



Technical Note

Validity and slopes of the linear equation of state for natural brines in salt lake systems

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SUMMARY

Many density-dependent groundwater flow simulations rely on a linear equation of state that relates the fluid density to the total dissolved solute content (TDS). This approach ignores non-linear volume of mixing effects, as well as the impact of any chemical reactions. These effects can be considered by using geochemical codes that implement algorithms that calculate the density of a fluid based on the concentration of individual solute species. While in principle such algorithms could be used in-lieu of a linear equation of state in a groundwater model, the computational overhead is such that the use of a more simplified equation of state is preferred. This requires that the assumption of linearity as well as the appropriate value of the linear slope have to be determined. Here, published density measurements of 7 chemically-distinct salt lake brines are compared with densities calculated by PHREEQC-3, confirming the applicability of PHREEQC's algorithm to salt lake brines, as well as to seawater brines and artificial brines from laboratory experiments. Further, calculations with PHREEQC-3 are used to assess the impact of mineral precipitation reactions during evaporative concentration. Results show that the density–TDS relationship is essentially linear over a wide concentration range, and that slopes range between 0.64 and 0.75, with the upper end of the range applying to Na–CO₃–Cl brines and the lower end to Na–Cl brines. Mineral precipitation of highly-soluble evaporate minerals such as halite and trona limit TDS, and may lead to considerable errors in coupled flow simulations based on a linear equation of state at high concentrations. Misrepresentation of the slope may lead to an error of up to 20% in the calculated length of the brine nose bordering a salt lake, or of the Rayleigh number, which indicates if a density stratification is stable or not.

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1. Introduction

Flow through geological media is influenced by the density and viscosity of the prevailing fluids. Groundwater density is a function of pressure, solute concentration and temperature (Diersch and Kolditz, 2002). This dependence is often described by a linear approximation of the equation of state for density:

$$\rho = \rho_0(1 + \gamma(P - P_0) + \alpha(\omega - \omega_0) + \beta(T - T_0)) \quad (1)$$

where ρ (M L⁻³) is the density, P is the fluid pressure (M L⁻¹ T⁻²), ω is the total dissolved solids concentration TDS (M L⁻³), T is temperature (K), γ is the fluid compressibility (L T² M⁻¹), and α (L³ M⁻¹)

and β (K⁻¹) are the solutal and thermal expansion coefficients, respectively (Diersch and Kolditz, 2002). The subscript 0 refers to the value of a parameter at the chosen reference state. For natural waters under isothermal conditions, and ignoring water's small compressibility (i.e., $\gamma = 0$), Eq. (1) reduces to:

$$\rho = \rho_0 + \alpha'\omega \quad (2)$$

where ρ_0 is the density of water at $\omega_0 = 0$ and α' is $\alpha \times \rho_0$ representing the slope of the equation of state (EOS). For seawater intrusion problems, Eq. (2) with $\alpha' \approx 0.71$ (when the density and TDS are expressed in g/L) is normally applicable (Langevin et al., 2007).

Adams and Bachu (2002) published several non-linear and linear expressions for the density of brines and NaCl solutions. They found that the relationship between measured density and salinity of water samples of brines from the Alberta Basin in Canada could

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be described using a linear regression of the data points. They also reviewed different algorithms that calculate brine density as a function of temperature, pressure and salinity, and noted that these underpredicted the measured density of brines at high salinity when other ions than Na^+ and Cl^- are present in significant amounts. This is because, depending on the relative proportions of the dissolved ions, different waters with the same TDS may have different densities due to the difference in mass and molar volume of the dissolved ions. For example, a CaCl_2 solution will have a higher density than a NaCl solution of the same TDS (Haynes, 2013). Empirical relationships based on NaCl -dominated solutions are therefore not expected to have generic applicability across the range of compositions of natural brines.

The selection of an appropriate equation of state for natural brines is thus not straightforward. Furthermore, the relationship between density and TDS in brines below evaporating salt lakes are confounded by the changing relative proportions of chemical components during evapoconcentration. This is related to the concept of chemical divides (Hardie and Eugster, 1970): As solute concentrations in a chemically closed system increase, mineral precipitation occurs and removes the constituent ions from the solution. The solute with a concentration-ratio that is lower in the solution than in the precipitate will decrease in concentration, while the remaining solutes increase in concentration as evaporation proceeds. As each solute influences the density in a different way depending on its partial molar volume and degree of hydration (Appelo et al., 2014; Millero, 2001), this may lead to a deviation from the linear relationship described by Eq. (2).

A number of algorithms exist that consider contribution of individual solutes to the density (see Appelo et al., 2014 and references therein for a recent overview). Monnin (1989), for example, presented a model for density calculation based on the ion-interaction approach by Pitzer (1979) that considers the major ions Na, K, Ca, Mg, Cl, SO_4 , HCO_3 , CO_3 and found that calculated densities compared well to measured densities of complex mixtures resembling Dead Sea waters up to ionic strengths of around 9. Marion (2007) presents an algorithm for calculating density and molal concentrations from molar data based on the Pitzer approach for density calculations. Millero (2001) described an algorithm that is based on the principle of additivity of the partial molar volumes of solute species. These partial molar volumes are calculated by the Redlich–Rosenfeld equation, which requires knowledge of the partial molar volume at infinite dilution, the Debye–Hückel limiting slope and the coefficients that describe the change of the molar volume with ionic strength (Appelo et al., 2014). The details of the algorithm and the fitting coefficients that describe the temperature dependence of its parameters are described in Millero (2001). The calculated density values have been compared with measurements of the density of seawater, estuaries and lagoons up to seawater ionic strength of 0.7. Recently, Appelo et al. (2014) published an algorithm based on a modified Redlich–Rosenfeld equation, which reduces the number of fitting parameters by using the Born equation to calculate the temperature dependence of the molar volumes at infinite dilution, and by constraining the limiting slope of the molar volume with ionic strength by differentiating the extended Debye–Hückel equation with respect to pressure.

These algorithms can be incorporated into numerical simulators of variable-density groundwater flow and solute transport, to study the potential feedbacks between chemical reactions and density-driven flow (e.g., Post and Prommer, 2007; Bauer-Gottwein et al., 2007). This, however, comes at a significant computational expense and in many instances a sufficiently accurate single-species simulation using a simple form of the equation of state for density as described by Eq. (2) would be preferable to avoid the complexities of simulating a comprehensive set of geochemical reactions. In modelling salt lake systems, which is

the focus of the present article, different slopes of the linear density function (Eq. (2)) have been applied. While there is abundant data on physical properties of single-salt solutions (e.g. Haynes, 2013), few studies have considered complex natural brines. Fan et al. (1997) used a coefficient of 0.756 taken from Cussler (1984) and Zimmermann et al. (2006) applied the value of 0.714 typical for seawater without providing references. Rogers and Dreiss (1995) defined a slope of 0.875 based on values of specific gravity and total dissolved solids from LADWP (1987).

Key metric attributes of numerical simulations of groundwater flow below salt lakes include the penetration of the brine toe into the freshwater part of the aquifer, and the critical Rayleigh number. This latter quantity determines the onset of free convection, i.e. the transition of a diffusion dominated stage to a convective phase of salt transport by density gradients (e.g., Simmons et al., 2001; Nield and Bejan, 1999). For groundwater below salt lakes, both the brine toe length and the Rayleigh number can be shown to be a function of $\Delta\rho = \rho - \rho_0$ (Duffy and Al-Hassan, 1988). From Eq. (2) it can be seen that the aforementioned range of slopes $0.714 < \alpha' < 0.875$ imparts an uncertainty in these parameters in the order of 20–25%.

A potential problem associated with the use of non-reactive numerical models of evapoconcentration in salt lake systems in combination with Eq. (2) is that these models may not properly capture the behaviour of the system as solute concentrations reach their solubility limits. As evapoconcentration progresses beyond the point where the most soluble minerals such as halite start to precipitate, TDS values asymptote with further evaporation because constituent ions transfer from the liquid into the solid phase. Failure to capture this behaviour may lead to an overestimation of TDS and, through Eq. (2), the groundwater density, which may in turn influence the simulated groundwater flow pattern through the coupled nature of variable-density flow problems (Diersch and Kolditz, 2002).

It is thus clear that an appropriate representation and parameterisation of the relationship between density and TDS is an important consideration for numerical modelling of aquifers interacting with salt lake systems and brines in general. The currently available literature provides no consensus on this aspect of the modelling process and the objective of the present study is to address this gap. Specifically, we assess the applicability of a linear equation of state for a range of natural brine compositions found beneath salt lakes, because for these environments reliable hydrochemical data are available for water compositions ranging from the initial freshwater to the highly mineralised brines formed by evaporation. First a comparison will be presented of the measured and calculated densities for different salt lake systems and holds for all brines within the investigated hydrochemical range including seawater brines and artificially brines from laboratory experiments. Secondly, the measured densities will be compared to calculated values based on geochemical codes that simulate the hydrochemical evolution of inflow water subject to evaporation and salt precipitation. Finally, based on these results, a set of simple guidelines are provided for incorporating evaporation-induced density variations in non-reactive solute transport models of groundwater systems below salt lakes.

2. Methodology

For this study a set of 273 water samples from 7 different locations spanning a wide range of hydrochemical conditions were compiled from the literature (Table 1; Fig. 1). All hydrochemical simulations were performed with PHREEQC-3, which calculates the density based on the algorithm proposed by Appelo et al. (2014). All simulations were carried out using the Pitzer.DAT database of PHREEQC-3.

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