A Numerical Method for Predicting Thermophysical Properties of Complex Chloride-Dominated Brines

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ABSTRACT

Complex aqueous solutions containing high concentrations of chloride ions are found throughout nature. Examples include seawater and geothermal brines. Accurate models of the thermophysical properties of such solutions are needed for numerous scientific and engineering disciplines; in particular, applications associated with geothermal energy and the oil and gas industry. Often however, it is either impossible or overly computationally taxing to determine the properties of such complex aqueous solutions from first principles considerations.

Instead, numerous tables and functions exist to empirically determine the properties of single-salt solutions or predefined mixtures. In general, such properties are expressed as a function of solute mass fraction. However, more descriptive models are needed that are capable of determining the thermophysical properties of fluids of arbitrary chemical composition.

Ideally, the model should be able to calculate the properties of aqueous solutions based on a consideration of the contributions of key aqueous components; it should contain fitting parameters that are easy to solve for new aqueous species; and the model should be easy to implement and extrapolate well. In this paper, we discuss a model that achieves these goals by deriving physical properties based on correlations at the ionic level, and accounting for the chloride-dominated nature of the brine.

1. INTRODUCTION

The behaviour of geothermal systems is intimately linked to the thermodynamic and fluid mechanical properties of subsurface brines. These thermophysical properties not only depend on the fluid's temperature and pressure, but also its chemical composition. Particularly as we venture deeper and explore new options for geothermal resources (such as mineral co-production and energy storage), the brines encountered become increasingly concentrated and complex in composition (D'Amore et al 1998, Michard et al 1996).

Thus there is a need to understand the thermophysical properties of complex aqueous solutions when modelling geothermal systems. However, it may be difficult or computationally taxing to determine the properties of such complex aqueous solutions from first principles considerations. Instead, we often rely on pre-existing empirical relationships to describe this behaviour. The difficulty with using such models is that they typically focus on single salt solutions, or solutions with only a few predefined components. In many cases, more comprehensive models are required that can represent the physical properties of fluids with arbitrary chemical composition.

In this paper, we outline such a model, and describe how the accuracy might be improved by focusing on a particular subset of aqueous solutions – namely chloride dominated brines. In doing so we build on previous work by Laliberte (2007,2009), who collated an open source database of around 6600 experimental data points for heat capacity, 10,700 points for viscosity and 16,300 for density, then established empirical expressions for thermophysical properties of 129 different salt solutions with a mixture model to combine these solutions. Other studies have also built empirical libraries describing the relationships between aqueous solutions of predefined salt solutions. Examples of this approach can be found in the work of Sharqway and co-workers (Sharqawy et al., 2010a, Sharqawy 2013) who collated and updated empirical expressions for the thermophysical properties of seawater, and that of Bell et al. (2014), who incorporated a similar database of expressions into the open-source thermophysical property library Coolprop.

Rather than employ a pre-existing set of pre-defined salt solutions, we instead define empirical mixture rules for thermophysical properties derived from the contributions from key aqueous components. In the sections below, using the heat capacity as an example, we outline our approach and compare it to Laliberte's original model and experimental data. The approach allows for integration of new experimental data from a range of different sources, and, importantly, provides a more consistent framework for predicting solution properties.

2. MODEL DESCRIPTION

Laliberte's original formulations are based on a consideration of the relative mass fraction of dissolved salts in solution (Laliberte 2007,2009). The approach uses empirically fitted laws for the heat capacity, viscosity and density of the solutions. For heat capacity (which we will focus on in the present paper), the salt solutions are fitted with an empirical model of the form:

$$Cp_{aq} = w_w Cp_w + w_s Cp_s$$

where Cp_{aq} is the heat capacity of the aqueous solution, Cp_w is the heat capacity of deionized water, w_w is the water mass fraction, w_s is the salt mass fraction, and Cp_s is the contribution to the heat capacity from the salt in solution, given by

$$Cp_s = a_1 \exp(a_2 t + a_3 \exp(0.01\, t) + a_4(1 - w_w)) + a_5(1 - w_w)^{a_6}$$

where $a_1 \dots a_6$ are empirical constants fitted to each single salt solution, and t is the temperature in Celsius.

The model may be extrapolated to more complex brines by employing mixture rules of the form:

$$Cp_m = w_w Cp_w + \sum_s w_s \, Cp_s$$

where w_s is the salt mass fraction, and Cp_s is the contribution to the heat capacity from each of the salts in solution.

Laliberte's approach is simple and effective for many aqueous solutions. In particular, it is capable of representing the behaviour of solutions of single salts to high degrees of accuracy, and as Laliberte demonstrates, it is also effective at capturing the behaviour of much of the published experimental data on multiple salt solutions.

However, this approach does have a slight disadvantage when it comes to more complex aqueous solutions – namely the formulation is ambiguous when defining the properties of solutions with more than one salt. To see this consider an aqueous solution with two distinct salts: for example, NaCl and KBr, in equal concentration. Under Laliberte's formulation, the heat capacity may be expressed as:

$$Cp_{NaCl,KBr} = w_w Cp_w + w_{NaCl} Cp_{NaCl} + w_{KBr} Cp_{KBr}$$

However, the thermophysical properties can also be expressed as the product of a conjugate set of salts: NaBr and KCl as

$$Cp_{NaBr,KCl} = w_w Cp_w + w_{NaBr} Cp_{NaBr} + w_{KCl} Cp_{KCl}$$

Though these expressions are similar in form, the contribution from the solute to the heat capacity can differ significantly as shown in Figure 1.

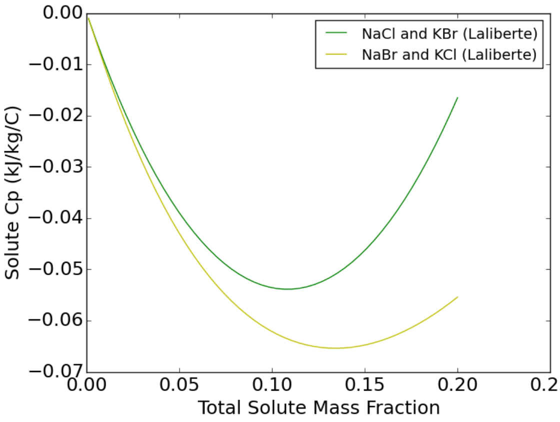


Figure 1: A comparison of solute contribution to the heat capacity from aqueous solutions with NaCl and KBr (green line), and KCl and NaBr (yellow line) in equal molarity following Laliberte (2009).

While this ambiguity is most easily demonstrated (and it's effect is strongest) in solutions comprising salts of equal molar concentration, it should be noted that it is also encountered in solutions with differing molar amounts of salts. Any aqueous solution created with salts AB & CD, can instead be expressed as a combination of three salts: AD, CB and AB (or CD – whichever has the greater concentration in the original solution), or indeed as a mixture of all four of the original salts. This can be used to check the accuracy of the empirical expressions derived in the Laliberte paper against salt solutions comprising mixtures of conjugate salts.

In Figure 2, for example we plot the difference in the heat capacity predicted for binary salt mixtures and their conjugate pairs.

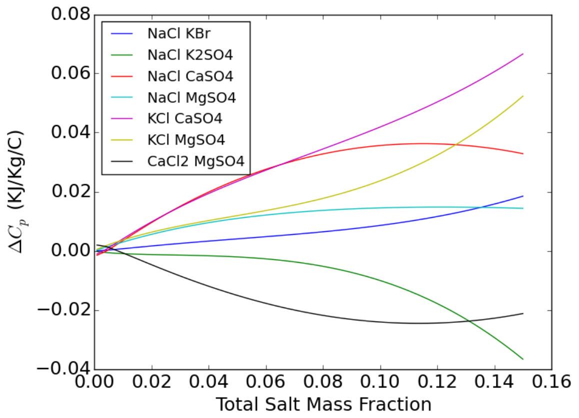


Figure 2: Plot showing the difference between the predicted heat capacities of binary salt solutions and those of their conjugate pairs using Laliberte's formulation.

The ambiguity in a salt-fraction based formulation stems from the fact that it is over determined. By introducing parameters for every single-salt-solution the empirical law over fits the available data. The ambiguity can be avoided by instead expressing the thermophysical properties as a function on the elemental composition of the aqueous solution. This removes the dependence on the origin salts of the thermophysical properties of the aqueous solution.

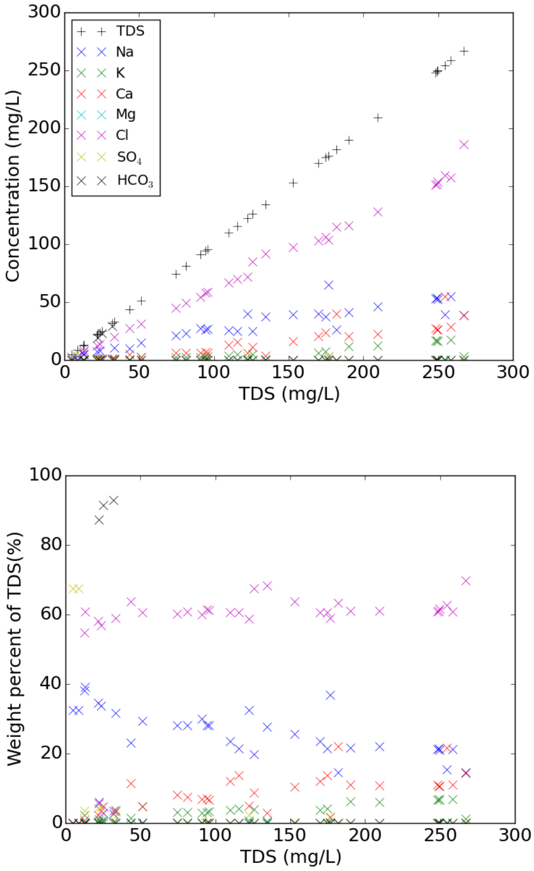
A similar approach was employed by Wang and coworkers (Wang and Anderko, 2008, 2012), who derived empirical relationships for a range of thermophysical properties based on the speciation of each solution. However, the majority of these properties are recorded in a proprietary library, preventing widespread use, and in many cases rely on empirical relationships based on cross-species interactions (i.e. between pairs of aqueous components). Moreover, because the relationships are derived for individual aqueous species, they are necessarily tied to a single speciation routine and accompanying database. The latter constraint in particular makes it difficult to extend the library without extensive testing to compare the properties of every species against every other previously tested combination.

Nevertheless, such an approach is advantageous for complex brines as it allows for estimation of thermophysical properties based solely on their composition. This is increasing necessary as we consider the more complex geothermal brines encountered at depth (Walsh et al 2017). As noted by Hu (2004, 2005), there is a need for practical means for accurately predicting the physical properties of such fluids without overly numerically-taxing computational methods.

To achieve this, we adopt an approach similar to Laliberte, in that we assume that the thermophysical properties can be represented through mixture models of the form:

$$Cp_m = w_w Cp_w + \sum_e w_e \, Cp_e$$

where w_e is the element mass fraction and Cp_e is the contribution to the heat capacity from each of the elements in solution. The key difference is that the formulation is based on the elemental mass fraction rather than that of the dissolved salts. The contributions from the individual elements to the heat capacity are once again fitted with empirical rules similar to those of the salt components. In this way the formulation avoids any ambiguity in the definition of the heat capacity for fluid mixtures.



a)

b)

Figure 3: Reported compositions of geothermal brines from various locations around the globe ordered according to the total dissolved salt (mg/l): a) absolution concentrations; b) relative concentrations as a proportion of the overall dissolved salts. Data from D'Amore et al. (1998); Bath et al. (1996); Edmunds et al. (1980), Gizaw (1996); Helgeson (1968); Hendenquist, (1990); Lippmann et al. (1999); Manning et al. (2007); McKibben et al. (1987); Michard et al. (1996); Regenspurgetal.,2010); Sanjuan et al., (2010); and Williams and McKibben (1989).

This approach introduces a single independent degree of freedom associated with a reference element. The choice of element allows the empirical model to be adjusted to preferentially fit aqueous solutions with predetermined compositions. Notably, chloride dominated brines are common in geothermal operations. Many geothermal brines are well approximated as mixtures of NaCl, KCl, $CaCl_2$ and $MgCl_2$ salts, with chloride the most prevalent anion. Moreover, as illustrated in Figure 2 (which plots elemental concentrations from geothermal brines sampled from around the globe) for all but the most dilute geothermal brines the chloride concentration is a remarkably constant fraction (around 60%) of the total dissolved salts. For this reason, we fix the contribution from chlorine to zero in the analysis of thermophysical properties. This has the effect of improving the accuracy of the empirical model for single salt solutions with chloride salts and chloride-dominated aqueous mixtures.

It should be noted that similar strategies are employed elsewhere in geochemical analysis. The B-dot model of ionic strength, for example, is most appropriate for brines with high NaCl concentrations (Helgeson 1969). Likewise, the same strategy of zeroing out the contribution from one species is also used with Riedel's approach for determining thermal conductivity, though in that case it is the contribution from sodium that is set to zero (Riedel 1951).

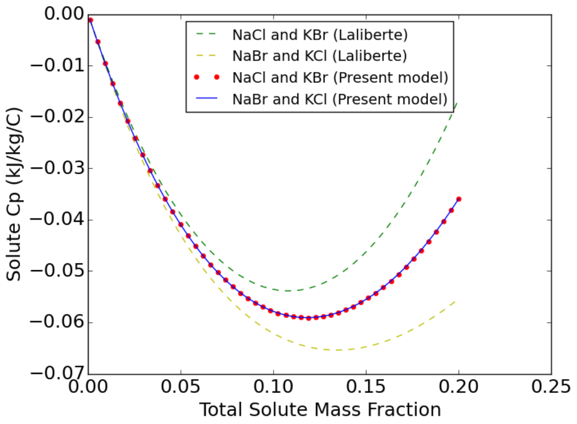


Figure 4: A comparison of solute contribution to the heat capacity from aqueous solutions with NaCl and KBr, and KCl and NaBr in equal concentrations. The heat capacity calculated with the Laliberte (2009) formulation (yellow and green dashed lines) is compared with the present approach (blue line and red dots).

3. COMPARISON OF MODEL RESULTS

In this section we compare results from the present model with those from chloride dominated brine mixtures.

In Figure 4, we repeat the analysis given earlier in Figure 2, but with the present formulation. The resulting curve is bounded by the two formulations from the salt-fraction based model. As expected, the elemental model predicts the same heat capacity regardless of the salt origins.

Figure 5 compares predicted heat capacities for aqueous NaCl solutions with experimental data provided in the Laliberte Database. As with Laliberte's original formulation there is an excellent fit between the experimental solution and the empirically fitted result.

Figure 6 provides a comparison between the calculated heat capacity for seawater (based on a three salt solution) and that given by the MIT seawater model (as implemented in Coolprop by Bell et al. 2014). There is remarkable consistency between the two formulations, in particular as the present model is derived from a consideration of the elemental composition, that is based on a three-salt "synthetic" sea water analogue.

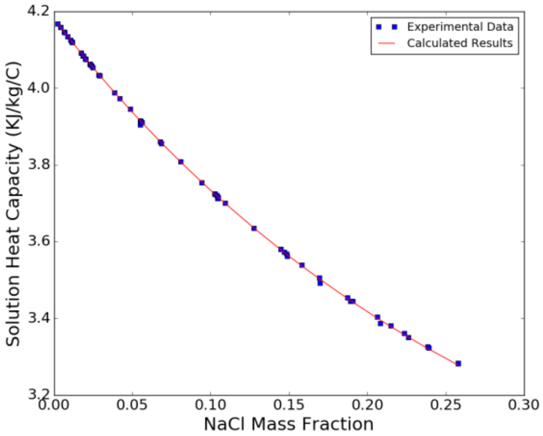


Figure 5: A comparison between experimentally measured (blue dots) and predicted (red lines) heat capacities for NaCl solutions.

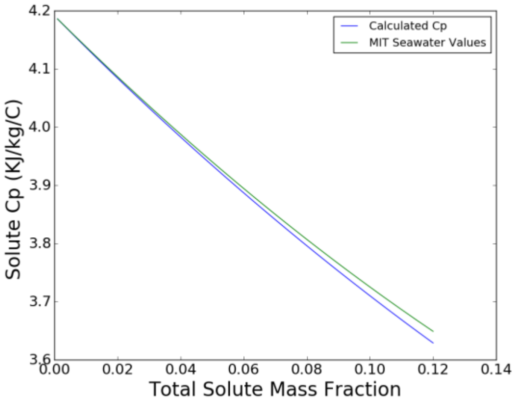


Figure 6: The heat capacity given by the MIT seawater model and that predicted using the present approach.

4. CONCLUSION

There is a growing need to form accurate models that can simulate the themophysical properties of complex aqueous solutions in geothermal systems. This is particularly true, as we look to deeper sources of geothermal power with in situ brines that are less affected by mixing with surface waters. However, these models can be difficult to come by for arbitrary aqueous solutions as most empirical thermophysical models are tailored around the properties of predefined salt mixtures.

In this paper, we have briefly outlined a strategy for obtaining the thermophysical properties of complex brines through a consideration of their chemical composition. The approach is based on a similar set of models originally developed by Laliberte, but uses a formulation based on individual element concentrations. This creates an unambiguous expression for the physical properties, and allows the model to be tailored to specific classes of aqueous solutions (eg. chloride-dominated brines).

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