USE OF MATHCAD FOR THE RESOLUTION OF IONIC EQUILIBRIA IN COMPLEX AQUEOUS SYSTEMS. APPLICATION TO SOLUBILITY CALCULATIONS IN $\{H_2O\text{-}Na^+\text{-}Ca^{2+}\text{-}Cl^-\text{-}SO_4^{2-}\text{-}OH^-\}$.

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Thanks to Mathcad, a calculation tool has been developed for the resolution of ionic equilibria in complex aqueous systems containing several cations and anions using Pitzer's model. This tool has been applied to solubility calculations in the $\{H_2O\text{-}Na^+\text{-}Ca^{2+}\text{-}Cl^-\text{-}SO_4^{2-}\text{-}OH^-\}$ system between 273.15 and 373.15 K. Using solubility data from the literature, the available parameter set (Pitzer parameters and equilibrium constants) has been extended. The obtained Mathcad application has been successfully tested for the representation of mineral solubilities in all sub-systems found in the literature. Our tool also allows the simple resolution of a tricky issue like the representation of the composition of a saturated aqueous solution in equilibrium with several solid phases.

1. INTRODUCTION

In most cases, the applications of mineral chemistry involve concentrated aqueous solutions of numerous electrolytes. The representation of thermodynamic properties of such systems is therefore of great importance in the design of industrial processes.

In particular, solid/liquid equilibria calculations are necessary for the design of separation devices. These calculations are usually difficult because they concern highly non-ideal mixtures in which many different equilibria between ionic species can take place. Subsequently an adequate thermodynamic model for the representation of activity coefficients is required along with an appropriate algorithm for the resolution of single or multiple non-linear equations.

The pionnering works in this field have been made by geochemists like Helgeson et al. (1969) who used extended Debye-Hückel equations. Since then, improvements have been significant thanks to the utilization of Pitzer's model [Harvie et al. (1984)] and to the stupendous development of computers and programmation languages [Plummer et al. (1990)]. However the realization of such software applications is time-consuming and requires computational skill. Advanced mathematical packages like Mathematica, MATLAB or Mathcad can be of great help because the algorithms necessary for the resolution of non-linear systems are defined as built-in functions. We have choosen Mathcad (because of its ease of use) to develop a simple tool to represent ionic equilibria in complex aqueous systems containing several cations and anions using Pitzer's model. As a part of an industrial collaboration, this tool has been applied to solubility calculations in the $\{H_2O\text{-}Na^+\text{-}Ca^{2+}\text{-}Cl^-\text{-}SO_4^{2-}\text{-}OH^-\}$ system between 273.15 and 373.15 K.

2. THERMODYNAMICAL BACKGROUND

The solubility of a mineral species in an aqueous solution containing several electrolytes is defined as the maximum amount of salt which is possible to dissolve before apparition of solid phase. From the thermodynamic point of view, the calculation of solubility data involves the resolution of equilibrium conditions between liquid phase solution and solid phase deposit.

2.1 Thermodynamics of solid/liquid equilibria in electrolyte aqueous solution

As strong electrolytes in liquid solution are totally dissociated into ionic species, the dissolution of a crystallized hydrated strong electrolyte of general formula $C_{\nu_c}A_{\nu_a}.\nu_w H_2O$ in water can be represented with the following chemical reaction :

$$C_{\nu_c}A_{\nu_a}.\nu_w H_2O_{(s)} = \nu_c C^{z_c}_{(aq)} + \nu_a A^{z_a}_{(aq)} + \nu_w H_2O_{(l)} \quad (1)$$

where z_c and z_a are respectively the (positive) number of electrical charges of formed cation (C) and anion (A). Equilibrium condition of reaction (1) at given temperature is related to solubility product, K_S :

$$K_S = \gamma_C{}^{\nu_c} \cdot m_C{}^{\nu_c} \cdot \gamma_A{}^{\nu_a} \cdot m_A{}^{\nu_a} \cdot a_w{}^{\nu_w} \quad (2)$$

In eq. 2, γ_i is the activity coefficient of ionic species i expressed according to unsymmetrical convention in the molality scale, m_i the molality of species i and a_w is the activity of water. K_S is defined with chemical potential of the species in their standard state :

$$K_S = \exp\left(-\frac{\nu_w \cdot \mu_w^0 + \nu_c \cdot \mu_C^0 + \nu_a \cdot \mu_A^0 - \mu_S^0}{RT}\right) \quad (3)$$

The values of solubility product are usually fitted with experimental solubility data.

2.2 The Pitzer ion interaction model

Activity coefficient of ions, γ_i, and activity of water, a_w, defined in the previous section can be related to the excess Gibbs Energy, G^E, of the liquid solution. The expression of G^E proposed by Pitzer (1991) is capable of accurately predicting thermodynamic properties in complex aqueous electrolyte solutions (Marliacy, 1999, Marliacy et al., 1999), especially activity coefficient, dissolution enthalpy and solubility data (Marliacy et al., 1998), but also activity of water (Hubert et al., 1997).

In this approach, the excess Gibbs energy of the electrolyte solution containing 1 kg of water (molal excess Gibbs energy) can be considered as the sum of a Debye-Huckel term which expresses the effect of long range interactions between ions and of a second term accounting for the short range binary and ternary interactions between solute ionic species. Corresponding expression is a function of temperature, of molality and ionic strength of each ionic species and of binary and ternary parameters. Binary parameters are relative to each binary aqueous system of type CA which is possible to form with ions present in the solution. They are fitted to thermodynamic properties of corresponding binary systems (Marliacy et al., 1998). Ternary parameter are, in first approximation, characteristic of ternary solutions with common ion, like for example CAA' or CC'A. Values of these parameters are adjusted on thermodynamic data of corresponding ternary system (Marliacy et al., 1998).

3. THE $\{H_2O\text{-}Na^+\text{-}Ca^{2+}\text{-}Cl^-\text{-}SO_4^{2-}\text{-}OH^-\}$ SYSTEM

3.1 List of species

The $\{H_2O\text{-}Na^+\text{-}Ca^{2+}\text{-}Cl^-\text{-}SO_4^{2-}\}$ system was already studied by Moller (1988). The behavior of ion OH^- in aqueous solution was investigated by Lambert and Clever (1992) who studied the solubility of $Ca(OH)_2$ in several aqueous solutions at different temperatures. From these works, it appears that numerous solid species can deposit in the $\{H_2O\text{-}Na^+\text{-}Ca^{2+}\text{-}Cl^-\text{-}SO_4^{2-}\text{-}OH^-\}$ system : hydrates, double salts, metastable salts... In this paper, we focused our attention on solutions very concentrated in chloride ions (especially NaCl). In these conditions, some mineral species like, for example,

Na_2SO_4, $Na_2SO_4.10H_2O$, $Na_2SO_4.CaSO_4$, NaOH... don't crystallize. Finally the mineral salts which were taken into account in this study are the following : halite (NaCl), anhydrite ($CaSO_4$), hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), lime ($Ca(OH)_2$).

3.2. Activity coefficients and equilibrium constants

The use of Pitzer's model for our study requires the knowledge of all adequate equilibrium constants and adjustable parameters. Because of the numerous ionic species in the system, the number of necessary parameters is rather high. Fortunately most of them can be found in the literature. Harvie et al. (1984), Pabalan and Pitzer (1987) and Greenberg and Moller (1989) give all the ternary parameters necessary for our study. Greenberg and Moller (1989) propose the binary parameters relative to the Na^+-Cl^-, Na^+-SO_4^{2-}, Ca^{2+}-Cl^- et Ca^{2+}-SO_4^{2-} interactions from 273.15 to 523.15 K. The interactions between Na^+ et OH^- are represented with binary parameters from Pabalan and Pitzer (1987). The binary parameters proposed by Harvie et al. (1984) for Ca^{2+}-OH^- are valid only at 298.15 K, therefore they cannot be used in our study.

We have fitted the binary parameters $\beta^0_{Ca(OH)_2}, \beta^1_{Ca(OH)_2}, \beta^2_{Ca(OH)_2}$ and the solubility product of lime with experimental solubility data in the H_2O-$CaCl_2$-$Ca(OH)_2$ system [Lambert and Clever (1992)].

The Pitzer type model proposed by Moller (1988) (which parameters have been revised by Greenberg and Moller (1989)) takes into account explicitly the neutral species $CaSO_4^0$. In addition to the different solid/liquid equilibria, it is then necessary to consider the dissociation of the associated species (ion pair) $CaSO_4^0$:

$$C_aSO_4 = C_a^{2+} + SO_4^{2-} \qquad (4)$$

4. RESOLUTION OF IONIC EQUILIBRIA WITH MATHCAD

4.1 Presentation of SolubLTS

The activities of species in solution depend strongly of the composition, therefore the resolution of ionic equilibria (eq. 2) is iterative. We have then choosed to solve the mass action law with the help of Mathcad solve blocks. The developed Mathcad application, SolubLTS, allows the simple calculation of solubilities in complex aqueous systems. These solve blocks use a Levenberg-Marquardt algorithm [Lawson and Hanson (1974)] for the resolution of non linear systems with or without constraints. Their use within Mathcad is particularly easy since it is only necessary to precise the system's constraints, its unknown values and the corresponding guess values.

In SolubLTS, the solubility calculations are defined as Mathcad solve blocks with the mass action law as constraint.

In the case of a solid/liquid equilibrium between a liquid solution and a crystallized salt i of chemical formula $C_{\nu_c}A_{\nu_a}.\nu_wH_2O$, the equilibrium composition is ruled by the mass action law (eq. 2) which is equivalent to :

$$\frac{\gamma_C{}^{\nu_c} \cdot m_C{}^{\nu_c} \cdot \gamma_A{}^{\nu_a} \cdot m_A{}^{\nu_a} \cdot a_w{}^{\nu_w}}{K_S} = 1 \qquad (5)$$

We have named this ratio "Equilibre_sel i": it's a function of composition and temperature (just as the activity coefficients). The equilibrium condition is then :

$$\text{Equilibre\_sel}_i\left(\begin{matrix} m_{Na^+}, m_{Ca^{2+}}, m_{Cl^-} \\ m_{SO4^{2-}}, m_{OH^-}, T \end{matrix}\right) = 1 \qquad (6)$$

In the main program "solub", we have defined the "Equilibre_sel$_i$" functions relative to all the mineral species considered within our study. Thanks to this mathematical trick, the user only specifies the solid/liquid equilibrium to take into account without writing the mass action law explicitly (see éq. 6). The molality of the neutral species $CaSO_4^0$ being low, we have neglected its influence on the activities of other species in solution, the "Equilibre_sel$_i$" functions are then independent of the molality of $CaSO_4^0$.

In a similar way, we have defined the "Equilibre_$CaSO_4^0$" function which is relative to the dissociation of the neutral species $CaSO_4^0$:

$$\text{Equilibre\_CaSO}_4{}^0\left(\begin{matrix} m_{Na^+}, m_{Ca^{2+}}, m_{Cl^-}, T \\ m_{SO4^{2-}}\, m_{OH^-}, m_{CaSO4^0} \end{matrix}\right) = \frac{\gamma_{ca^{2+}} \cdot m_{Ca^{2+}} \cdot \gamma_{SO4^{2-}} \cdot m_{SO4^{2-}}}{\gamma_{CaSO4^0} \cdot m_{CaSO4^0} \cdot K_d} \quad (7)$$

4.2. Comparison of calculated solubilities with experimental values

The ion interaction model has been successfully tested up to 18 mol·kg^{-1} ionic strengths with experimental solubility data from binary (water + 1 salt) to quaternary (water + 3 salts) systems [Linke and Seidell (1958), Linke (1965), Lambert and Clever (1992)]. As an example, Figures 1a and 1b represent the calculated solubilities in H_2O-NaCl-Na_2SO_4-$CaSO_4$ at 373.15 K.

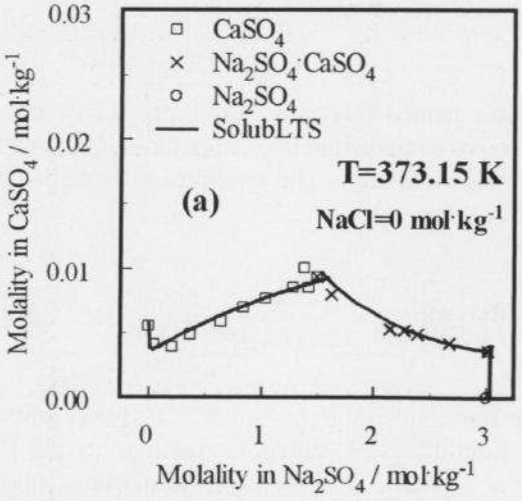

Figure 1a: Solubility of $CaSO_4$ in H_2O-Na_2SO_4 at 373.15 K. (experimental data from Block and Waters, 1968).

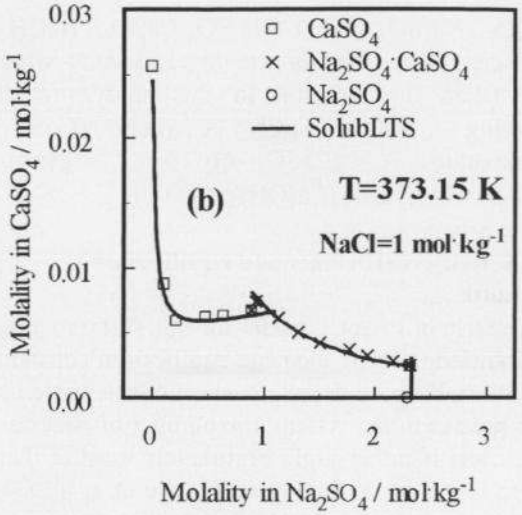

Figure 1b. Solubility of $CaSO_4$ in H_2O-NaCl-Na_2SO_4 at 373.15 K. (experimental data from Block and Waters, 1968).

4.3. Example of industrial interest

Industrial fluids are often composed of an aqueous solution in equilibrium with several solid phases. Let us consider the example of an aqueous solution containing one mole of dissolved calcium chloride per kilogram of water, in equilibrium with halite (NaCl), lime ($Ca(OH)_2$) and a $CaSO_4$ dérivative (anhydrite, gypsum or hemihydrate). The computation of the system's composition requires the definition of the corresponding ionic equilibria and of an adequate solve block.

According to the model used in our study, the system's composition is ruled by three solid/liquid equilibria and a dissociation equilibrium (four ionic equilibria). In the case where the calcium sulfate derivative is gypsum ($CaSO_4 \cdot 2H_2O$), the corresponding solve block to use within SolubLTS is presented in Table 1.

Table 1
Resolution of four simultaneous ionic equilibria with SolubLTS (see text for details).

Référence : c:\SolubLTS\Modèle\solubMCD

Initial value :

cacl2 :=1 (dissolved $CaCl_2$)

Guess values :

caso4dis :=0.010 (dissociated $CaSO_4$)
caso4neu := 0.001 (neutral species $CaSO_4$)
caoh2 :=0.010 (dissociated $Ca(OH)_2$)
nacl :=5 (dissociated NaCl)

Solve block :

Given

Equilibre_Gypse(nacl,cacl2+caso4dis+caoh2,nacl+2.cacl2,caso4dis,2.caoh2,T)=1
Equilibre_CaSO4°aq(nacl,cacl2+caso4dis+caoh2,nacl+2.cacl2,caso4dis,2.caoh2,T,caso4neu)=1
Equilibre_Chaux(nacl,cacl2+caso4dis+caoh2,nacl+2.cacl2,caso4dis,2.caoh2,T)=1
Equilibre_Halite(nacl,cacl2+caso4dis+caoh2,nacl+2.cacl2,caso4dis,2.caoh2,T)=1

composition(T) :=trouver(caso4dis,caso4neu,caoh2,nacl)

Solubilities of gypsum, of lime and halite as functions of temperature :

gypsum(T) :=composition(T)$_0$ + composition(T)$_1$ lime(T) :=composition(T)$_2$ halite(T):=composition(T)$_3$
gypsum(298.15) :=0.0039 lime(298.15) :=0.0071 halite(298.15) :=4.4093

Similarly we have considered the case where the calcium sulfate derivative is anhydrite ($CaSO_4$) or hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$).

Figures 2a and 2b present the solubilities of the calcium sulfate derivatives (anhydrite, gypsum or hemihydrate) respectively in pure water and in the solution in equilibrium with the three solids simultaneously. As conclusion it can be seen that the influence of temperature on gypsum solubility is not the same in both cases.

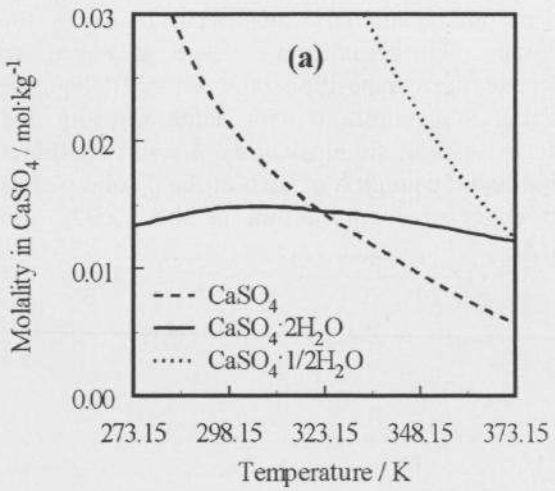

Figure 2a. Solubility of calcium sulfate in pure water

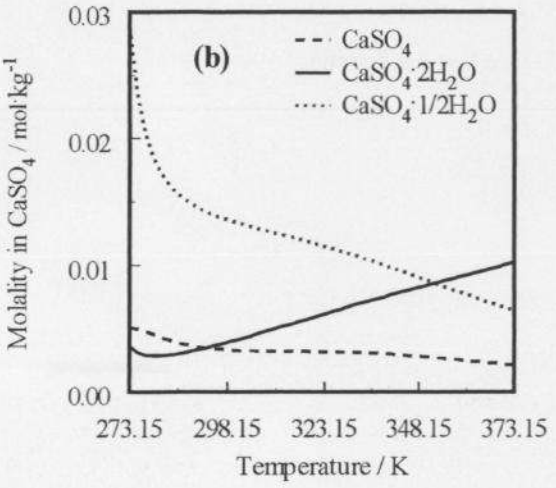

Figure 2b. Solubility of calcium sulfate in a molal calcium chloride aqueous solution saturated with NaCl, $Ca(OH)_2$ and a $CaSO_4$ derivative .

5. CONCLUSION

Using solubility data taken from Lambert and Clever (1992), we have extended the parameter set (Pitzer parameters and equilibrium constants) proposed by Greenberg and Moller (1989). The Mathcad application with the extended parameter set has been successfully tested for the representation of mineral solubilities in each binary, ternary and quaternary sub-system found in the literature. Furthermore we have managed to calculate the composition of a saturated aqueous solution in equilibrium with halite, gypsum and lime by solving simultaneously 4 ionic equilibria (solid/liquid equilibria of each of the 3 solid phases and dissociation equilibrium of the $CaSO_4^0$ ion pair).

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