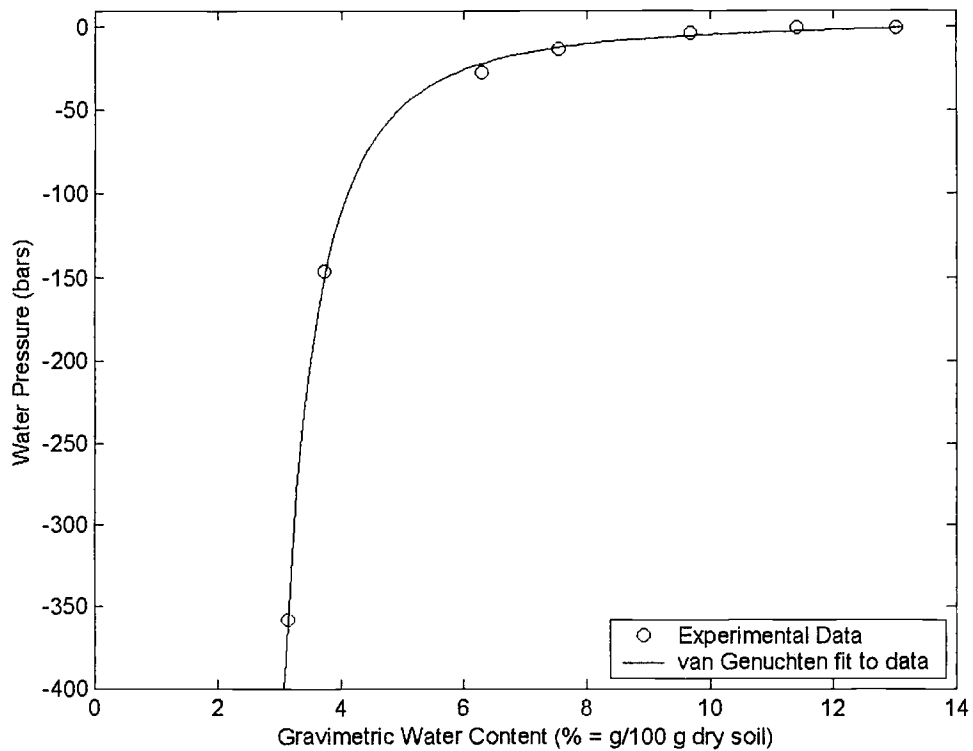


Figure 18: Fit of the van Genuchten relationship to the experimental data of Scotter. The data is for very low strength or pure water.

Since Scotter's experiments were all conducted at 25 C (298.15 K), it is assumed that the straight line in Figure 4 is sufficient for this example. For the remaining estimates and conversions from the gravimetric data of Scotter, a porosity of 0.3 and a density for the dry soil of 2.65 g/cm^3 were used. Equation 6 of Heyrovska (1996) was used to compute a^{wL} (using linear interpolation of α from the closely spaced tabulated values), providing the last required information. If desired, the method of Pitzer (Pitzer and Peiper 1984) could be used to get all 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.

Equation (78) may again be employed to perform an order of magnitude analysis and to plot vapor pressure. Figure 19 shows that the linear approximation is valid for Scotter's soil. The remaining plots in Figure 19 are analogous to those shown in Figures 8a through 8c for comparison. Figure 20a shows that the liquid saturations and the equivalent water saturations are different in the wet region, and Figure 20b shows the resulting liquid pressure profiles (computed using equation (55b)). Figure 21 shows the resulting vapor pressure profile for the Scotter data (i.e., equation (78) solved for vapor pressure). The vapor pressure of pure water over a flat interface is available in any chemistry handbook, and the vapor pressure over a saturated salt

solution is an approximate value taken from the compilation of Appelblat and Korin (1998).

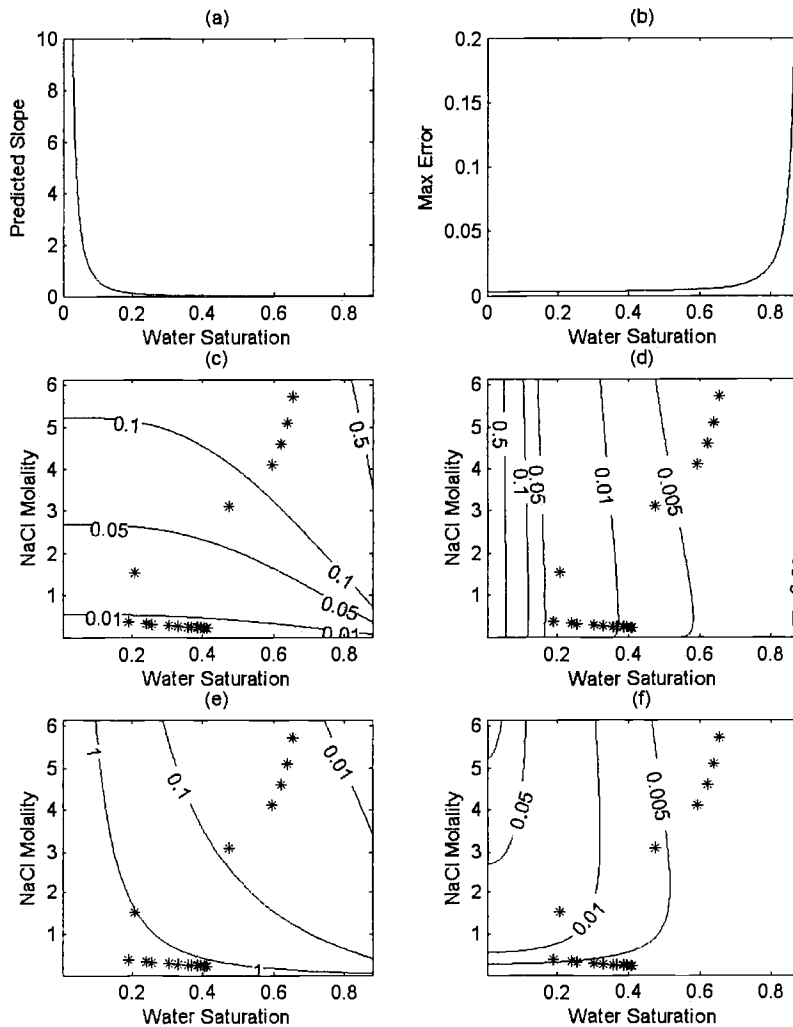


Figure 19: Plots for Scotter's soil: (a) The slope of the linear approximation ($b(S_0^L)$) to the pressure function. (b) The error (eqn (66)) between the linear fit and the computed pressure. (c) The absolute value of the ratio of the volume correction term to the dilute approximation term for equation (47). (d) The absolute value of the ratio of the volume correction term to the activity term for equation (47). (e) The absolute value of the ratio of the dilute approximation term to the activity term for equation (47). (f) Plot of equation (65): The absolute value of the ratio of the volume correction term to the sum of the dilute approximation and activity terms for equation (47). The asterisks are the experiment 1 data.

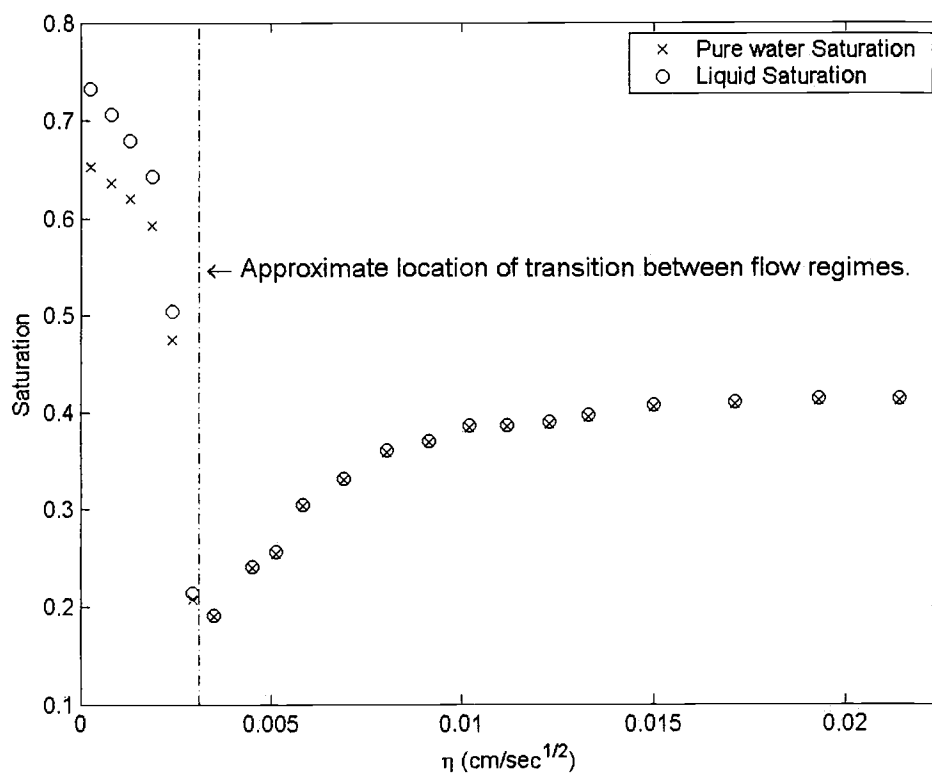


Figure 20a: Scotter data: Pure water saturation and saline liquid saturation as a function of position.

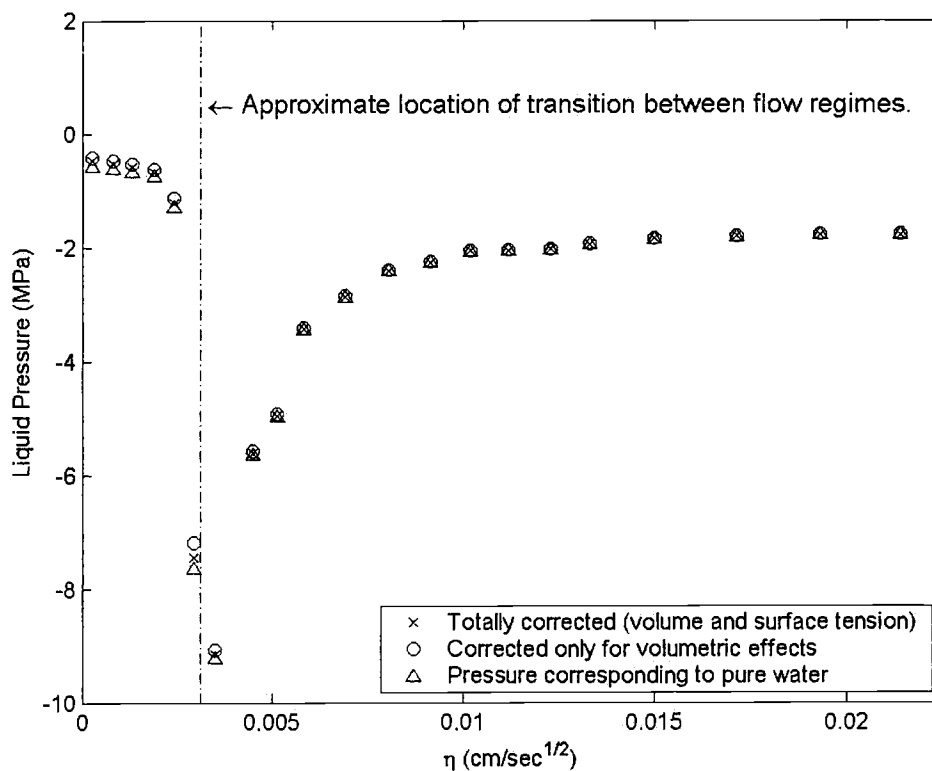


Figure 20b: Scotter data: Computed liquid pressures using equation (55b) and the data in Figure 17: equation (55b) is shown with x's, not correcting for salt at all shown with triangles, and correcting for changes in volume, but not surface tension shown by o's. Evidently, the volume effect is larger, but the increase in surface tension lessens the effect.

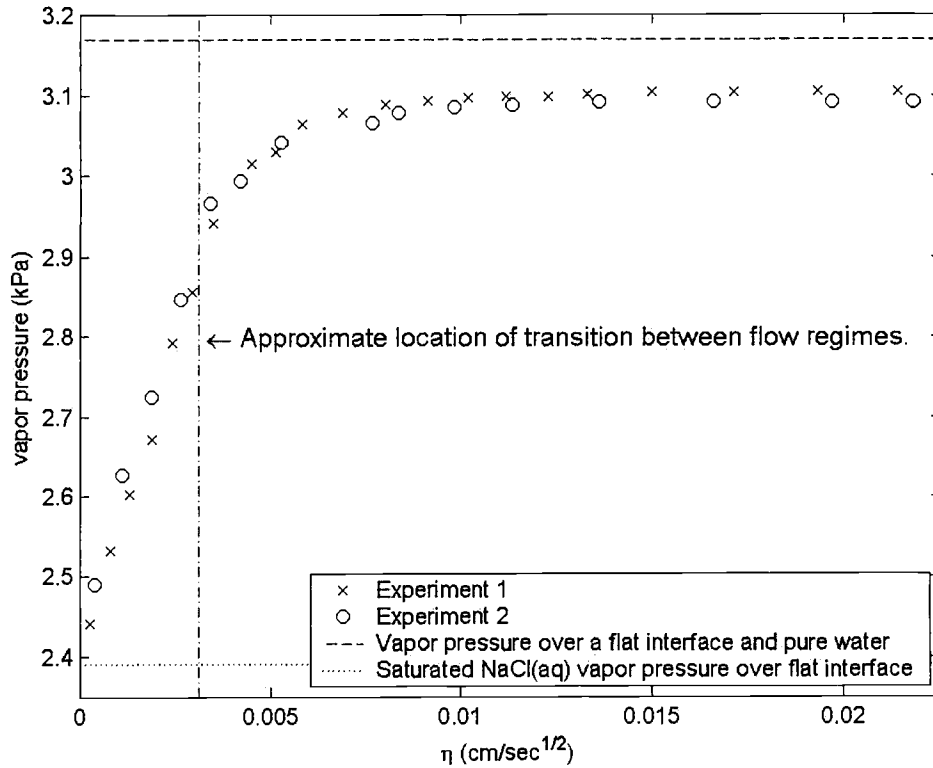


Figure 21: Computed vapor pressure (equation (55a)) as a function of position.

Clearly, there is a large effect of the salt content on the vapor pressure. To emphasize this, the vapor pressure is plotted in Figure 22 with various terms assumed to be negligible. There appears to be little effect due to neglecting the volume correction term. In Figure 19, the data points have been plotted in (S_0^L, m) space, and Figure 18(f) shows that the point $\eta \approx 2.9$ is the point expected to be most dramatically influenced. A blow-up detail of the wet region (Figure 23) shows that this is the case, but that the effect is still relatively small. Figure 24 shows the errors (analogous to the errors plotted in Figures 10a through 10c) for comparison. From Figures 19 and 24, it is likely that the volume correction term may be neglected for computation of vapor

pressures, with only one data point falling in a region where the error is $>1\%$. As expected, in the dry region, it may be allowable to neglect the activity term (due to low salt content); and in most of the wet region, interface curvature may be neglected (due to high salt content).

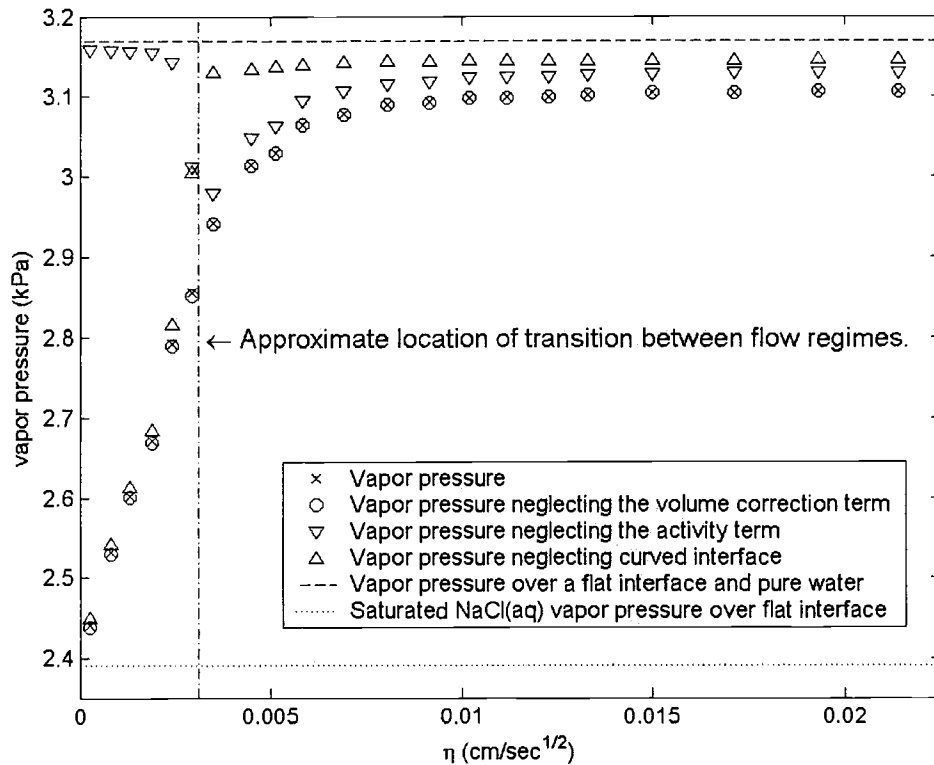


Figure 22: Computed vapor pressure (equation (55a)) from experiment 1 for four cases: 1) the full equation, 2) neglecting only the volume correction term (equation (57) or more specifically equation (66)), 3) neglecting the activity term (activity = 1), and 4) neglecting the entire exponential term (curved interface correction).

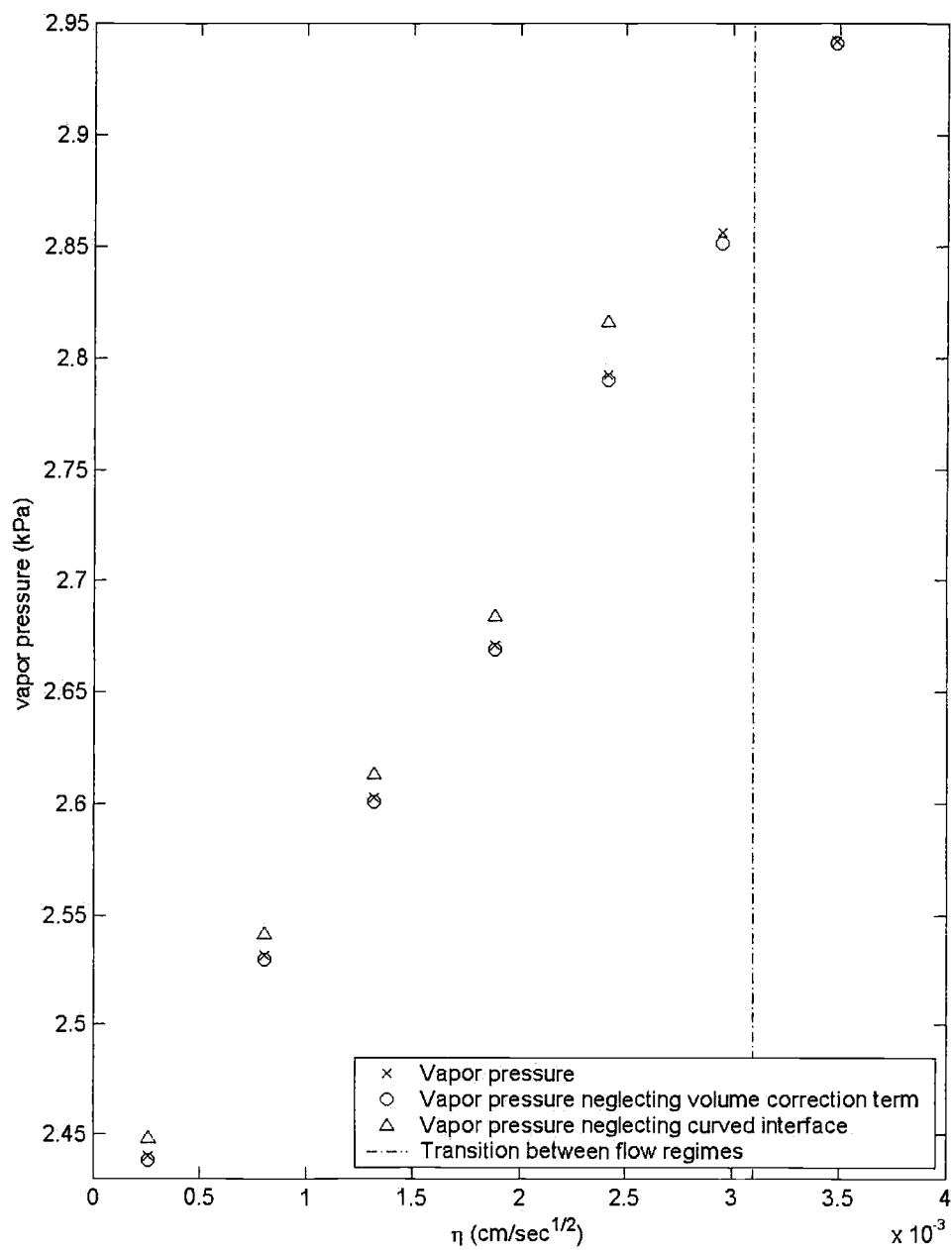


Figure 23: Blow-up detail of Figure 22 for the wet region with the activity term included.

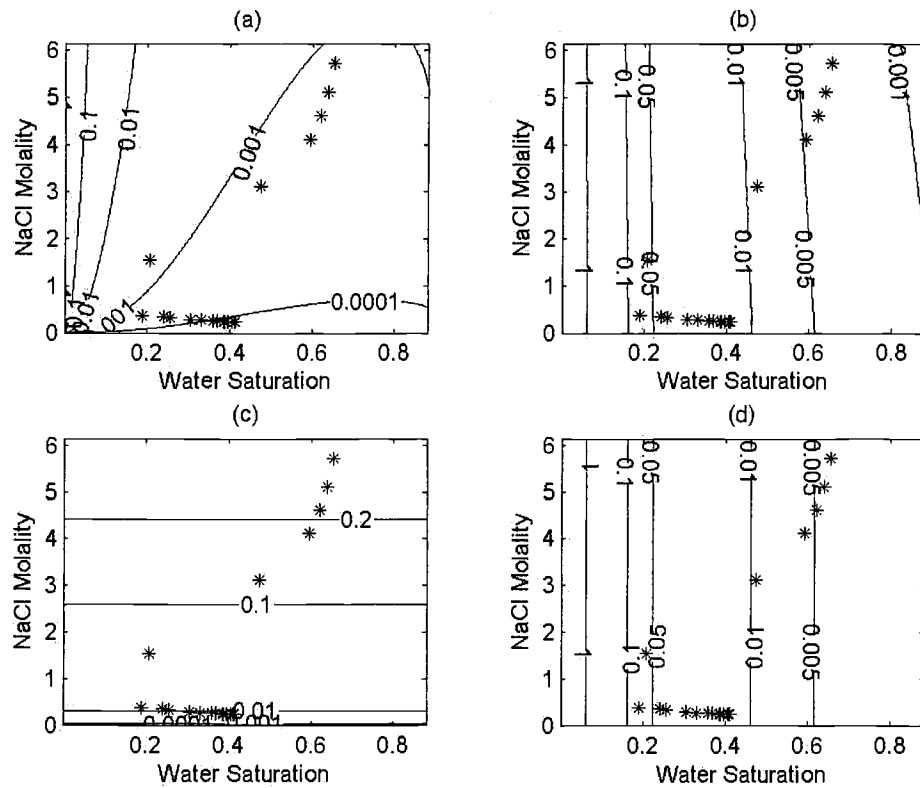


Figure 24: Scotter's data: Plots of the error (equation (66)) induced by neglecting one or more terms in equation (55a): (a) only the volume correction term is neglected (worked example equation (67)); (b) interface curvature is neglected (both dilute approximation term and volume correction term); (c) only the activity term is neglected; and (d) only the dilute approximation is neglected. The asterisks are data from experiment 1.

Figure 25 (analogous to Figure 12a plots (b) through (d) for comparison) shows that the volume correction term needs to be accounted for when computing equation (59a).

This is further supported by Figure 26 (analogous to Figures 13a and 13b).

Examination of Figure 12b shows that the volume correction term will need to be accounted for when computing equation (59b) for Scotter's soil. This implies that accounting for the volume correction term is necessary when computing the conversions between gradients in vapor pressure and gradients in water and salt contents.

Examination of Figure 27 (analogous to Figures 15a through 15c) shows that equation (80) is a good approximation for equation (62a) for the Scotter data. Examination of Figures 16a through 16c makes it obvious that neither the volume correction nor the surface tension correction may be neglected for equation (62b).

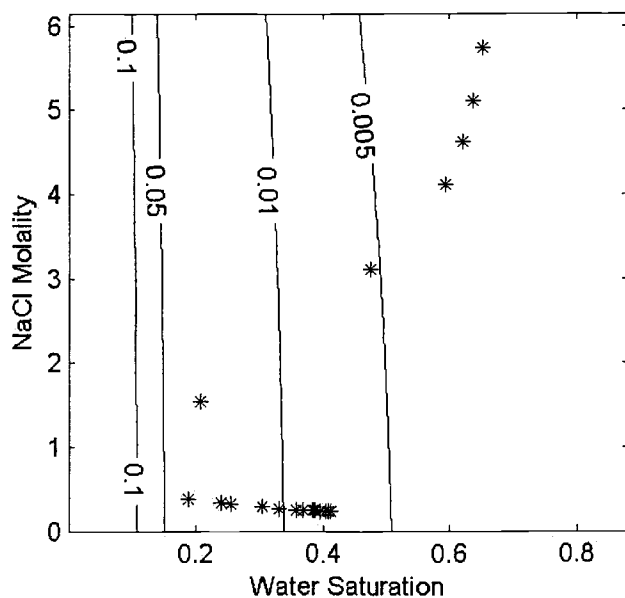


Figure 25: Plot of the magnitude of the volume correction term relative to the activity term for Scotter's data for equation (59a).

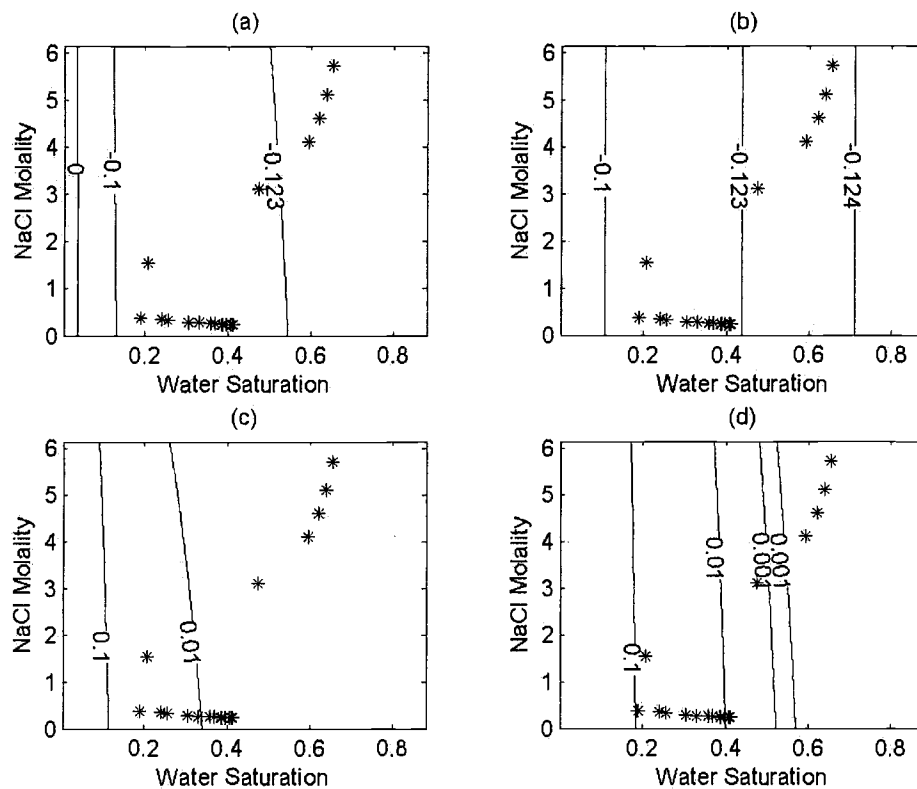


Figure 26: Plots for **Scotter's soil**: (a) Plot of equation (59a); (b) plot of equation (59a), but neglecting the volume correction terms; (c) error (eqn (66)) induced by neglecting volume correction terms; (d) error (eqn (66)) induced by approximating equation (59a) with the constant -0.123. Asterisks are data from experiment 1.

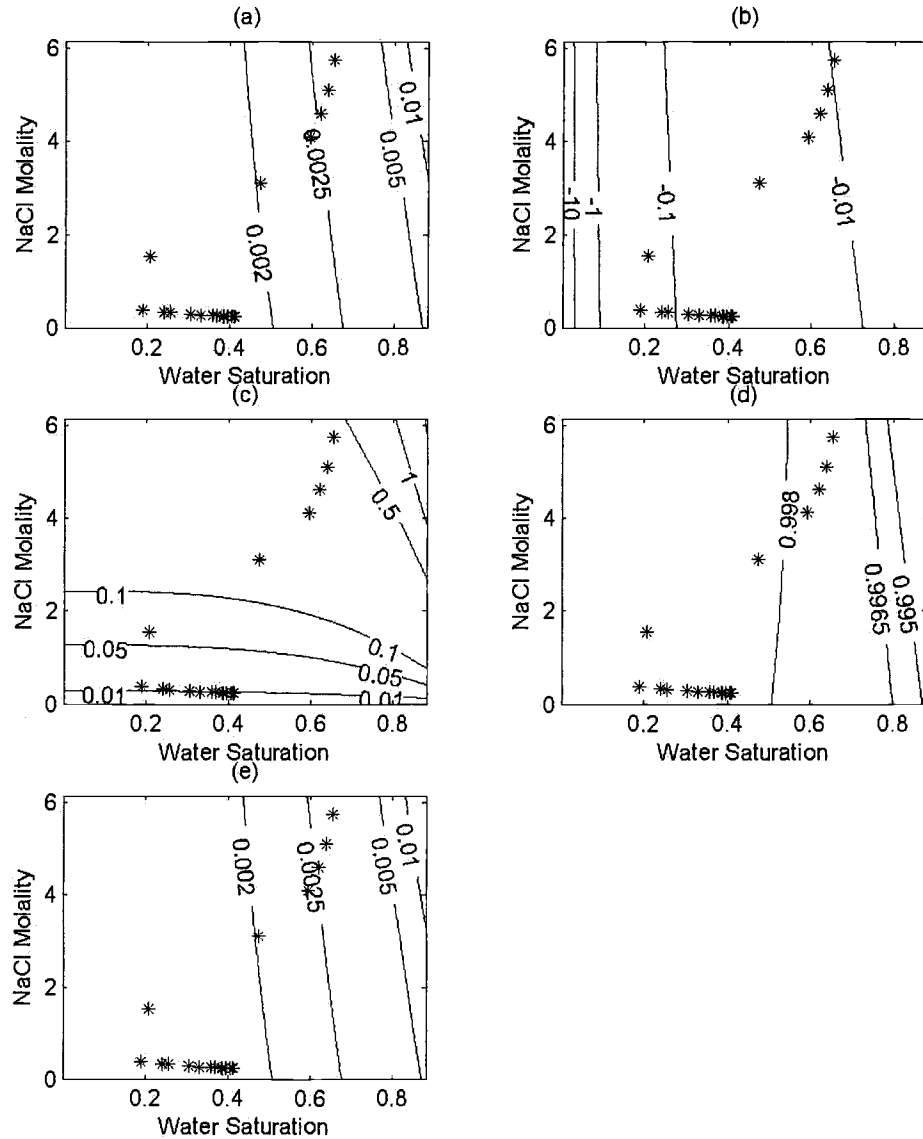


Figure 27: Plots for equation (62a) for **Scotter's soil**: (a) ratio of the magnitudes of the pressure differential term to the surface tension differential term; (b) plot of equation (62a); (c) error (eqn (66)) induced by assuming \tilde{P}^L is not a function of salt content (i.e., there is no correction of saturation for salt content); (d) error induced by assuming the surface tension is constant, but that saturation changes with salt content; (e) error induced by assuming 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). Asterisks are data from experiment 1.

Discussion

Constitutive relationships have been defined for various purposes by Olivella et al. (1996), Bear and Gilman (1995), and Nassar and Horton (1989), but the detail and method of determination of these relationships was dictated by the level of detail necessary to accomplish specific tasks. None of the relationships presented in the aforementioned papers were completely derived from first principles, but there are many similarities to certain results from this paper.

Olivella et al. (1996) use a very similar functional form to the dilute solution approximation equations derived in this paper (equation (64)). In the references they cite, the relationships for salt and for curvature are derived separately, so it seems likely that Olivella et al. combined the functional forms in a reasonable way, getting the form they use in their model CODE_BRIGHT.

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. Certainly such an approximation is likely reasonable for cases where salt gradients dominate in the region of interest. The resulting equation is similar to the one derived here for dilute solutions 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 of the water, and so is comparable to the salt correction in equation (36). There is also a temperature correction term that includes the latent

heat of vaporization. Olivella et al. and Nassar and Horton both compensate for temperature with empirical relations, but energy conservation equations are used to account for latent heats and other energy transfers.

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.

None of the papers reviewed presented a methodology for handling non-dilute effects on the integrand in equation (46). The methodology developed herein results in the general relations equations (55a) (equivalently (47)) and (55b). These results are very general, and the fourteen assumptions leading to their derivation are broadly satisfied in natural unsaturated porous media.

The relations developed herein are applicable for high-strength contaminants that may be well-represented by a single concentration parameter (N^{hL} or m are used here). When it becomes necessary to use multiple concentration parameters (i.e., for multiple independent salts), the above derivations will yield results in terms of affinities (c.f. DeHoff (1993)). Since the goal of this paper was to describe the method and to show that non-dilute effects are appreciable under some circumstances, the single concentration derivation was used for clarity.

Examination of the NaCl example above shows that non-dilute effects are generally more profound in dryer, fine textured soils. For dryer soils, the approximation scheme above provides a simple and effective first-order correction for the volumetric effects. The slope function, $b(S_0^L)$, appears to be a well-behaved function that would be easy to approximate analytically for any fixed soil type of interest.

When considering flow in a porous media, it should also be noted that at high saturations, vapor flow due to vapor pressure gradients will be negligible due to a negligibly small diffusion coefficient resulting from lack of connection between gas filled voids. Also, any water mass in the vapor state is negligible compared to the liquid water mass (due to low volumes of gas and low specific volumes of water in the gas phase), so errors introduced by the departure from linearity at high saturations should have a negligible effect on water flow in a porous media. For this reason and the fact that the activity term dominates at high saturations, it is postulated that the linear approximation for NaCl given by equation (76) is sufficient for modeling flow and transport of saline fluids in many porous mediums.

As a final note, one becomes interested in the extension of the above derivation to an-isothermal conditions (where changes in temperature occur via a quasi-static path). Obviously, it is possible to conduct the experiments necessary to repeat the above for other temperatures. If sufficient other temperatures are used, a functional form for the temperature dependence may be derived. In this way, a constitutive relation for mass exchange between the phases may be developed for an-isothermal conditions.

Conclusion

A very general relationship describing the equilibrium vapor content in the gas phase above a saline liquid and across a curved interface has been developed. Also, a method to compute the appropriate salt corrections to the constitutive relation is derived. The resulting equations are valid for salt concentrations between zero and saturation, and for any temperatures that nominally occur in near surface geologic materials. High strength salt effects are most profound in fine textured soils that are very dry. If it becomes necessary to account for high strength salt effects for NaCl, equation (76) may be used as a first-order approximation. This approximation is trivial to use with numerical models.

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Appendices

Appendix 1 - Notation

Variables

U = the internal energy

H = entropy

T = absolute temperature

P = pressure

V = volume

S = saturation

m = molality

$\mu^{i\alpha}$ = 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

$v^{iL} \equiv \frac{V^L}{N^{iL}}$ = 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 (51)).

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

∂ = partial differential

δ = imperfect differential

Superscripts

L, G = liquid and gas phase respectively

wL, wG = water in liquid and water in gas respectively

hL = salt in liquid

aG = air in gas

LG = gas-liquid interface

sys = system total

α = an arbitrary phase or sub-system

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)

Appendix 2 – Sample Matlab code that shows method of computing the volume correction term.

Sample Matlab code for plot 7a:

```
clear
```

```
% List constants and parameters.
```

```
% Molecular weight of water in g/mol.
```

```
MW=18.015;
```

```
% density of pure water at 25C in g/cubic cm
```

```
rho=.997044;
```

```
% R is gas constant. Units=J/mol*K. T is temp in K.
```

```
R=8.314;
```

```
T=298.15;
```

```
% van Genuchten parameters for the pressure-saturation relationship for silt.
```

```
% vGalpha has units of 1/cm.
```

```
vGalpha=.016;
```

```
n=1.37;
```

```
% Data for NaCl from Heyrovská [1996]: Tabulated values of Heyrovská's alpha as a  
% function of molality (m).
```

```
m1=[.001 .002 .005 .01 .02 .05 .1];
```

```
m2=[.2 .3 .4 .5 .6 .7 .8 .9 1 1.2 1.4 1.6 1.8 2 2.5 3 3.5 4 4.5 5 5.5 6 6.144];
```

```
m=[m1 m2];
```

```
alpha1=[.976 .968 .952 .935 .916 .884 .858];
```

```
alpha2=[.832 .818 .807 .801 .797 .795 .792 .79 .789 .788 .788 .788 .791 .794 .802  
.812 .825 .837 .847 .855 .863 .865 .865];
```



```

alpha=[alpha1 alpha2];

% Compute the activities using Heyrovsk's equation.
activity=55.51-3.348*m;
denominator=alpha.*m;
denominator=55.51-2.348*m+denominator;
activity=activity./denominator;

% Compute the "molal volumes" (units of cubic cm/kg water) using Heyrovsk's
functional fits. The exception to Heyrovsk's methodology is that
% Heyrovsk changes the calculation at 2 molal, while we choose 0.1506
% because this is where the curves cross. This ensures V is continuous.
V1=1002.86+26.8*m1-10.55*alpha1.*m1;
V2=1002.38+24.74*alpha2.*m2;
V=[V1 V2];

% So is the water saturation assuming zero salt. The following creates a
% vector of saturations for looping the calculations and subsequent contour
% plots. Notice that 0.884 is the maximum value allowed since the addition
% of salt to 6.144 m (saturation) will increase saturation to 100%.
So=.001:.001:.88;

% The following is a linear fit of surface tension as a function of m
% divided by the zero salt surface tension at 25 C (i.e., 72 dynes/cm).
surf=m*1.7/72+1;

% Loop over the water contents.
M=length(So);
for i=1:M

    % Call the function "saturation" that computes the change in saturation
    % that results by adding salt.
    s=saturation(So(i),V);

    % Call the van Genuchten Pressure function for set values of van
    % Genuchten's alpha (vGamma) and n. This function returns the change in
    % pressure with s.

    P= -vG_press(s,vGamma,n);

    % Correct for surface tension effects.
    P=surf.*P;

    % This performs a linear fit to P as a function of m, then computes the

```

```

% relative maximum error defined as the difference between the line and the
% computed pressure divided by the computed pressure.
fit = polyfit(m,P,1);
slope(i)=fit(1);
y=fit(1)*m+fit(2);
B=P-y;
B=B./P;
B=abs(B);
H(i)=max(B);

% error is the value of the salt correction integral. error4 is this
% value divided by the dilute solution approximation plus the activity term.
% error1 is only divided by the dilute approximation. error2 is only
% divided by the activity term. The salt correction
% integral is the integral of a linear function (i.e., a quadratic term)
% times the slope of the linear fit above (which is only a function of
% water content which is constant in the correction integral).
error(i,:)=(m.^2)*0.38151/2;
error(i,:)=error(i,)+(18.043*m);
error(i,:)=slope(i)*error(i,:);
denominator=-vG_press(So(i),vGalpha,n);
denominator=MW*denominator/rho+R*T*log(activity);
error4(i,:)=abs(error(i,:)/denominator);
denominator=-vG_press(So(i),vGalpha,n);
denominator=MW*denominator/rho;
error1(i,:)=abs(error(i,:)/denominator);
denominator=R*T*log(activity);
error2(i,:)=abs(error(i,:)/denominator);

end

% Loop over the molal strengths, and compute the dilute approximation
% divided by the activity term.
N=length(m);
for i=1:M
    for j=1:N
        error3(i,j)=-vG_press(So(i),vGalpha,n);
        error3(i,j)=MW*error3(i,j)/rho;
        denominator=R*T*log(activity(j));
        error3(i,j)=abs(error3(i,j)/denominator);
    end
end

end

```

% Plot the results.

% Plot (a) is a plot of the slopes of the linear fit as a function of water

% (pure) saturation.

```
subplot(3,2,1); plot(So,slope)
```

```
xlabel('Water Saturation'); ylabel('Predicted Slope');
```

```
xlim([0 .88]);
```

```
ylim([0 1]);
```

```
title('(a)');
```

% Plot (b) is a plot of the error of the linear fit as a function of water

% (pure) saturation.

```
subplot(3,2,2); plot(So,H)
```

```
xlabel('Water Saturation'); ylabel('Max Error');
```

```
xlim([0 .88]);
```

```
ylim([0 .5]);
```

```
title('(b)');
```

% Plot (c) is a contour plot of the salt correction integral divided by the

% dilute approximation. It shows the relative magnitude of the salt

% correction compared to the dilute approximation.

```
v=[.01 .05 .1 .5 1];
```

```
subplot(3,2,3); [C,h] = contour(So,m,error1',v);
```

```
clabel(C,h)
```

```
xlabel('Water Saturation'); ylabel('NaCl Molality');
```

```
title('(c)');
```

% Plot (d) is a contour plot of the salt correction integral divided by the

% activity term. It shows the relative magnitude of the salt

% correction compared to the activity term.

```
v=[.001 .01 .1 1];
```

```
subplot(3,2,4); [C,h] = contour(So,m,error2',v);
```

```
clabel(C,h)
```

```
xlabel('Water Saturation'); ylabel('NaCl Molality');
```

```
title('(d)');
```

% Plot (e) is a contour plot of the dilute approximation term divided by the

% activity term. It shows the relative magnitude of the dilute

% approximation term compared to the activity term.

```
v=[.001 .01 .1 1];
```

```
subplot(3,2,5); [C,h] = contour(So,m,error3',v);
```

```
clabel(C,h)
```

```
xlabel('Water Saturation'); ylabel('NaCl Molality');
```

```
title('(e)');
```

```
% Plot (f) is a contour plot of the salt correction integral divided by the
% dilute approximation plus activity terms. It shows the relative magnitude of the salt
% correction compared to the other terms that may dominate.
v=[.001 .01 .1];
subplot(3,2,6); [C,h] = contour(So,m,error4',v);
clabel(C,h)
xlabel('Water Saturation'); ylabel('NaCl Molality');
title('(f)');
```

The code for the function “saturation”:

```
% This function takes any saturation between zero and one, plus the molar
% volume from Heyrovská [1996] to compute the change in saturation as salt
% is added to pure water.
```

```
function [s] = saturation(So,V)
```

```
% Molecular weight of water.
MW=18.015;
```

```
% Number of moles of water in 1 cubic cm.
NwL=.05551;
```

```
% Corrected saturation for salt content.
s=V*So*NwL*MW/1000;
```

The code for the function “vG_press”:

```
function [P] = vG_press(s,alpha,n)
```

```
% s is saturation, alpha is van Genuchten alpha in 1/cm, n is unitless.
```

```
% This function calculates the water pressure (in positive MPa) of a soil using the van
% Genuchten relationship.
```

```
% density of pure water at 25C in kg/cubic meter
rho=997.044;
```

```
% gravity constant in m/square sec
g=9.80665;
```

```
% van Genuchten pressure in MPa
```

```
P=s.^(n/(1-n));
```

```
P=P-1;
```

```
P=P.^(1/n);
```

```
P=P*rho*g/alpha/1e8;
```