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## Considerations about the building of a thermodynamic database for the chemical description of highly saline systems

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### Abstract

Amongst the existing models able to describe highly concentrated aqueous systems and solid-liquid or gas-liquid equilibria up to elevated temperatures and pressures, the semi-empirical Pitzer model has been shown to be powerful. Calculation codes are now available for applying this model to such complex natural and industrial systems. The key point remains the building of related thermodynamic databases of high quality. In this work, we present elements of a strategy to build and extend such a database for widespread use.

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*Keywords:* Saline systems; Pitzer model; Thermodynamic database; Parameter estimation; Ion-pairing

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### 1. Introduction

More and more attention is paid to the description of brine chemistry for various reasons. Natural brines can constitute interesting reserves for valuable chemical elements or chemical products such as lithium, potash, and other various salts. In some instances they are considered as cumbersome by-products of industrial processes or resulting from the exploitation of the subsurface (examples can be found in the context of CO<sub>2</sub> geological storage). Besides, the context of global climate change may induce new problematics regarding the chemistry of atmospheric aerosols and their potential impact on the soils, sub-soils and building materials. On the other hand, numerical tools and computers now allow performing complex calculations so that sophisticated models can be run quite fast. This permits the extension of thermodynamic databases necessary for describing the behavior of increasingly complex geochemical systems at very high salinity. In this work, we present a strategy for developing new sets of specific

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interaction parameters consistent with the Pitzer model<sup>1</sup>.

## 2. Theoretical background

### 2.1. History of the Pitzer model: a rapid overview

The Pitzer model is a semi-empirical approach that considers specific interactions between dissolved species in an aqueous solution<sup>1</sup>. It uses interaction parameters, thermodynamic constants for aqueous complexation reactions, and mineral (respectively, gas) solubility products for dissolution/precipitation (respectively dissolution/degassing) reactions. It is one of the most promising and frequently used models as it was shown to represent the physico-chemical solution properties from very low to very high salinities<sup>2</sup> in complex systems<sup>3</sup>, from low to high temperatures<sup>2,4</sup>, and it has been applied to many different chemical systems<sup>5</sup> (and references therein).

In its first developments for binary systems (i.e., containing one single electrolyte), the Pitzer model considered full dissociation of the dissolved electrolyte, giving one anion and one cation. Their behavior was described in terms of mean activity coefficients and osmotic coefficient of the aqueous solution and calculated, using specific interaction parameters only (namely,  $\beta^{(0)}$ ,  $\beta^{(1)}$  and  $C^\phi$ ). For 2:2 type electrolytes, a fourth binary interaction parameter was required:  $\beta^{(2)}$ . The description of mixed systems, involves ternary interaction parameters between two like-charge ions ( $\theta$ ), and between two like-charge ions and an opposite charge ion ( $\psi$ ).

But, for weak electrolytes, the full dissociation assumption failed to describe correctly the solution properties and solid-liquid equilibria. The possibility to form ion pairs was then introduced in the model, and allowed in particular the description of pH-sensitive systems. A formation constant is attributed to the formation reaction of the ion pair. And, since some ion pairs can have a zero net charge, new specific ternary interaction parameters were introduced for neutral-ion or neutral-neutral ( $\lambda$ ), neutral-cation-anion ( $\zeta$ ), neutral-cation-cation or neutral-anion-anion ( $\eta$ ), and neutral-neutral-ion or neutral-neutral-neutral ( $\mu$ ).

In the end, there are 11 possible types of interaction parameters to describe complex aqueous systems. A 12<sup>th</sup> one, namely the solubility product (for solids) or the Henry's constant (for gases), is required to describe the liquid-solid or the liquid-gas equilibria, respectively. Furthermore, the dependence to temperature ( $T$ ) and pressure ( $P$ ) implies that any of these specific interaction parameters and equilibrium constants may be expressed as functions of these properties. Considering the works of<sup>6,7</sup>, a 9-coefficient equation can be used to describe interaction parameters variations from 0 to 250°C, and possibly down to subzero values according to<sup>4</sup>. A 5-coefficient equation is used for describing equilibrium constants in the same range of  $T$ . On the other hand, including  $P$  potentially involves 6 additional coefficients for each interaction parameter. This impressive inflation of coefficients makes their determination (by fitting) a key task that must ensure the internal consistency of the resulting database. This justifies developing an adequate strategy, depending on the capabilities of the calculation tools and on the type of experimental data that can be considered to constrain the model.

### 2.2. Solid-liquid and/or gas-liquid system useful properties

Among the most widespread information available for aqueous systems, osmotic coefficient of the aqueous solutions, and activity of water (or vapor partial pressure) can characterize either binary systems or mixtures. Mean activity coefficient of electrolytes rather concerns binary systems. When available, aqueous speciation data can provide useful supplementary information. Solubility data of solids and gases complete the characterization of the systems at given temperatures and pressures. In order to improve the description of the system additional constraints can be considered. In particular, the enthalpy of dilution and the heat capacity of aqueous solutions can be used to constrain the temperature dependence of the interaction parameters<sup>8</sup>. On the other hand, the density and compressibility of solutions can be used to constrain the pressure dependence of the interactions parameters<sup>9</sup>.

### 2.3. Parameter estimation

Specific interaction parameters and equilibrium constants can be fitted as soon as the related properties can be described by numerical tools. The well-known Phreeqc geochemical code<sup>10</sup> can handle the full Pitzer model, that is

the 11 types of interaction parameters, as well as the equilibrium constants. However, the  $T$  and  $P$  dependence is not consistent with the Pitzer model as applied in the literature, and the code cannot calculate the solutions enthalpy and heat capacity. A code, derived from PhreeqC and called PhreeSCALE, has been developed recently to address these deficiencies<sup>11</sup>. Coupling the use of one of these two codes with a parameter estimation code like PEST<sup>12</sup> allows fitting combinations of interaction parameters and equilibrium constants<sup>13</sup>, provided enough experimental data are available. However, a strategy for building sets of parameters must be established in order to fulfil a number of criteria that warranty the quality of the resulting database and, thus, the confidence in the subsequent geochemical calculations. Some of these criteria are given below.

The *internal consistency of the database* is an obvious major point. It can be preserved by realizing incremental extensions of the same database. In particular, binary systems should be dealt with ternary systems in order to insure the connection with chemical systems considered earlier and the consistent extension of the database.

It is preferable to describe *systems of highest solubility* first. Such systems can then be used as pillars on which less soluble systems can lean on. Here, we give the example of the NaOH-Na<sub>2</sub>SO<sub>4</sub> ternary system that has been revised in this work, compared to the model of<sup>3</sup>, on the basis of the recently revised models for NaOH<sup>14</sup> and Na<sub>2</sub>SO<sub>4</sub><sup>11</sup> (see § 3).

For highly soluble binary systems, *allowing for ion-pairing* can help describing ternary systems. Indeed, osmotic and mean activity coefficients can be satisfactorily described without ion-pairing but problems arise when ternary systems are considered. If no aqueous speciation data are available, the simultaneous parameterization of a binary and of one or several ternary systems can help solving the problem. An example of improved description of the KNO<sub>3</sub>-Ca(NO<sub>3</sub>)<sub>2</sub> ternary system is given in § 3.

For *low soluble binary systems*, where the extended Debye-Hückel approximation holds, it may be of interest to avoid as much as possible the use of binary interaction parameters. Ternary interaction parameters can suffice for describing the chemical behavior of ternary systems involving such binary systems. Here again, it is encouraged to limit as far as possible the number of interaction parameters to fit, when considering ternary systems.

### 3. Results

The first case of application is that of the NaOH-Na<sub>2</sub>SO<sub>4</sub> ternary system, at 25°C. In Fig. 1 is plotted the phase diagram at 25°C. It points out that the former model<sup>3</sup> fails in describing the behavior of the system above 6 M NaOH. The new models for the NaOH<sup>14</sup> and Na<sub>2</sub>SO<sub>4</sub><sup>11</sup> binary systems are used to re-parameterize the ternary system. Then, the adjustment of ternary interaction parameters suffices to reproduce solubility data of thenardite and NaOH:H<sub>2</sub>O over the whole range of concentrations.

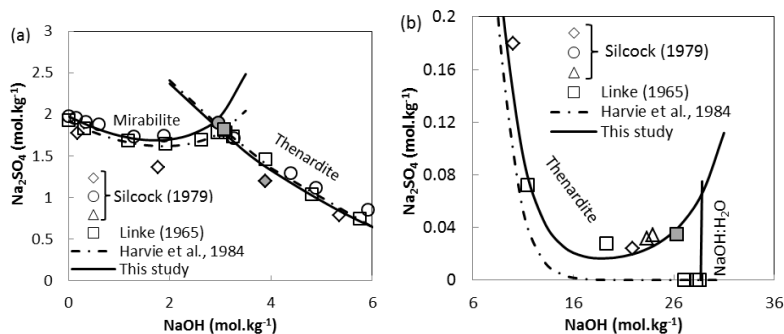


Fig. 1. Phase diagram of the NaOH-Na<sub>2</sub>SO<sub>4</sub> ternary system at 25°C, (a) at moderate NaOH concentrations; (b) at high NaOH concentrations. Symbols are bibliographic experimental data; dot-dash line is the model of<sup>3</sup>, full line is this study.

The second case considers the KNO<sub>3</sub>-Ca(NO<sub>3</sub>)<sub>2</sub> ternary system at 25°C which, to our knowledge, has never been fully described with the Pitzer model. Indeed, the full dissociation of both KNO<sub>3</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> binary systems cannot match the phase diagram (Fig. 2). When the KNO<sub>3</sub><sup>0</sup> ion pair is implemented and both the KNO<sub>3</sub> binary and KNO<sub>3</sub>-Ca(NO<sub>3</sub>)<sub>2</sub> ternary systems are parametrized simultaneously, the phase diagram is successfully described.

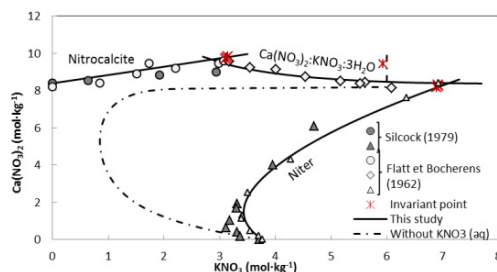


Fig. 2. Phase diagram of the  $\text{KNO}_3$ - $\text{Ca}(\text{NO}_3)_2$  ternary system at 25°C. Symbols are bibliographic experimental data; dot-dash line is the model assuming full dissociation, full line is the model assuming ion-pairing of  $\text{KNO}_3$ .

#### 4. Concluding remarks

The original Pitzer model is able to describe complex aqueous systems and solid-liquid or gas-liquid equilibria up to very high salinities provided the relevant strategy for estimating interaction parameters is applied. Existing calculation tools are now able to describe such systems but caution must be paid to some criteria so that numerical stability is preserved. One way to do this is to implement ion-pairing. Indeed, this allows lowering the charge concentration in the aqueous solution, and thus the ionic strength. Second, this lowers the number of aqueous species in solution and thus maintains a higher water content compared to full dissociation. Moreover, it is physically more reasonable to allow for ion-pairing when two oppositely charged species are close to each other in solution, which is not allowed in the full dissociation assumption. Another way (which is not exclusive) is to limit the number of interaction parameters. Because of the non-linearity of Pitzer equations, an increased number of parameters would favor inflation of parameters requirement.

Finally, provided experimental data are available, it is now possible to tackle the description of numerous complex chemical systems up to very high salinity, temperatures and pressures. This versatility is of interest for many scientific domains ranging from geochemistry to industrial chemistry.

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