Estimation of salt solubilities in hydrothermal systems

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Abstract - In this work we analyze the calculation of the solubility of salts at high temperatures and pressures. The prediction of solubility constants relies on the knowledge of the standard properties of the ions in water, while the calculation of ion concentration and speciation in solution at saturation requires a method to estimate activity coefficients and association constants. We discuss the achievements and limitations of the ion-specific interaction and the mean spherical models to estimate activity coefficients in pure and mixed electrolyte systems. We emphasizes the importance of simple models depending on few molecular parameters and having a reasonable physical behaviour as a function of pressure and temperature.

INTRODUCTION

The solubility of salts in aqueous ionic systems at high temperatures and pressures is relevant in geochemistry to understand the formation and transformation of evaporative mineral deposits in natural environments. The formation of scales in petroleum reservoirs and steam generators is also an important process which sometime determines the life time of the installation.

Although there is now a large body of experimental data dealing with the solubility of salts in hydrothermal solutions, thermodynamics models are still required to estimate the solubility in multicomponent systems (brines) under high temperature and pressure conditions.

Accurate calculations of mineral solubilities in hydrothermal solutions rely on the knowledge of activity coefficients and ion-pair or complexation constants. The Pitzer equations for the activity coefficients of the aqueous species provide a means to extrapolate low concentration data to high concentrations and the temperature dependence of the model parameters have also been reported for a number of electrolytes (1). However, these parameters can not be estimated beyond the range of temperatures and pressures where they have been fitted, limiting the predictive power of the approach.

The prediction of solubilities using the Pitzer formalism for the activity coefficients in mixed aqueous electrolytes have been summarized sometime ago (2) and used to estimate mineral solubilities at ambient and high temperatures (3-6). In this work we present some alternative procedures to estimate salt solubilities in mixed systems, the pressure effect and the speciation in ionic solutions when ion association is present.

THEORY

The basic equation for the solubility of an ionic solid $M_{\nu_+}X_{\nu_-}$ in equilibrium with ions ν_+ ions M^{z+} and ν_- ions X^{z-} follows from the chemical potentials of the phases:

$$(\mu_s^\ominus - \nu_+\mu_+^\ominus - \nu_-\mu_-^\ominus)/RT = \nu_+ \ln(m_+\gamma_+) + \nu_- \ln(m_-\gamma_-) \tag{1}$$

where $\mu_s^\ominus$ is the chemical potential of the solid pure phase and $\mu_i^\ominus$ is the chemical potential for the aqueous i ion at the hypothetical standard state (one molal referenced to infinite dilution), in both cases at pressure p and temperature T.

The left hand term in equation (1) is $\ln K$, being K the equilibrium constant at p, T for the dissolution reaction. It follows from the equilibrium condition that, once the standard state properties at a given p, T

have been calculated, the molality of the salt at saturation can be obtained if we are able to estimate the value of the ionic activity coefficients or the mean activity coefficient of the electrolyte

The chemical potentials of the solid and aqueous species at the temperature and pressure of interest are obtained from the values reported in literature at reference temperature and pressure (normally 25°C and 1 bar), provided that the heat capacities and volumes of those substances are well known in the interval (T, T_o) and (p, p_o).

$$\mu_i^\ominus(p,T) = \mu_i^\ominus(p_o, T_o) - (T - T_o)S_i^\ominus(T_o) + \int_{T_o}^{T} C_{p,i}^\ominus dT - T \int_{T_o}^{T} C_{p,i}^\ominus d\ln T + \int_{p_o}^{p} V_i^\ominus dp \qquad (2)$$

For the solid phase it is common the use of the Maier-Kelley equation for the heat capacity ($C_p = a + bT + c/T^2$) along with thermal expansion data. The experimental information about $C_{p,i}$ and V_i for aqueous ions is abundant up to 373K and normal pressure, being scarce at higher temperatures and pressures.

The electrolytes whose heat capacities in water are well-known at high temperature (6) are: NaCl, KCl, NaOH, MgCl$_2$, CaCl$_2$, Na$_2$SO$_4$, K$_2$SO$_4$ and MgSO$_4$. Volumetric data on aqueous electrolytes at high temperature it is also restricted to few substances. Thus, the equations developed for Helgeson, Kirkham and Flowers (7) to estimate the standard state chemical potentials of aqueous ions (HKF model) at high temperature and pressure are very useful above 373K and 1 bar.

The HKF model or its modified version (8) is based on an extended Born model, where the electrostatic part of the Gibbs energy change of dissolution of an ion in the continuum dielectric medium is given by the equation of Born (9) with an effective ionic radii. It is well known that the Born model describes very adequately the main features of the high temperature properties of electrolytes (10).

The HKF model is completed with an empirical expression for the non-electrostatic part of the chemical potential. It should be noted that the equation used for the non-electrostatic contribution is not based on physical considerations on the short range solute-solvent interactions, but it has several adjustable parameters which have been fitted (11) using all the experimental information available for aqueous electrolytes at high temperatures and pressures. The data set of HKF model parameters comprises 55 cations and 68 anions and they can be used to calculate standard state properties to 1273K and 5 kbar.

The results of the HKF model calculation of the equilibrium constants are in very good agreement with the experimental results up to 473K, as shown in Figure 1 for NaCl and BaSO$_4$. At higher temperatures the predictions of this model deteriorates, although they are qualitatively correct.
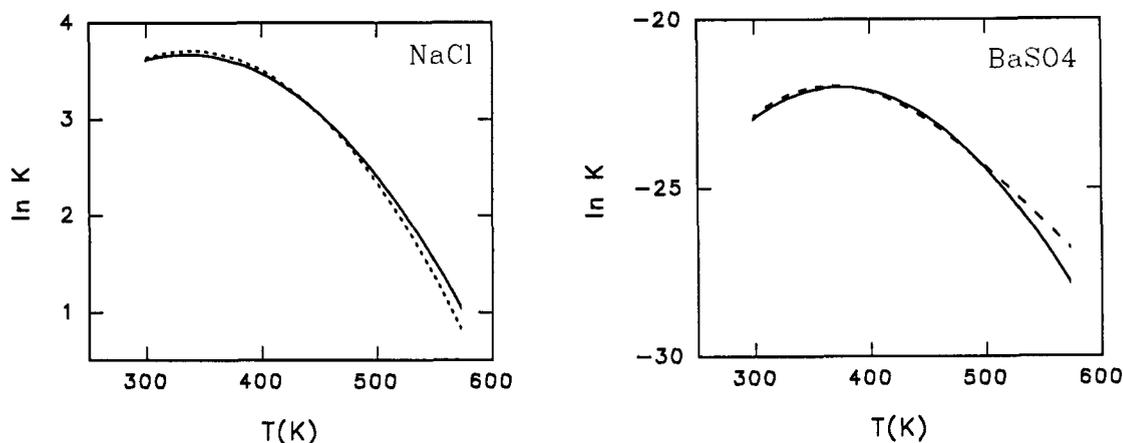

Fig. 1 Equilibrium constants for the dissolution of NaCl and BaSO$_4$. Predicted by the HKF model (——); Experimental values (••••), ref.12 and ref.13.

The principle of balance of identical like charges formulated by Lindsay (14) is therefore a good alternative to estimate equilibrium constants at high temperatures. It is based on the fact that ΔC_p for a dissolution reaction written in the isocoulombic form is almost independent of temperature.

Figures 2 shows the results of the application of this simple approximation to the isocoulombic reaction involving barite and anhydrite. A plot of pK$_s$ vs. 1/T for the exchange reaction deviates only slightly from the linearity, which would correspond to $\Delta C_p = 0$ (dashed line). If we adopt $\Delta C_p = -32$ J/(K mol) (solid line),

the heat capacity of reaction at 298K, the agreement with the experimental results is quite satisfactory (18).
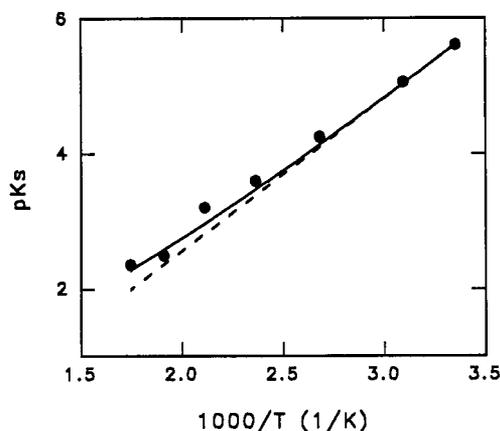
Fig. 2 Predicted and experimental pK for the isocoulombic reaction $BaSO_4(s) + Ca^{2+}(aq) = Ba^{2+}(aq) + CaSO_4(s)$. Experimental data (●) from refs. 15 and 16.
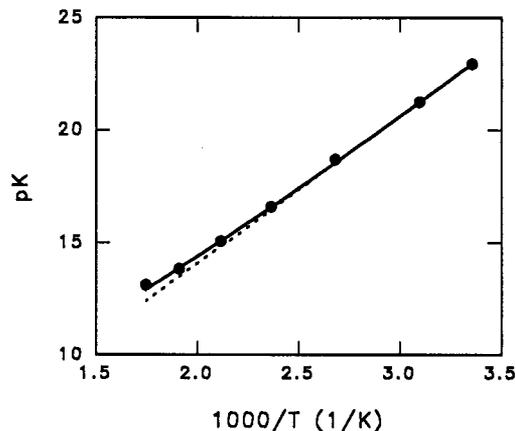
Fig. 3 Predicted and experimental pK for the reaction: $Ca^{2+}(aq) + 2H_2O = Ca(OH)_2(s) + 2H^+(aq)$. Symbols as in Fig. 2. Experimental data (●) from ref. 17.

Figure 3 shows the result for the dissolution reaction of $Ca(OH)_2$ combined with the autoprotolysis of water. In this case we have used ΔC_p=-48.2 J/(K mol) (solid line), the value at 298 K, to reproduce the experimental results.

We have used the model substance approach (14) to estimate the solubility of $Mg(OH)_2$ from the former result (10). In this case the model substance is $Ca(OH)_2$, whose solubility is well known at high temperature. From the estimated equilibrium constant for the isocoulombic reaction $Ca(OH)_2(s) + Mg^{2+}(aq) = Ba(OH)_2(s) + Ca^{2+}(aq)$ we calculated the solubility product of $Mg(OH)_2$ up to 573K, by combining this equilibria with the dissolution reaction of $Ca(OH)_2$. The experimental results reported in the literature for the solubility of $Mg(OH)_2$ above 423K differ more than one order of magnitude, so the model substance approach has helped us to identify the more reliable solubility values.

ACTIVITY COEFFICIENTS ESTIMATION

Pitzer's equations

Undoubtedly, the Pitzer's ion-interaction model (19) is the most successful approach for the excess properties of electrolytes. In this model the mean activity coefficient of the electrolyte is expressed as a virial expansion which includes the Debye-Huckel term plus concentration independent coefficients: $\beta_{MX}^{(o)}$, $\beta_{MX}^{(1)}$ and C_{MX}, which are temperature dependent and specific for each electrolyte. A fourth coefficient, $\beta_{MX}^{(2)}$, must be added to the expansion in order to fit the high concentration data of 2-2 or higher valence electrolytes, where ion-pair formation is important.

While the Pitzer's expansion of the excess Gibbs free energy relies on the McMillan-Mayer formalism, which assumes the solution in equilibrium with the pure solvent at the osmotic pressure, the coefficients of the Pitzer equation were obtained by fitting the practical Lewis-Randall activity coefficients. Thus, these coefficients absorb the correction term accounting for the change of the reference system. This correction is not easy to estimate and become important for concentrated solutions. Nevertheless, at high temperature there is same kind of compensation which prevents this correction to be very large (10).

For mixed electrolytes the interaction coefficients θ_{ij} and ψ_{ijk} complete the expansion. They are evaluated from osmotic or activity coefficients of mixtures containing a common-ion. The values of these parameters for mixtures containing Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, OH^- and SO_4^{2-} at high temperature has been reported (5,6). Some of them have been obtained by adjusting solubility data in ternary mixtures, limiting the predictive power of the model.

For instance, the solubility of halite (NaCl) in $NaCl-NaOH-H_2O$ mixtures was reproduced up to 453K using a temperature dependent ternary coefficient $\psi_{Na,OH,Cl}$. Without this ternary parameter the predictions of the model leads to differences of up to 20% with the experimental data.

The use of Pitzer equations in systems containing mixtures of electrolytes and non-electrolytes has not been

well explored. An example is our study of the solubility of salts in aqueous systems containing CO_2 (20). In this case, the activity coefficients for the mixture of the nonionic solute [1] with the salt [2] are given by:

$$\ln \gamma_1 = \ln \gamma_1^* + 2m_2\Lambda_{12} + 3\nu_+\nu_- m_2^2\Gamma_{122} + 6m_1m_2\Gamma_{112} \tag{3}$$

$$\ln \gamma_2 = \ln \gamma_2^* + \frac{2}{\nu}m_1\Lambda_{12} + \frac{3}{\nu}m_1^2\Gamma_{112} + 6\frac{\nu_+\nu_-}{\nu}m_1m_2\Gamma_{122} \tag{4}$$

where γ_i^* is the activity coefficient of the pure binary solution. For the nonionic solute:

$$\ln \gamma_1^* = 2m_1\lambda_{11} + 3m_1^2\tau_{111} \tag{5}$$

The Pitzer parameters for CO_2 were obtained from the solubility data in water. It was found that $\ln \gamma_1^*$ is a linear function of concentration ($\tau_{111}=0$) and the binary interaction parameter, λ_{11}, is negative and increases with temperature.

By analyzing the NaCl-CO_2 and Na$_2$SO$_4$-CO_2 mixtures, we found that $\ln(\gamma_1/\gamma_1^*)$ is independent of the CO_2 concentration ($\Lambda_{112}=0$) and Γ_{12} is almost independent of temperature. Moreover, the contribution of Λ_{122} is negative and very small. More systems should be studied before generalizing these conclusions.

Integral equation theories: MSA

The term integral theories refers to solutions models based in an approximation (closure) for the direct correlation function, $c_{ij}(r)$, in order to solve the Ornstein-Zernike equation (10), which relates $c_{ij}(r)$ with the total distribution function, $h_{ij}(r)$.

For electrolytes, the simplest closure relationship is given by the Debye-Hückel (DH) model:

$$c_{ij}(r) = -\beta u_{ij}(r); \qquad r \geq 0 \tag{6}$$

where u_{ij} is the coulombic potential between ion i and j.

The logical extension to the DH model is the mean spherical approximation (MSA), where the former closure applies for $r \geq \sigma_{ij}$. Therefore, the hard core size of the ions is included in the treatment of the electrostatic part of the ion-ion interactions. MSA is a linearized theory which yields to analytical expressions for the excess thermodynamic properties (21) even in the unrestricted case (different ion sizes). Similarly to the DH model, the MSA is based on the calculation of a shielding parameter, Γ, given by

$$4\Gamma^2 = \alpha^2 \sum_i^s (\rho_i a_i^2/(1 + \Gamma\sigma_i)^2 \tag{7}$$

where:

$$\alpha^2 = (4\pi e^2)/(\epsilon kT)$$

and

$$a_i = z_i - (\pi P_n \sigma_i^2)/(2\Delta)$$

where P_n is a function of the particles densities (ρ_i), charges (z_i) and diameters (σ_i). P_n is very small in dilute solutions and even in concentrated solutions if the ion sizes are not too different.

Once Γ is evaluated by a simple iteration method, the activity coefficient of the ion i in the mixture is calculated as,

$$\ln \gamma_i^{MSA} = (\alpha^2 z_i M_i/4\pi) - (\alpha^2 P_n \sigma_i/8\Delta)(1/(1 + \Gamma\sigma_i) + (\pi\alpha^2 P_n \sigma_i^2)/(6\Delta)) \tag{8}$$

where $M_i = (2\,\Gamma a_i\,/\,\alpha^2\,$-$\,z_i)/\,\sigma_i$.

The MSA has been used to analyze the excess properties of pure binary electrolytes and ternary mixtures (22) at 298K. The results lead to the following conclusions:

a) In pure electrolyte solutions where the diameter of the anion was fixed at its crystalographic value, the best fit to the activity or osmotic coefficient, requieres the cation diameter to decrease with concentration.

b) A single adjusted cation diameter can be used in the 0-1 molal region to obtain activity coefficients of 1-1 and 1-2 electrolytes which agree within 5% to the experimental values.

c) In ternary mixtures with common anion, the mean activity coefficients of both electrolytes can be fitted quite satisfactorily at moderate concentrations by using constant effective values for the cation diameters. The fit is improved and even extended to higher concentrations if ion sizes are taken as in the pure electrolyte at the same total anion concentration.

It is clear that the need of effective diameter for ions in MSA is the result of the fail of the primitive model to capture specific interactions of the ion with the solvent. Therefore, this effective ion size should be taken as an hydrated ion size, and it is reasonable that its value decrease with concentration due to decreased availability of solvent molecules.

This approach has been extended at high temperature NaCl aqueous solutions (10) with the purpose of estimating activity coefficients close to saturation. It is concluded that a concentration-dependent diameter must be used to fit experimental activity coefficients within 1%. Figure 4 shows the $Na^+(aq)$ diameter as a function of concentration at two temperatures and several pressures (the Cl^- diameter was fixed at 3.60 A). It is worthy to note that the effect of pressure on the effective diameters is very small.
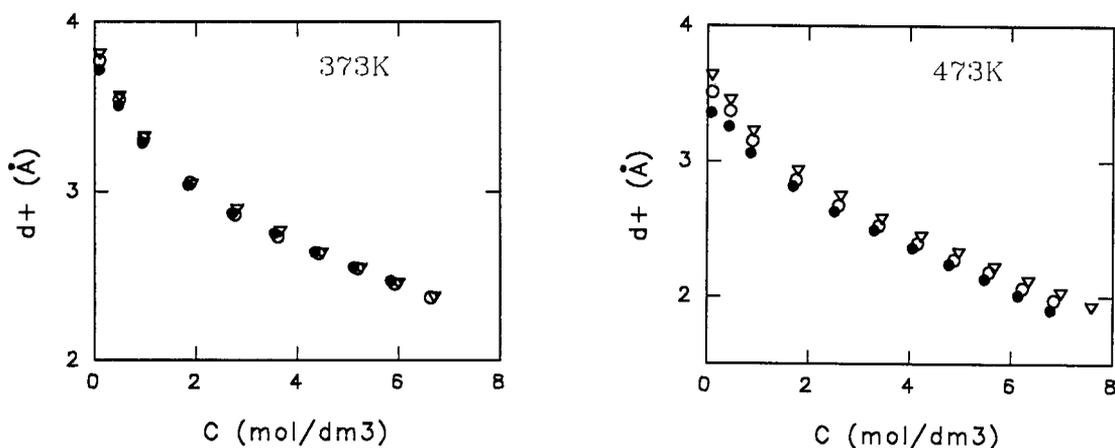

Fig. 4 Effective diameter of $Na^+(aq)$ obtained by fitting NaCl(aq) activity coefficients to equation (8) at 373K and 473K. (●) saturation pressure; (◉) 50 MPa; (▽) 100 MPa.

In the case of mixed electrolytes this approach has an important advantage on the Pitzer's model: it is not necessary to invoke specific interactions between ions; the ion sizes used as adjustable parameters are fixed at the values in its binary solution at the ionic strength of the mixture.

We have calculated the solubility of halite (NaCl) in the ternary system $NaCl-NaOH-H_2O$ at 298K and 423K using the effective diameters for $Na^+(aq)$ obtained from NaCl. The effective diameter of $OH^-(aq)$ was fitted from the activity coefficients data for NaOH(aq) (23) using the Na^+ diameters calculated from NaCl(aq). The experimental activity coefficients values for NaOH(aq) could be reproduced quite well by using a concentration independent diameter for OH^- (3.78 Å at 298K and 3.34 Å at 423K, as shown in Figure 5.

ION ASSOCIATION

In systems with strong ionic association it has been shown that the inclusion of a $\beta^{(2)}$ parameter in the specific ion-interaction model is not enough to obtain a good representation of the data (25). For ion pairing of M^{2+} cations with X^- anions a reliable criteria suggest that for association constant K_a larger than 100 the ion pairs must be included in the model.

This criteria has been found to be valid by Moller (5), analyzing the the solubility of $CaSO_4$ and $BaSO_4$ at high temperature. The SO_4^{2-} association with divalent cations become stronger at higher temperatures and it requires the inclusion of the associated species in the treatment. However, the values asigned to the association constants are largely arbitrary since the ion-pair formation is not a true chemical equilibrium. Any intent to define an association constant in the sense of the Bjerrum model, face the problem of the ambiguity of the ion-pair definition. A theory of ionic association based on thermodynamic criteria, such as free energy minimization, is then required.
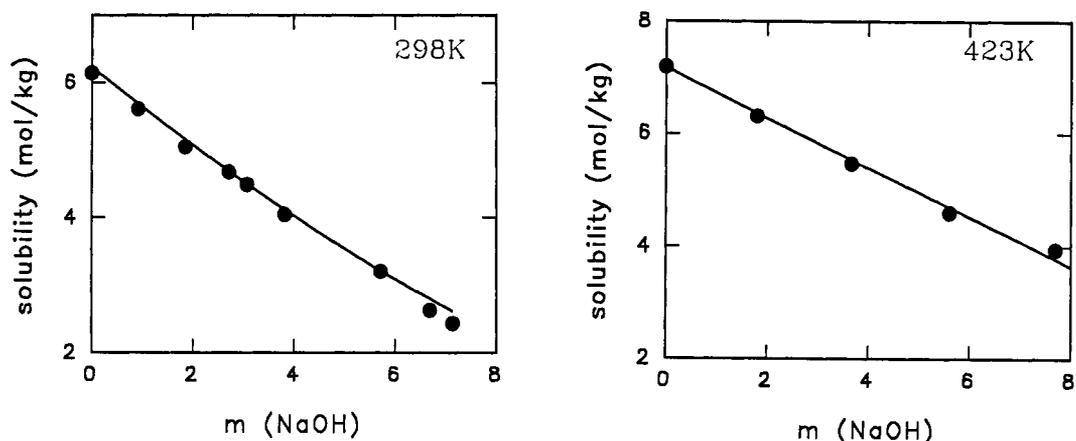
Fig. 5 Solubility of halite in the system NaCl-NaOII-H$_2$O calculated by MSA (━━━).
Experimental data from ref. 24

The cluster theory of electrolytes (26) is a generalization of the Bjerrum model in the sense that the system is viewed as a mixture of free ions and clusters (s,t) formed by s cations and t anions. Two or more ions form a cluster if distance between each ion center and the mass center of the cluster is shorter than d, the cluster distance. The difference with the Bjerrum model is that the cluster distance is used as a parameter in the minimization of the free energy of the system.

The free ions and charged or neutral clusters interact each other, and the configuration partition function is given by,

$$Q_N = Q_{cl} \prod_{s,t}(Q_{s,t}^{N(s,t)}/N(s,t)\,) \qquad (9)$$

Q_{cl} can be written as the product of the MSA and hard sphere partition functions and the integrals $Q_{s,t} = \int_V \exp(\beta U(r))dr$ can be evaluated by standard Monte Carlo sampling.

It is well known that the clusters population depend on the particle density and the reduced temperature ($T_r = \epsilon kT \, \sigma/(|\,z_i z_j\,| \, e^2)$). The speciation of the ionic systems is determined by the product ϵT (decrease with temperature for water) and the effective size of the ions, which can be obtained by a self consistent procedure by fitting activity or osmotic coefficients of the pure electrolyte.

The cluster theory has been extended to the unrestricted case (27) and tested with success for real 1:1 and 2:2 electrolytes at high temperature (28).

PRESSURE EFFECT ON SOLUBILITY

The pressure effect on the solubility of salts in aqueous solutions can be estimated (29) from the partial molar volume of the salt in the solution (V_2), the molar volume of the solid salt (V_2^*) and the concentration dependence of the activity coefficient of the salt:

$$\left(\frac{\partial m_2}{\partial p}\right)_{T,sat} = -\frac{V_2 - V_2^*}{\nu RT} \left(\frac{1}{m_2} + \frac{\partial ln\gamma_2}{\partial m_2}\right)^{-1}_{sat} \qquad (10)$$

The Pitzer equations for the partial molar volume and the activity coefficient of the salt can be used to estimate the pressure effect on the solubility. Thus, the estimated solubility of NaCl in water at 298 K increases 3% when the pressure is raised from 1 bar to 1000 bars, while the calculated increment is 4%. At higher temperatures the pressure effect on solubility is reverted around 473 K, and at 523 K the solubility decrease as pressure is raised. The predicted behaviour at 573 K is complex, as shown in Figure 6, the solubility of NaCl increases with pressure up to around 350 bar, decreasing at higher pressures.

Unfortunately the Pitzer equation is not useful for predictions out of the range of temperatures and pressures where the parameters have been fitted. As an example, Figure 7 shows the estimated solubility of NaCl at 298 K along with the experimental values up to 10 kbars.
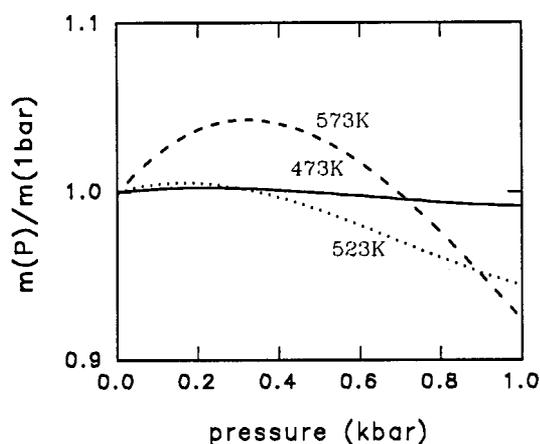
Fig. 6 Solubility of NaCl as a function of pressure at several temperatures as predicted by Pitzer equations (ref. 12)
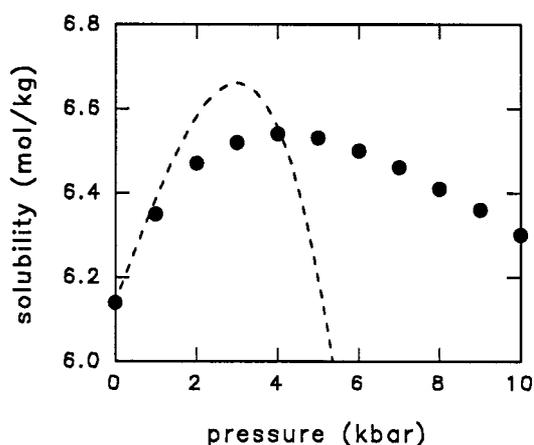

Fig. 7 Solubility of NaCl at 298K as a function of pressure Experimental results from ref. 30 (●). Dashed line correspond to predicted values.

A different approach to the estimation of pressure effect on salt solubility is the use of a primitive model (continuum solvent), such as MSA, for the electrostatic contribution to the partial molar volume combined with a hard sphere term which consideres the solvent on a molecular basis. Thus, the excess partial molar volume of the electrolyte can be calculated with the relationship:

$$V_2^{ex} = V_2^{ex,MSA} + V_2^{ex,HS} + \Delta V_2^{LRMM} \tag{11}$$

where the first term on the right side is the electrostatic contribution to V_2. The following expressions for the excess partial molar volume and the derivative of $\ln \gamma_\pm$ of an electrolyte have been derived from the mean spherical approximation (31):

$$V_2^{ex,MSA} = -\frac{3}{2}\nu kT \ln \gamma_\pm \left(\frac{\partial \ln \epsilon}{\partial p}\right)_{T,\rho_2} - kT\kappa_T \left(\frac{\alpha^2 P_n^2}{4\rho_2 \Delta^3 \Omega} + \frac{\rho_2 \Phi^2}{4\pi\Psi}\right) \tag{12}$$

$$\frac{\partial \ln \gamma_\pm}{\partial \rho_2} = -\frac{\alpha^2 P_n^2}{4\nu\rho_2^2 \Delta^3 \Omega} - \frac{\Phi^2}{4\pi\nu\Psi} \tag{13}$$

where ρ_2 is the particle density of ions in the solution, simply related to the salt molality. Φ and Ψ are functions of the particle densities and diameters.
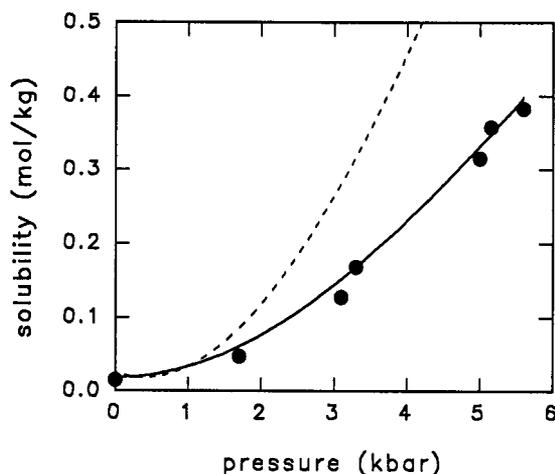
Fig. 8 Solubility of gypsum as a function of pressure at 298K. Dashed line correspond to the undissociated case ($K_a=0$). Full line calculated with $K_a =200$, $\sigma_-=4.75$ A and $\sigma_+=4.00$ A. Experimental results from ref.24

The first term in Eqn.[12] is important at infinite dilution and the limiting slope for the MSA partial molar volume of the electrolyte is equal to that given by the Debye-Hückel theory.

The the hard sphere contribution to the partial molar volume is calculated from the equation of Mansoori et al (32) for the pressure of a mixture of an ion i and the solvent (s), recalling that $V_i/\kappa_T = (\partial p/\partial \rho_i)_T$.

Finally, the last term in Eqn.[11] accounts for the convertion from the McMillan-Mayer to the Lewis-Randall reference system. For the sake of simplicity we have ignored this contribution which is only important (higher than 1 cm^3) at temperatures above 473K (10).

It has been probed that this approach is able to describe the excess partial volume of electrolytes at high temperatures and pressures for concentrations up to around 1 molal. It will be used here to assess the effect of pressure on salt solubility, by resorting to Eqn.[11] and to the infinite dilution partial volume of the electrolyte, obtained from the HKF equations.

Figure 8 shows the results obtained for the solubilty of gypsum at 298K as a function of pressure compared to the experimental results (33). It can be seen that the agreement is good if ionic association is allowed (Ka=200 was assumed), in such a way that ion pairs contribute to the hard sphere part of V_2 with a diameter which was taken as the sum of the ionic components.

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