

MODELS OF SUBSURFACE ROCK-WATER PROCESSES AFFECTING FLUID FLOW

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ABSTRACT

The TEQUIL rock-water interaction models (MOLLER et al., 1998) developed at UCSD include most of the solution species necessary to describe the saturation status of hydrothermal fluids for the temperature, pressure, and concentration (TPX) conditions encountered in natural and enhanced geothermal systems (EGS). Important solutes not incorporated are the various hydrolysis products of the Al^{3+} ion. These are needed to predict the chemical behavior of hydrothermal fluids in contact with aluminosilicate minerals, which are found throughout the earth's surface and crust.

The aqueous chemistry of aluminum is extremely complicated. The species in solution include mononuclear (e.g., $Al(OH)_n^{(3-n)+}$, $n = 0 - 4$) and polynuclear (e.g., $Al_{13}O_4(OH)_{24}^{7+}$) aluminum ions and neutral species. Recently, great progress has been made measuring the thermodynamic properties of the mononuclear species in the aluminum-water system. However, the data base for modeling the polynuclear species is far from complete. In this article, using an approximate model, we show that polynuclear aluminum species are not expected to be present in high concentration in hydrothermal fluids that are in near chemical equilibrium with the mineral phases commonly present in reservoir formations. This finding is important for interpreting the data used in the model parameterization. It also indicates that we can develop a highly accurate hydrothermal fluid model containing only mononuclear aluminum solution species for rock-water applications. Our initial efforts to model the aluminum-water system up to 125°C are reported. Results show that the modeling phenomenology we have developed can predict the complicated chemical behavior of this system with accuracies near that of the experimental data.

INTRODUCTION

The successful enhancement of fluid flow in high temperature, low permeability reservoirs (EGS) would significantly advance geothermal energy as an economically competitive contributor to the nation's energy supply. However, progress in this approach is limited by insufficient knowledge about the

subsurface rock-water chemical processes controlling fluid flow in high temperature formations. The purpose of our research is to provide new modeling technologies that accurately characterize the reservoir rock-water chemistry of EGS systems. An initial objective is to construct an accurate variable temperature (0-250°C) model of the H-Na-K-Al-OH-Cl-H₂O system to add to our TEQUIL models that include the aqueous chemistry of silica. This model will adapt the Pitzer (PITZER, 1987) liquid density free energy representation to the complicated chemistry of the aluminum system. When completed, it will be the first model that can accurately calculate the activities of aluminum species in hydrothermal fluids to high concentration and temperature. Our suite of solution models will then include the components necessary to describe the interaction of many hydrothermal minerals (e.g., those compiled in the report of Browne (BROWNE, 1978)) with formation fluids. This model will provide an important tool for understanding the behavior of hydrothermal systems and EGS applications. It will be made available to many users via our web site, geotherm.ucsd.edu.

METHODOLOGY

The temperatures addressed in the model discussed here are below the critical temperature of aqueous natural fluid mixtures. The pressures considered are along the aqueous mixture saturation line. Although pressure can also affect equilibria under these TPX conditions, the largest variation of the solution free energy comes from changes in X and T (e.g., changes in pH, mineral/solution and solution/gas solubilities, etc.). In order to provide the highest accuracy, we have tailored our selection of equations of state to reflect the important properties of each phase in this TPX range. The aqueous phase activities are based on the solution free energy equations introduced by Pitzer (PITZER, 1987). An ideal mixture or mixing equation of state is used for the vapor phase.

The equilibrium compositions of all the phases in the system can be found by minimizing the free energy of the total system for constant T and P subject to the conditions of conservation of mass and charge balance for each solution phase (HARVIE et al.,

1984). The chemical potential (activity) of each species in a solution phase is given by,

$$\mu_i = \mu_i^o + RT \ln \gamma_i m_i, \quad (1)$$

where μ_i^o is the standard chemical potential of species i , usually referred to infinite dilution. γ_i is the activity coefficient for species i , and m_i is the molal concentration. The Gibbs free energy may be written in terms of the chemical potentials as,

$$G = \sum_{\text{species}} \mu_i n_i. \quad (2)$$

n_i is the number of moles of species i and the sum is over all species (HARVIE et al., 1984).

Theoretical results can provide general guidance as to the form of the expression used for μ^o and γ as a function of TPX (e.g., the equation of state, EOS). However, to achieve the accuracy needed in geochemical applications it is necessary to adjust parameters in the EOS to obtain agreement with experimental data.

The range and variation in solution composition encountered in possible EGS applications is very large. Formation waters with ionic strengths up to ≈ 10 m have been reported (SHVARTSEV and BUKATY, 1995; WHITE et al., 1963). Values of pH can vary from 0.4 (WHITE et al., 1963) to 10.0 (HENLEY and ELLIS, 1983; WHITE et al., 1963). The ability to provide accurate chemical predictions for such large composition variation is a requirement of the phenomenology that we are developing.

Aqueous solutions models usually begin with a Debye-Huckel ionic strength dependent contribution, ($\ln \gamma_{DH} = -A_\gamma |z_+ z_-| I^{.5} / (1 + I^{.5})$), which provides reasonable predictions for very low ionic strength solutions ($I \approx .01$ m). To treat higher ionic strengths, it is necessary to account for specific ion interactions.

In the model we are developing, our (HARVIE and WEARE, 1980; HARVIE et al., 1984; WEARE, 1987) implementation of the Pitzer activity expressions for the aqueous solution phase is used. Because this formalism is based on the excess free energy, all the activity expressions are consistent, allowing different kinds of data (e.g., osmotic, e.m.f., and solubility measurements) to be used in the parameter evaluations. These equations have been given in many publications. Here, we give only the activity coefficient expression for the interaction of cation, M , with the other solute species.

$$\begin{aligned} \ln \gamma_M = & z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \\ & \sum_c m_c (2\Phi_{Mc} + \sum_a m_a \psi_{Mca}) + \\ & \sum_a \sum_{a' < a} m_a m_{a'} \psi_{Maa'} + |z_M| \sum_c \sum_a m_c m_a C_{ca} \\ & + \sum_n m_n (2\lambda_{nM}) + \sum_n \sum_a m_n m_a \zeta_{naM} \end{aligned} \quad (3)$$

$$\begin{aligned} F = & -A^\phi \{ I^{.5} / (1 + 1.2I^{.5}) + \\ & (2/1.2) \ln(1 + 1.2I^{.5}) \} \\ & + \sum_c \sum_a m_c m_a B'_{ca} + \sum_c \sum_{c' < c} m_c m_{c'} \Phi'_{cc'} \\ & + \sum_a \sum_{a' < a} m_a m_{a'} \Phi'_{a,a'} \end{aligned} \quad (4)$$

$$\begin{aligned} B_{ma} = & \beta_{Ma}^0 + \beta_{Ma}^1 g(\alpha, I^{.5}) + \beta_{Ma}^2 g(12I^{.5}), \\ g(x) = & 2(1 - (1+x)e^{-x}) / x^2, \\ \Phi_{ij} = & \Theta_{ij} + {}^E \Theta_{ij}(I), Z = \sum_i |z_i| m_i \end{aligned} \quad (5)$$

This expression is symmetric for an anion. The B coefficients describe the ionic strength dependence of binary solutions. When either the cation or anion for an electrolyte is univalent, we set α equal to 2.0 and omit the $\beta^{(2)}$ term. For 2-2 or higher valence pairs, $\alpha = 1.4$. In addition the $\beta^{(2)}$ term accounts for the increased tendency of these higher charged species to associate in solution. When strong ion association is present (e.g., HCO_3^-) the ion pair species must be added to the species list (HARVIE et al., 1984). The ionic strength dependence of the ternary mixing coefficients is found in the Φ terms, which account for mixing between two ions of like charges. In Φ_{ij} , Θ_{ij} is the only adjustable parameter. The ionic strength dependent ${}^E \Theta_{ij}(I)$ term accounts for electrostatic unsymmetric mixing effects that depend only on the charges of ions i and j and the total ionic strength. The terms with λ and ζ account for neutral species interactions with anions and cations (FELMY and WEARE, 1986). In this model the third virial coefficients, C , and the ψ terms, are independent of ionic strength. All these parameters are adjusted to fit the available data in binary and ternary systems using a non-linear least squares method (HARVIE et al., 1987). We note that only binary and ternary data are required to evaluate all the parameters in the Pitzer equations described here no matter how many components are in the solution. This formalism, Eqs. 3-5, therefore, provides a means to extrapolate data from ternary and lower systems to systems of higher order. We (CHRISTOV and MOLLER, 2004; HARVIE et al., 1984) have shown that these equations can provide solubility predictions for a range of ionic strengths that include most of the compositions found

in nature. Temperature dependence (MOLLER, 1988; MOLLER and GREENBERG, 1989; CHRISTOV and MOLLER, 2004) of the solution parameters is built into the model by adjusting selected constants in the following equation,

$$\text{parameter}(T) = a_1 + a_2T + a_3(T^2) + a_4(T^3) + a_5/T + a_6 \ln T + a_7(1/(T-263)) + a_8(1/(680-T)). \quad (6)$$

This equation is consistent with the temperature dependence reported by other workers both for heat properties and free energy properties.

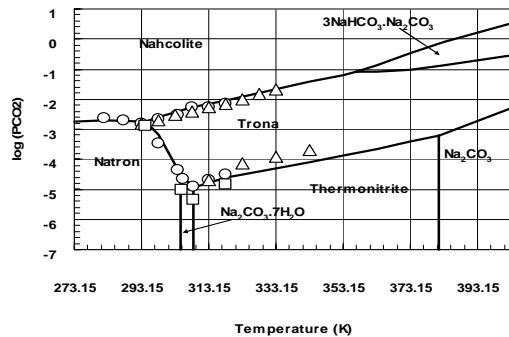


Figure 1

Fig. 1 above and Fig. 2 below illustrate that our modeling strategy has the capability of calculating the solubilities (Fig. 1: solubility of carbonate minerals as a function of CO_2 and T) and weak acid/base properties (Fig. 2) in hydrothermal fluids (solid lines are model predictions; symbols are experimental data).

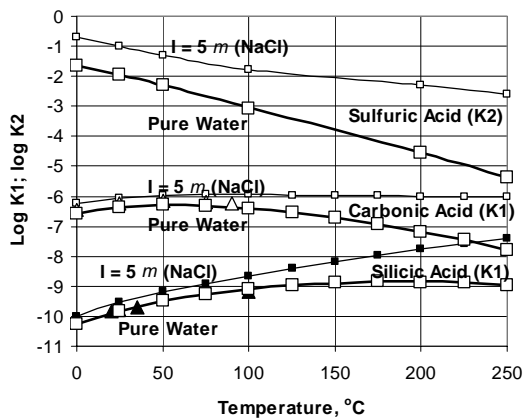


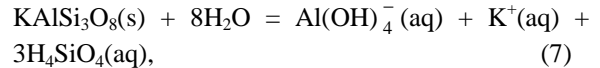
Figure 2

DEVELOPMENT OF THERMODYNAMIC MODEL FOR ALUMINUM

Aluminosilicate minerals are found throughout the earth's surface and crust (commonly as feldspars; e.g., alkali feldspar, $\text{Na/KAlSi}_3\text{O}_8$) in metamorphic and igneous rock (DEER et al., 1966), as clays in well-weathered soils (DRISCOLL and SCHECHER, 1989) and as authigenic constituents of evaporites

(KASTNER, 1971)). The ability to correctly model the solubility of these minerals as a function of fluid composition and temperature is critical to understanding the formation and evolution of rock- and soil-forming minerals and flow properties such as reservoir permeability in hydrothermal systems.

The condition determining equilibrium between a mineral phase and a solution phase can be written in terms of a free energy balance equation. For example, for the dissolution of K-feldspar ($\text{KAlSi}_3\text{O}_8(\text{s})$) via the reaction,



this free energy condition leads to the equation,

$$\Delta G_f(T, P)(K - \text{spar}) = \mu_{\text{Al}(\text{OH})_4^-} + \mu_{\text{K}^+} + 3\mu_{\text{H}_4\text{SiO}_4} - 8\mu_{\text{H}_2\text{O}}. \quad (8)$$

$\Delta G_f(T, P)$ is the free energy of formation of K-spar. In order to use this expression to determine the solubility status of the K-spar mineral, we need models for the chemical potentials or activity coefficients of the species in solution. In our prior work we have developed TPX dependent model parameterizations for all the species (see, for example, Fig. 1) in Eq. (8) except $\text{Al}(\text{OH})_4^-(\text{aq})$. The activity of this species is a function of TP and all the composition variables in the solution.

The aqueous chemistry of aluminum is highly complicated. Thermodynamic and spectroscopic evidence for several mononuclear (MN) hydrolysis products (e.g., $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$, and $\text{Al}(\text{OH})_4^-$) has been reported. Less well defined polynuclear (PN) hydrolysis species (e.g. $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ or $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$) have been proposed to explain data in concentrated aluminum solutions in certain pH ranges (BAES and MESMER, 1986). Experimental data available for parameterization in the high and low pH region include osmotic, potentiometric and solubility measurements. In the near neutral pH region, most commonly encountered in hydrothermal systems, the low solubility and complex solution chemistry of aluminum have made the determination of activity and formation constants of the various aluminum solutes difficult. However, recent advances in potentiometric titration methods and in determining effective formation constants for aluminum speciation reactions via solubility studies of aluminum (oxy)hydroxide minerals are now providing the data needed to characterize the thermodynamics of Al^{3+} and its mononuclear hydrolysis products. The data base available defining the activities of the polynuclear hydrolysis products on the other hand is still very incomplete.

The role of polynuclear aluminum species

Since the data required to define a high accuracy model including PN species is not available, a first step in the development of a model for natural water applications is to determine the composition ranges where these species do not play an important role. Obviously, the model we develop using only the well determined MN species will produce highly accurate predictions only for hydrothermal solutions with these compositions.

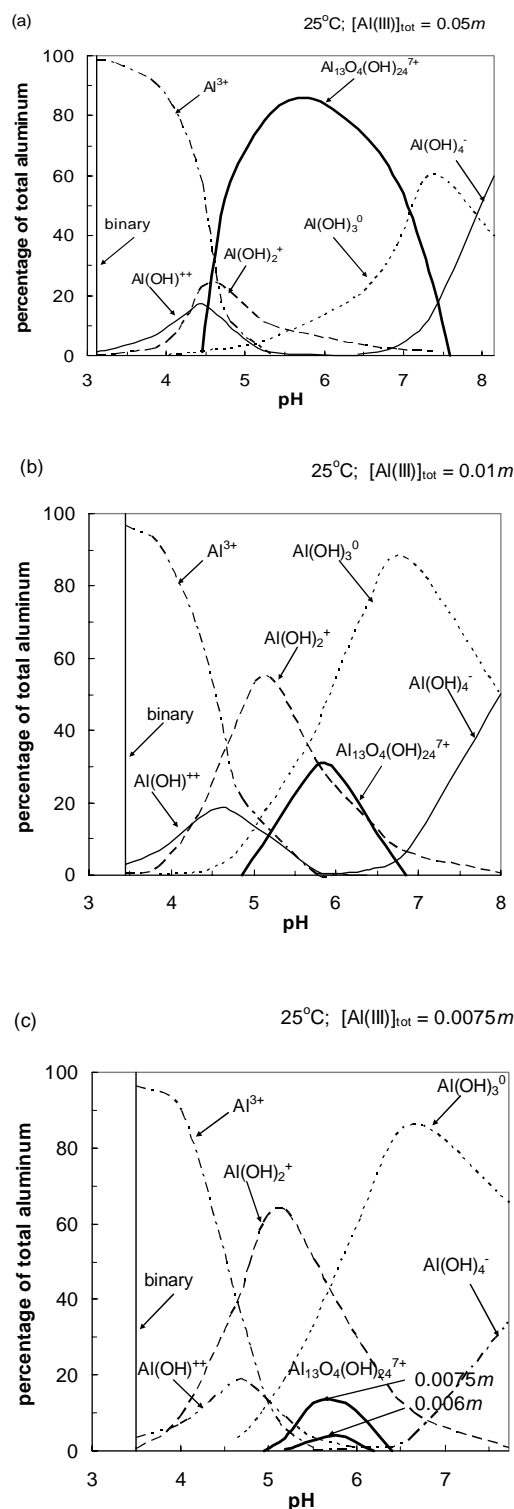
For our modeling effort there is an additional problem. The stoichiometry of the PN species suggests that they will be more important at high aluminum concentrations and high OH^- concentrations. In the high and low pH region we rely heavily on high aluminum concentration data to evaluate parameters in our model. If PN species are important in these solutions, it would be necessary to take them into account in the data analyses. With the present understanding of the aluminum system this would be difficult to do.

Because of the possible nonlinear hydrolysis effects at high aluminum and OH^- concentrations and the competition of the various solution species for Al^{3+} and OH^- , it is difficult to estimate aluminum speciation in solution without a computational model. Fortunately, enough data has been reported to allow the development of an *approximate* model including both the MN and PN species.

To test the impact of neglecting PN species in our high accuracy model and data analyses, we constructed an approximate model at 25° and 100°C using the concentration products for Al^{3+} hydrolysis and polymerization reactions ($\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ or $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$) taken from Baes and Mesmer (BAES and MESMER, 1986) and Furrer et al. (FURRER et al., 1992). Examples of the predictions of this model for 25°C (where the approximate model is better determined) are given in Fig's. 3a-c below. In these figures, the pH of a binary $\text{AlCl}_3\text{-H}_2\text{O}$ solution has the pH indicated by the line marked binary. The graphs are made by titrating these solutions with base to obtain the speciation for higher pH solutions predicted by the model.

There are several important observations to make about the results illustrated in Fig's. 3a-c. First, the $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ species, which is the only PN species that appears in significant concentrations, can play a dominant role in the pH range from 4.5 to 7.5, at total aluminum concentrations above about 0.01 m. (see Fig's. 3ab). Since most natural waters have pHs in the intermediate pH range (4-8), this would suggest

that it is necessary to include this species in a model for hydrothermal applications. However, we note from Fig. 3c that as the amount of total aluminum in solution decreases the model predicts that the concentration of this PN is quite low (e.g., $\text{PN} < 9\%$; see the solid line in the 5 to 6 pH range).



Figures 3 a-c

For applications in which the formation water is in near chemical equilibrium with formation minerals, the neglect of polynuclear species is justified because the solubility of the hydroxide minerals, such as gibbsite and kaolinite, common to most hydrothermal reservoir keeps the total concentration of aluminum very low ($<10^{-5} m$) (NORDSTROM, 1982). For these solutions, the PN concentration is negligible.

For acid mine and volcanic waters, which can have low pH values (BIRD et al., 1989; ROCHELLE et al., 1989; WHITE et al., 1963), and carbonate rich waters, which can have high pH values (WHITE et al., 1963), the concentration of aluminum can become quite high (WHITE et al., 1963). The stoichiometry of the species, $Al_{13}O_4(OH)_{24}^{7+}$ is also high in OH. Therefore, at low pH, the low OH concentration destabilizes this species as illustrated in the low pH region of Fig's. 3a-c. At high pH, the dominant species is the MN species $Al(OH)_4^-$ for which we have data.

These results at 25°C suggest that an accurate model of aluminum speciation using only MN species can be developed and has wide application to formation water problems. In Fig. 4 the results of a similar (but less well defined) model at 100°C are reported. For this temperature, the aluminum concentration at which the PN species become important is higher than for 25°C, supporting the use of a model containing only MN species for high temperatures.

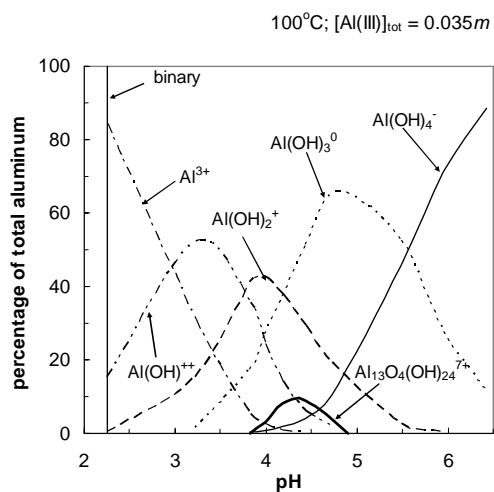


Figure 4

Development of a high accuracy aluminum speciation model (MN only):

Our development of a high accuracy model begins with aluminum speciation in low pH aqueous sodium chloride solutions. For these solutions we assume the only solutes are H, Na, Al and Cl, as justified by Fig's. 3a-c and 4. We used e.m.f., osmotic and solubility data in the literature and unpublished e.m.f.

data (Andrew Dickson) to establish temperature functions for the binary interaction parameters β^0_{AlCl} , β^1_{AlCl} , and C^0_{AlCl} and the ternary mixing parameters θ_{AlNa} , θ_{AlH} , ψ_{AlHCl} and ψ_{AlNaCl} . An example of this model's agreement with solubility data for solid $AlCl_3 \cdot 6H_2O$ in the low pH region is given in Fig. 5. Having established these parameters in the low pH regions, they are used for all compositions in the model.

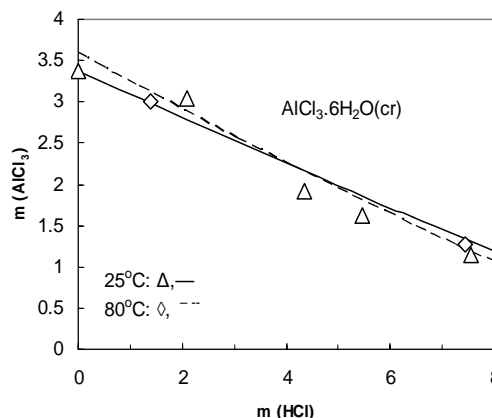


Figure 5

The complex aqueous chemistry of aluminum and its low solubility in the near neutral region common to natural systems have made model development difficult. However, recent advances in determining molal equilibrium quotients as a function of composition for aluminum speciation reactions via solubility studies of aluminum (oxy)hydroxide minerals (e.g., gibbsite $Al(OH)_3(cr)$; boehmite $AlOOH(cr)$) and potentiometric titration are now providing the data needed to characterize the activities of Al^{3+} and its MN hydrolysis products in this difficult region (BENEZETH et al., 1997; BENEZETH et al., 2001; BOURCIER et al., 1993; CASTET et al., 1993; PALMER et al., 2001; PALMER and WESOLOWSKI, 1992; PALMER and WESOLOWSKI, 1993; WESOLOWSKI, 1992; WESOLOWSKI and PALMER, 1994).

Using these data and the acid-side parameterization described above, we constructed a Pitzer ion interaction model of aluminum speciation (Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$ and $Al(OH)_4^-$) in H-Na-Al-OH-Cl- H_2O solutions ($NaCl \approx 0-5m$) as a function of pH and temperature from 0° to 125°C. In Fig. 6 the agreement of the model with the observed aluminum hydrolysis quotients (WESOLOWSKI and PALMER, 1994) as a function of NaCl concentration and temperature is reported. In Fig's. 7ab, the predicted distribution of aqueous aluminum species as a function of pH in $10^{-7}m$ $AlCl_3$ solutions at 25° and 90°C is shown. Note the movement of the hydrolysis reactions to lower pH with temperature. With small exceptions, the model predictions are in

good agreement with the hydrolysis curves estimated from experimental data (e.g., Castet et al., 1993).

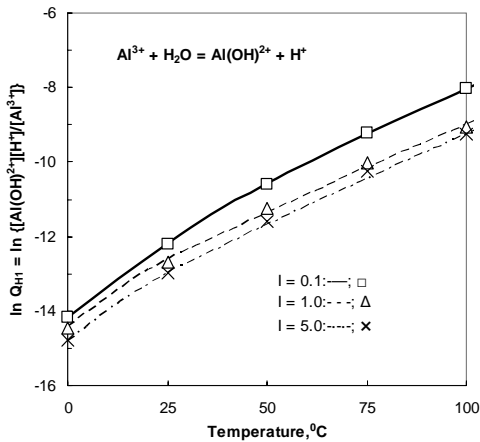
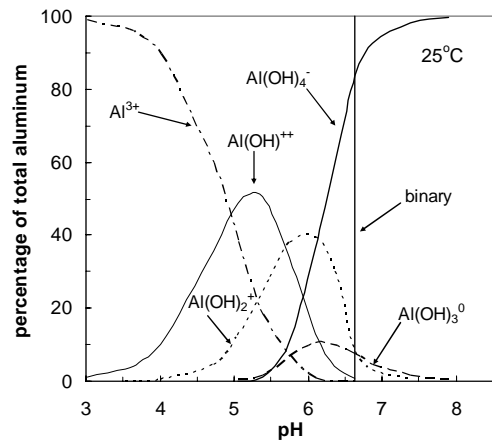
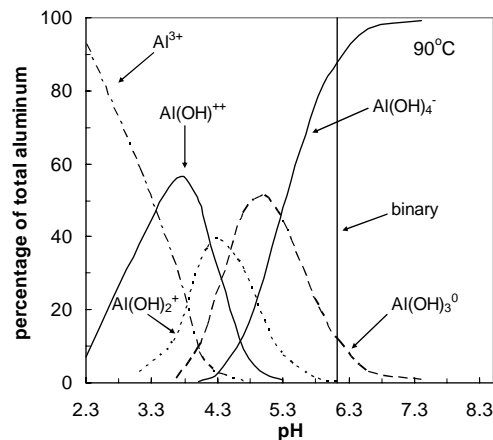


Figure 6

(a)



(b)



Figures 7ab

SUMMARY

Using an approximate model based on “best possible” estimates in the literature of equilibrium constants for polynuclear and mononuclear aluminum hydrolysis species, we demonstrate that for applications to hydrothermal fluids near chemical equilibrium with reservoir rocks a chemical model based only on mononuclear species should provide a very accurate description of the reservoir chemistry. Based on this assessment, a Pitzer type model has been constructed using only mononuclear species. This model accurately reproduces the data for aluminum speciation in high concentration aqueous NaCl solutions to high temperature. This is the first model to summarize these data. The results reported in Fig. 6 demonstrate that our modeling strategy is capable of very accurately representing existing data. The theoretical structure of the model, Eq’s. 3-4, and our experience with other systems suggest that use of this parameterization in much more compositionally complicated hydrothermal fluids will produce a highly accurate model of the solubility status of hydrothermal minerals for EGS applications.

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