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The effect of temperature and ionic strength on iron carbonate ($FeCO_3$) solubility limit

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ABSTRACT

In CO_2 corrosion, precipitation of iron carbonate can significantly reduce the corrosion rate of the underlying steel. Precipitation rate depends on a reliable calculation of the iron carbonate solubility limit. The open literature does not provide an expression for iron carbonate solubility that covers a wide enough range of parameters. In this study a unified iron carbonate solubility (K_{sp} in mol^2/L^2) expression is developed based on the literature data:

$$\log K_{sp} = -59.3498 - 0.041377T_k - \frac{2.1963}{T_k} + 24.5724\log(T_k) + 2.518I^{0.5} - 0.657I$$

which accounts for both temperature and ionic strength effects. The predictions made with this unified equation agree well with the published experimental data.

1. Introduction

The thermodynamics of iron carbonate ($FeCO_3$), also called siderite, has been studied in many research fields, such as geology, oceanography, sedimentology, water treatment, and is of high importance in carbon dioxide (CO_2) corrosion [1–11] of mild steel. Solid iron carbonate precipitates in an aqueous solution, when the concentrations of Fe^{2+} and CO_3^{2-} ions exceed the solubility limit K_{sp} (also called the solubility product constant).

$$Fe^{2+}_{(aq)} + CO^{2-}_{3(aq)} \rightarrow FeCO_{3(s)} \tag{1}$$

In CO_2 corrosion, this precipitation can significantly reduce the corrosion rate of the underlying steel. It is therefore important to determine the precipitation rate which heavily depends on a reliable calculation of the iron carbonate solubility limit. A number of research studies [1–3,6–20] have been dedicated to the investigation of iron carbonate solubility at different conditions. However, none of them presented an expression for iron carbonate solubility that covers a wide enough range of parameters required for example in CO_2 corrosion. Therefore, as a part of a larger project focusing on the precipitation of iron carbonate as related to CO_2 corrosion of oil and gas pipelines made from mild steel, this study aimed at developing a more general expression for iron carbonate solubility based on the literature data.

The solubility limit K_{sp} (in mol^2/L^2) which is a function of both temperature and ionic strength can be obtained from the experimental results using the following expression [13]:

$$K_{sp} = [Fe^{2+}][CO_3^{2-}] = f(T, I) \tag{2}$$

where $[Fe^{2+}]$ and $[CO_3^{2-}]$ are the equilibrium aqueous concentrations of Fe^{2+} and CO_3^{2-} in the solution in mol/L, i.e. those at the solubility limit. The ionic strength is defined as [14]:

$$I = \frac{1}{2}\sum_i c_i z_i^2 = \frac{1}{2}(c_1 z_1^2 + c_2 z_2^2 + \ldots) \tag{3}$$

where c_i are the concentrations of different species in the aqueous solution, all of which are in mol/L, and z_i are the species charges.

2. Overview of the previous studies

The rather large body of work on iron carbonate solubility limit previously reported is here divided in three groups:

1. studies of the solubility limit at room temperature and very low ionic strength,
2. studies of the temperature dependence of the solubility limit, and
3. studies of the ionic strength dependence of the solubility limit.

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2.1. Solubility at room temperature and $I \approx 0$

The iron carbonate solubility limit at room temperature and ionic strength $I \approx 0$ is reported to be in the range from 3.72×10^{-11} to 9.33×10^{-12} mol^2/L^2, as shown in Fig. 1. The results, provided by different researchers [1,6–15], were obtained by various experimental techniques, including precipitation of iron carbonate from supersaturated solutions, re-suspension of wet crystals and re-suspension of dry crystals. Theoretically the iron carbonate solubility limit should not be affected by the experimental method. However, Jensen et al. [6] reported that the iron carbonate solubility limit was 3.72×10^{-11} mol^2/L^2 when using wet crystals and 9.33×10^{-12} mol^2/L^2 for dry crystals. When a broader comparison is made, it has been found that other sources of uncertainty may lead to the experimental error. For example, at $T = 25$ °C and $I \approx 0$, Smith [7] found that iron carbonate solubility limit is 1.29×10^{-11} mol^2/L^2; Ptacek and Reardon [8] reported the solubility limit of 1.17×10^{-11} mol^2/L^2 which are both different from 3.72×10^{-11} mol^2/L^2 reported by Jensen et al. [6], while all used the same method of wet crystal re-suspension.

After careful analysis of the various techniques, it has been suggested that when using the wet crystal technique (such as in Jensen and coworkers' experiments [6]) the measurement of Fe^{2+} concentration may lead to an overestimate of the solubility limit. Therefore, the two extreme values reported for the solubility limit: 3.72×10^{-11} and 3.55×10^{-11} mol^2/L^2 (the first two sets of data in Fig. 1), were excluded when calculating the average solubility limit of iron carbonate at room temperature and $I \approx 0$. Accounting for all other reported values as shown in Fig. 1, an average solubility limit for iron carbonate at $T = 25$ °C and $I \approx 0$ is calculated to be 1.28×10^{-11} mol^2/L^2.

2.2. Temperature dependence

Several researchers investigated the effect of temperature on iron carbonate solubility limit by conducting experiments or by using theoretical thermodynamic models. Braun [13] performed experiments to determine the effect of temperature (in the range 30–80 °C) on iron carbonate solubility limit and proposed Eq. (4).

$$\log K_{sp} = -10.2 - 0.0314 T_c \tag{4}$$

Here temperature T_c is in °C. Using this equation to extrapolate iron carbonate solubility limit at room temperature (25 °C and $I \approx 0$) gives 1.04×10^{-11} mol^2/L^2 which is close to the average value identified above.

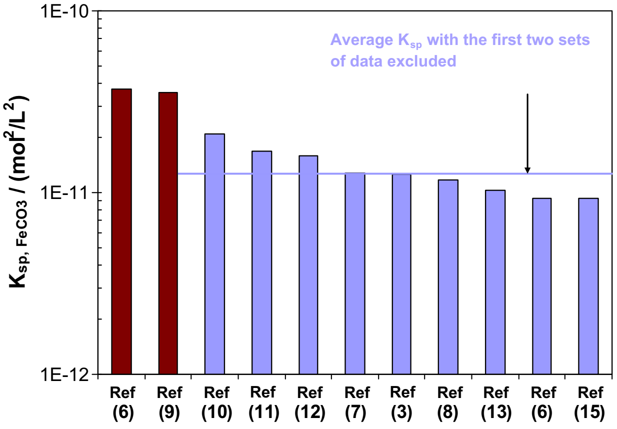

Fig. 1. The published data for iron carbonate solubility limit (shown as bars) at room temperature (25 °C) and ionic strength of $I \approx 0$ and the average value (shown as line) which excludes the first two sets.

Greenberg and Tomson [11] conducted a series of experiments to determine the iron carbonate solubility limit from 25 to 94 °C. The temperature dependence of the solubility constants was fitted to the Eq. (5) as suggested by Nordstrom et al. [1]:

$$\log K_{sp} = a + bT_k + c/T_k + d\log(T_k) \tag{5}$$

using the rigorous nonlinear least squares regression, results in Eq. (6):

$$\log K_{sp} = -59.2385 - 0.041377 T_k - \frac{2.1963}{T_k} + 24.5724\log(T_k) \tag{6}$$

where T_k is in Kelvin.

Besides the temperature dependent experimental data provided by Braun [13], and Greenberg and Tomson [11], several other research groups investigated the iron carbonate solubility limit dependence on temperature by using thermodynamic models. Helgeson [17] calculated the iron carbonate solubility limit in the temperature range from 50 to 300 °C using the van't Hoff equation:

$$\frac{d\ln K_{sp}}{dT_k} = \frac{\Delta H}{RT_k^2} \tag{7}$$

In the equation, K_{sp} at room temperature and $I = 0$ was 2.04×10^{-11} mol^2/L^2. They integrated Eq. (7) to obtain:

$$\begin{aligned}\log K_{sp} = \; & \log K_{298.15} - \tfrac{\Delta H^0}{2.303R}\left(\tfrac{1}{T_k} - \tfrac{1}{298.15}\right) - \tfrac{1}{2.303RT_k}\int_{298.15}^{T_k} \Delta C dT_k \\ & + \tfrac{1}{2.303RT_k}\int_{298.15}^{T_k} \Delta C d\ln T_k\end{aligned} \tag{8}$$

where T_k is the temperature in Kelvin

R is the gas constant, 8.3145 J/mol/K
ΔH^0 is the standard enthalpy of reaction in J/mol
ΔC is the standard heat capacity of reaction in J/mol/K.

In this equation, average heat capacities were employed to estimate the value of ΔC because the required heat capacity functions are not available. Their predicted results (for the temperature range 50–300 °C) were later cited by IUPAC [18]. Based on this work IFE [19] had developed a simplified equation:

$$\log K_{sp} = -10.13 - 0.0182 T_c \tag{9}$$

However, using Eq. (9), the predicted iron carbonate solubility limit at room temperature is 2.60×10^{-11} mol^2/L^2 which is somewhat higher than the value used by Helgeson [17] and much higher than the empirical data.

Marion et al. [2] also determined an iron carbonate solubility limit expression based on van't Hoff equation (7). They assumed that ΔH was a constant ΔH^0 and used the value for $MgCO_3^o$ because ΔH^0 for $FeCO_3^o$ is unknown [2]. This Eq. (8) is simplified to read:

$$\ln K_{sp} = \ln K_{298.15} + \frac{\Delta H^0}{R}\left(\frac{1}{298.15} - \frac{1}{T_k}\right) \tag{10}$$

Eq. (10) can be further simplified:

$$\log K_{sp} = -14.66 + \frac{1365.17}{T_k}. \tag{11}$$

Due to the fact that Marion et al. [2] assumed a constant ΔH^0, serious errors in calculated K_{sp} values occur at the elevated temperatures, as described by Helgeson [17]. At room temperature, iron carbonate solubility limit obtained by using this expression is 8.32×10^{-11} mol^2/L^2 which is much higher than all values reported above.

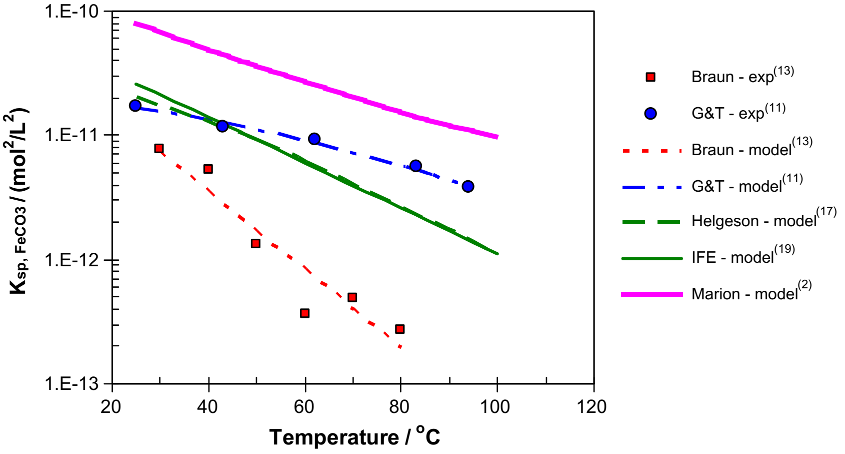

Fig. 2. The experimental and calculated solubility data of iron carbonate vs. temperatures at $I \approx 0$.

Preis and Gamsjager [16] used a similar thermodynamic model to Eq. (8) to predict the iron carbonate solubility limit, which is related to the standard enthalpy of solution ΔH^0 (at 298.15 K) in J/mol and the standard entropy of solution ΔS^0 (at 298.15 K) in J/mol/K by:

$$\log K_{sp} = \frac{\Delta S^0(298.15)}{2.303R} - \frac{\Delta H^0(298.15)}{2.303R}\frac{1}{T_k} - \frac{1}{2.303RT_k}\int_{298.15}^{T_k} \Delta C dT_k + \frac{1}{2.303RT_k}\int_{298.15}^{T_k} \Delta C d\ln T_k \quad (12)$$

However, using their equation in this form turned out to be cumbersome and was not included in the comparisons presented below.

A comparison of the iron carbonate solubility limit experimental data and values calculated by the various expressions discussed above at different temperatures is shown in Fig. 2. It should be noted here that Braun [13] and Greenberg & Tomson [11] empirical data are not in agreement. The reason may be that Braun [13] used an artificial buffer solution in order to control the pH, which might have introduced errors. Hence, Greenberg and Tomson data [11] are considered as being more reliable and were used as a reference for the comparisons below.

When comparing the equations provided by Greenberg and Tomson [11] (Eq. (6)), Helgeson [17] (Eq. (8)), IFE [19] (Eq. (9)) and Marion [2] (Eq. (12)) it can be seen in Fig. 2 that the Greenberg and Tomson [11] expression (Eq. (6)) fits their own experimental data best, and therefore was selected as the basis for the unified model proposed below.

2.3. Ionic strength dependence

There are very few data available for the effect of ionic strength. Silva et al. [3] experimentally investigated the iron carbonate solubility limit as a function of ionic strength in the range $I = 0.1$–5.5 mol/L and proposed the following equation for room temperature (25 °C):

$$\log K_{sp} = -10.9 + 2.518 I^{0.5} - 0.657 I \quad (13)$$

This equation gives similar values as the expression provided by the Norsok Standard [20].

When using the expression of Silva et al. [3] (Eq. (13)) to extrapolate the solubility limit to ionic strength of zero, one obtains 1.26×10^{-11} mol^2/L^2 which is in good agreement with the averaged experimental value reported above.

3. Unified equation

From the literature review, it is found that the Greenberg and Tomson equation [11] is the best choice for describing iron carbonate solubility limit as a function of temperature. It should be noted here that Greenberg and Tomson's experiments [11] used a de-ionized water solution and assumed that ionic strength is zero.

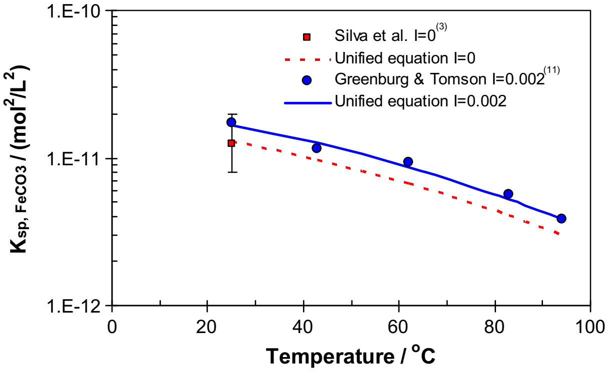

Fig. 3. The experimental and calculated solubility of iron carbonate at different temperatures and ionic strength of 0 and 0.002 mol/L.

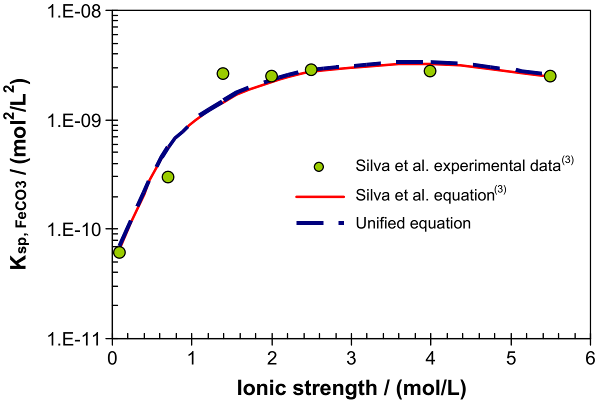

Fig. 4. The experimental and calculated solubility of iron carbonate vs. ionic strength at room temperature.

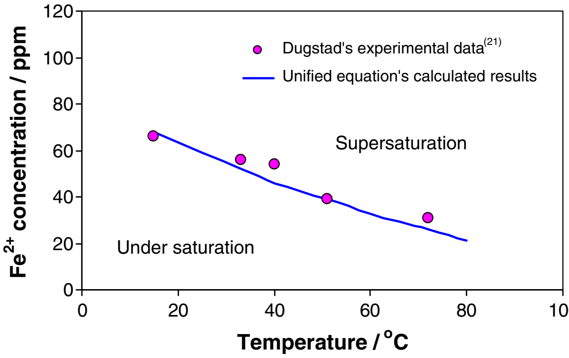

Fig. 5. A comparison of the experimental saturated Fe^{2+} concentration provided by Dugstad [21] and the calculated saturated Fe^{2+} concentration by using the unified equation at different temperatures.

However, it can be calculated that the ionic strength in their aqueous solution was actually $I = 0.002$ mol/L because of the other ions present in the solution, such as H^+, HCO_3^-, CO_3^{2-}, and OH^-, Fe^{2+}. When this is accounted for, a slightly revised equation is obtained:

$$\log K_{sp} = -59.3498 - 0.041377T_k - \frac{2.1963}{T_k} + 24.5724\log(T_k) \tag{14}$$

which is valid for $I \equiv 0$.

When the effect of ionic strength is added by combining the revised Eq. (14) with the Silva et al. [3] Eq. (13), the final unified equation is obtained which now includes the effects of both temperature and ionic strength:

$$\log K_{sp} = -59.3498 - 0.041377T_k - \frac{2.1963}{T_k} + 24.5724 \times \log(T_k) + 2.518I^{0.5} - 0.657I \tag{15}$$

4. Verification

The unified Eq. (15) was compared with empirical data at different temperatures (Fig. 3) and ionic strength (Fig. 4). The predicted values using the new Eq. (15) correlate well with the experimental results provided by Greenberg and Tomson [11] and Silva [3]. The new equation was also employed in a water chemistry model to predict the saturation Fe^{2+} concentration in a CO_2 solution as reported by Dugstad [21]. It was found that the calculated values at different temperatures are in good agreement with the experimental data provided by Dugstad [21] (Fig. 5).

5. Conclusions

A unified iron carbonate solubility expression (15) which accounts for both temperature and ionic strength effects was developed based on the literature data. The predictions made with this unified equation agree well with the published experimental data.

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