

Zinc Sulfide Solubility Modeling in Aqueous Solution at High Temperature, Pressure, and Ionic Strength

Xin Wang, Zhaoyi Dai, Yue Zhao, Chong Dai, Saebom Ko, Samridhdi Paudyal, Xuanzhu Yao, Cianna Leschied, Amy T. Kan, and Mason B. Tomson
Rice University - Brine Chemistry Consortium
6100 Main Street.
Houston, Texas, 77005

ABSTRACT

In this study, the solubility of zinc sulfide has been collected from the literature at pH 2 to 11, temperature 23 to 250 °C, pressure 0.6 to 150 bar, and ionic strength 0 to 4.6 m. A solubility model has been developed based on the combination of Pitzer theory calculated activity coefficient and speciation of the Zn-HS-OH-Cl aqueous system. In total, around 230 solubility data were collected as the input database, the model was fitted in Matalab 2020a with the particle-swarm optimization. The updated model is able to predict the ZnS solubility saturation index (SI) with 95% confidence interval 0.04 SI unit, which suggested good accuracy under model conditions. Due to the extremely low solubility of the ZnS itself, these errors correspond to only around 0.07 ppm of [Zn(II)], which is less than the error of measurement for field samples. For all pH conditions, Zn-HS complexes and Zn-Cl complexes have strong influence on the aqueous soluble zinc solubility. This new model with accurate ZnS solubility prediction will help field operators to better control the ZnS scaling and corrosion problem.

Keywords: zinc sulfide, scale, solubility modeling, high temperature, high pressure, high TDS, ion complexes

INTRODUCTION

The increasing need for fossil fuels has resulted in more aggressive drilling and exploitation in oil and gas production industry ^{1,2}. As new explorations at more extreme conditions (i.e. high temperature and high pressure) become more frequent, new challenges arise in terms of drilling equipment, operation conditions and safe production ³⁻⁶. Among those challenges, the mineral scale deposition, as one of the serious problems both for the surface and subsurface oilfields, can cause pipelines plugging, equipment failure and decrease in production efficiency, even emergency shutdown ⁶⁻¹⁰. Compared to the conventional drilling conditions, the scaling problems in these extreme conditions are mainly caused by changes in temperature and pressure during the production. The rapid temperature and pressure drop from the reservoir to the surface: 1. alters the equilibrium of the ions in the formation water; 2. causes water evaporation; and 3. redistributes the balance with CO₂ and/or H₂S gases. These changes result in mineral scale formation ^{6,11,12}.

In addition to the common oilfield scales such as barite, calcite and gypsum, zinc sulfide (ZnS) and lead sulfide (PbS) have been observed in high-temperature and high-pressure oil and gas fields. These sulfides are often referred to as “exotic” scales ^{8,12}. Due to their extremely low solubilities, which is even orders of magnitude lower than iron sulfide ^{10,13,14}, ZnS and PbS scale are easy to form and almost inevitable under oilfield conditions. Also, since solubility of both ZnS and PbS decrease with decreased temperature, they form easily in the pipelines during transportation from the downhole to the surface ¹⁵⁻¹⁷. These exotic scales have become an increased concern in a number of oil and gas fields within the North Sea and the Gulf of Mexico: the zinc and lead ion concentrations within the formation of Gulf of Mexico were reported to be as high as 245 ppm and 70 ppm ^{12,16,18}.

The presence of zinc also influences the scale control strategies of other minerals. It was found that even a few ppm of Zn ions could significantly improve the inhibition efficiency of the phosphonate inhibitor (i.e. DTPMP, BHPMP) to stop the barite scale precipitation ¹⁹. The presence of zinc sulfide was found to accelerate CO₂ corrosion and the formation of CaCO₃ scaling, which subsequently increased the requirement of both the scale and the corrosion inhibitor ²⁰.

Even though there is an urgent need for accurate ZnS scale control strategies at elevated temperature, pressure, and TDS, the solubility prediction of zinc sulfide challenging due to the complexity of the zinc and sulfide chemistry in brine solutions. The zinc ion is very active in brine and can undergo complicated speciation with chloride, sulfide and hydroxide anions ^{6,21}. The complexation of Zn-Cl-OH-HS system have been studied frequently with various methods including solubility modeling, voltammetry and EXAFS ^{13,22-26}. Unfortunately, these studies do not agree with each other well, and the stoichiometry and the stability constant of zinc aqueous complexes still have large uncertainties ^{13,21}. These aqueous complexes are important to the calculation of total soluble Zn(II). The concentration of free Zn²⁺ is usually about 10⁵ to 10⁷ times lower than the total soluble Zn(II) in seawater conditions ²⁴. It is suggested that the

major soluble Zn(II) species in the produced water is the stable aqueous complexes with chloride and bisulfide ions ⁶. The produced water from Elgin-Franklin Field in the North Sea has reported a high concentration of chloride (170 g/L), which also found ZnS formation in the field ^{6,12}. Due to the fact that chloride and bisulfide form stable species, causes large uncertainty in the solubility modeling of the zinc sulfide.

To fill the gap mentioned above, in this study, the solubility and the speciation of zinc sulfide has been studied by combining literature study and modeling. After careful review and data cleaning, the solubility data of ZnS has been collected from the literature at pH from 2 to 11, temperature from 23 to 250°C, pressure from 0.6 to 150 bar, and ionic strength 0 to 4.6 m. A novel ZnS solubility model has been developed based on the combination of the Pitzer theory and the speciation of Zn-HS-OH-Cl aqueous system. This new model is able to predict the ZnS solubility saturation index with 95% confidence interval ± 0.04 SI unit, which suggests good accuracy under model conditions. Due to the extremely low solubility of the ZnS itself, these errors only correspond to around 0.07 ppm of [Zn(II)], which is much less than the error of measurement for field samples. This model has been included in our recent version of ScaleSoftPitzer.

Solubility model of ZnS

At equilibrium conditions, the solubility product of ZnS can be expressed as in equation (1)

$$\text{ZnS} + \text{H}^+ \rightarrow \text{Zn}^{2+} + \text{HS}^- \quad K_{sp,\text{ZnS}}(T, P) = \frac{[\text{Zn}^{2+}]_{eq} [\text{HS}^-]_{eq} \gamma_{\text{Zn}^{2+}} \gamma_{\text{HS}^-}}{a_{\text{H}^+}} \quad (1)$$

Similar to other sulfide scale models, due to the large uncertainty of the second dissociation constant of hydrogen sulfide, the solubility product constant of the zinc sulfide is usually expressed with a proton addition and bisulfide release ^{21,27}. Thus, the saturation index of zinc sulfide can be expressed as in equation (2), below. If the solution is at equilibrium with ZnS solid, the SI should be 0.

$$SI_{\text{ZnS}} \equiv \log_{10} \frac{[\text{Zn}^{2+}]_{eq} [\text{HS}^-]_{eq} \gamma_{\text{Zn}^{2+}} \gamma_{\text{HS}^-} (T, P, \text{Composition})}{a_{\text{H}^+} K_{sp,\text{ZnS}}(T, P)} = 0 \quad (2)$$

As in equation (2), the saturation index of ZnS is a function of solubility product (K_{sp}), ion concentrations, and the activity coefficient (γ) of each species and the activity of the hydrogen ion (a_{H^+}). Since the measured pH is related to the hydrogen ion activity, it is customary to use only activity for the hydrogen ion. Where the activity coefficients are also function of temperature, pressure and composition, which is fitted by Pitzer model in this study. The solubility product is a function of temperature and pressure, only. The temperature dependence of zinc sulfide from various literature sources are plotted in Figure 1 ^{21,24,28,29}. All the values are re-calculated with the format of the reaction in equation (1), and the

first order dissociation constant of H₂S from Suleimenov and Seward (1997)²⁷. Most experimentally measured solubility products agreed well with each other up to 150 °C ($\Delta \log_{10} K_{sp} = 0.2$). At higher temperatures the deviation is relatively larger ($\Delta \log_{10} K_{sp} = 0.5$ at 250 °C). Due to the extremely low solubility, these differences are still acceptable. Thus, in this study, the temperature dependence of zinc sulfide reported by Tagirov and Seward (2010) is used for solubility modeling, as shown in equation (3). The pressure dependence of zinc sulfide is fitted from Solmineq 88³⁰, as shown in equation (4).

$$pK_{sp,ZnS} = -138.1059 + 8665.5519/TK + 21.0391 * \ln(TK) \quad (3)$$

$$\Delta \log_{10} K_{sp,ZnS}^P = -(0.198 + 9.4 * 10^{-6} * TC + 9.142 * 10^{-16} * TC^6) * P_{bar}/500 \quad (4)$$

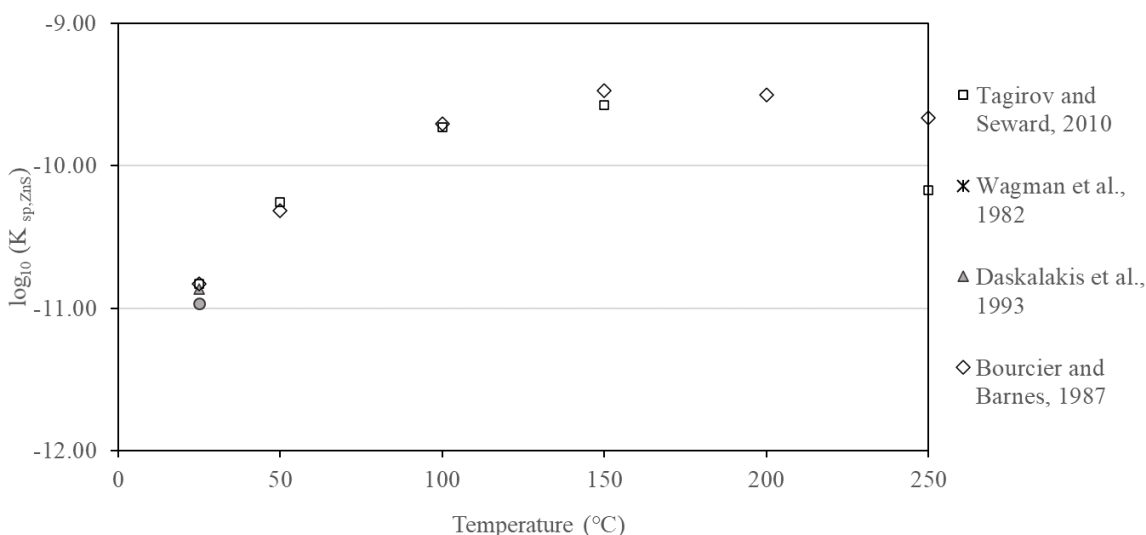


Figure 1, Solubility product constant of zinc sulfide from different literature sources.

As mentioned previously, the speciation of the Zn-Cl-OH-HS system is not in good agreement with respect to the major species and their stability constants, especially for the Zn-HS-S complexes and Zn-OH complexes. Thus, in this study the speciation of Zn-Cl-OH-HS system has been calculated based on B-dot method^{30–32}. Under common conditions, the Zn(II) concentration is usually orders of magnitude lower than the total sulfide concentration, and therefore zinc will have negligible influence on sulfide speciation. Thus, with the B-dot approach, the equilibrium zinc and bisulfide ions used in the saturation index calculation were determined via equations (5) to (7).

$$[HS^-]_{eq} = [total\ S(-II)] / \left(1 + \frac{a_{H^+} \cdot \gamma_{HS^-}}{\gamma_{H_2S} \cdot K_{a1,H_2S}} \right) \quad (5)$$

$$[Zn^{2+}]_{eq} = [total\ Zn(II)] / (1 + Z_{Cl} + Z_{HS} + Z_{OH}) \quad (6)$$

$$Z_Y(Y = \text{OH}, \text{HS or Cl}) = \sum_{n=1}^4 (\beta_n \gamma_{\text{Zn}}^* \gamma_Y^{*n} * [\text{Y}]_{\text{eq}}^n) / \gamma_{\text{ZnY}_n}^* \quad (7)$$

Where Z_Y represent the contribution of the zinc and anion Y complexes. The γ_i^* represents (Solmineq88 notation) the activity coefficient of the subscripted species, which are calculated using Solmineq88 B-dot approach³⁰. The β values with temperature dependence, represent the overall association constant of the corresponding complex, as shown in equations (8) and (9). The β coefficient for Zn-Cl (including ZnCl^+ , ZnCl_2 , ZnCl_3^- , ZnCl_4^{2-}) speciation were fitted based on Solmineq88³⁰, also included in our previous research⁶. The β coefficient for Zn-HS (including Zn(HS)^+ , Zn(HS)_2 , Zn(HS)_3^- , Zn(HS)_4^{2-}) and Zn-OH (including Zn(OH)^+ , Zn(OH)_2 , Zn(OH)_3^- , Zn(OH)_4^{2-}) are fitted in this work.

$$\text{Zn}^{2+} + n\text{Y}^- (\text{Y}^- = \text{Cl}^-, \text{OH}^-, \text{or HS}^-) \rightarrow \text{ZnY}_n^{2-n} \quad \beta_{\text{ZnY}_n^{2-n}} = \frac{[\text{ZnY}_n^{2-n}] * \gamma_{\text{ZnY}_n}^*}{[\text{Y}^-]^n * [\text{Zn}^{2+}] * \gamma_{\text{Zn}}^* \gamma_{\text{Y}}^{*n}} \quad (8)$$

$$\log_{10} \beta (\text{TK}) = z_1 + \frac{z_2}{\text{TK}} + z_3 * \log(\text{TK}) + z_4 * \text{TK} + z_5 * \text{TK}^2 + z_6 * \text{TK}^3 + z_7 * \text{TK}^4 + z_8 * \text{TK}^5 \quad (9)$$

The activity of hydrogen ion (a_{H^+}) is also involved in the saturation index calculation. A potential source of error in pH measurement is the residual liquid junction potential (RLJP), which is the difference of junction potentials between the standard solutions and the experimental solution. The RLJP would be especially important at high ionic strength conditions^{33,34}, which would be important in the field brine conditions. In this study, the junction potential was corrected as in equation (10).

$$\text{pH} = \text{pH}_m + 0.129 * (\text{IS})^{0.5} \quad (10)$$

Where pH_m is the measured pH value, reported in literature; IS is the ionic strength of the solution in molality (mol/Kg H_2O); and pH is the true pH value to be used in model calculations.

The objective of this modeling process is to minimize the summation of the square of the SI values by adjusting the temperature dependent β values of Zn-HS and Zn-OH complexes, and temperature dependent parameters of the Zn^{2+} -HS⁻, Zn^{2+} -Cl⁻ coefficient (i.e., $\beta^{(0)}_{\text{ZnHS}}$, $\beta^{(1)}_{\text{ZnHS}}$ and $\beta^{(2)}_{\text{ZnHS}}$). The optimization process was conducted with the particle swarm algorithm on Matlab 2020a.

RESULTS and DISCUSSION

Solubility modeling of ZnS

The solubility data of zinc sulfide along with the corresponding testing conditions and their suggested major complexes are summarized in Table 1. After careful review, only the solubility data that have clear water composition (including all other ion like Na^+ , Cl^-), pH, pressure, temperature and solid phase identified as pure sphalerite were selected for solubility modeling. Thus, the data from Hayashi et al. (1990), Tagirov et al. (2007) and Tagirov and Seward (2010) were selected in our modeling^{13,21,23}.