Absorption of Sulfur Dioxide in Water with High Salinity

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Understanding the absorption behaviour of sulphur dioxide in aqueous electrolyte solutions is of major interest for the design of flue gas desulphurization processes, as for example wet flue gas desulphurization of coal fired power plants or municipal solid waste incineration plants. In the present paper the influence of the water salinity on SO2 absorption is studied. The SO2 absorption was performed in equilibrium condition. The variation of marine solubility from 10 g/L to 40 g/L determines the variation of SO2 concentration in water from 2.6 mol/L to about 3.2 mol/L. In consequence, the variation of water salinity in these limits can determine a quite big difference of water pollution.

Keywords: SO2, salinity, desulphurization processes

The importance of studied problem consists in the fact that the majority of planet water is of high salinity varying between 12 g/L (Black Sea) and 35 g/L (Atlantic Ocean). It results that the pollution of such waters with SO2 is quite different, varying in large limits [1].

Sulfur dioxide is removed from flue gas by absorption processes because of its toxicity. In fossil-fired power plants at the coast, alkaline seawater is often used as a scrubber agent to chemisorb the acid SO2. In arid regions frequently energy-intensive seawater desalination plants which produce fresh water and brine as a waste product are connected with the power plants. The brine is able to substitute seawater in flue gas desulfurization. However, for the design of such a process, systematic investigations of the influence of ions in the brine on SO2 absorption are lacking. Hence, a reliable process modeling and prediction of the brine’s absorption capacity are not possible. Several working groups have modeled the solubility of SO2 in sea water on the basis of available models. Abdulsattar [3] has modeled the SO2 solubility in seawater in a temperature range from 10 to 25 °C. The activity coefficients of the ions were calculated from the Bromley model using an extended Debye–Hückel term [4], and the activity coefficients of the molecularly dissolved components were determined on basis of the coefficients of Rabe and Harris [5] as well as Garrels and Christ [6]. Al-Enezi [7] investigated the solubility of SO2 in sea water solutions at salinities from 0 to 65 g/kg, temperatures between 10 °C and 40 °C and constant SO2 partial pressure of 22.4 Pa. The applied model is based on the approach of Abdulsattar [3] and includes an extended Debye–Hückel term to describe the activity coefficients. As a result, a quadratic equation of the SO2 solubility was fitted as a function of temperature and salinity. However, the equation allows no extrapolations to other SO2 partial pressures and is therefore limited in their applicability [8-17].

Sulfur dioxide affects the environment in different ways, like direct absorption in water, acid rains and health damages [2, 18-19]. The concentration of SO2 in residual gases emitted by thermal power plants is about 0.15-0.25%. The SO2 concentration can to attain bigger values, like in metallurgical ones (1-2 %).

In contrast to the work cited above, in this work the absorption of SO2 in fundamental binary systems (water + 1 salt) present in seawater was experimentally investigated and modeled first to determine reliable model parameters for the main components of the electrolyte systems seawater.

Theoretical approach

The SO2 absorption in water is a phisicochemical process developed as follows:

\[
\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3 \rightleftharpoons \text{H}^+ + \text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}
\]

(1)

In the equation (1) the proton H+ represents the strongly hydrated ion H3O+.

\[K_1 = \frac{[\text{H}_2\text{SO}_3]}{[\text{SO}_2][\text{H}_2\text{O}]}\]

(2)

\[K_2 = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]}\]

(3)

\[K_3 = \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]}\]

(4)

where: [SO2] is the physically absorbed sulfur dioxide concentration;

[H2SO3] - the chemically absorbed sulfur dioxide concentration;

[HSO3] - concentration of ions resulting from the first step of H2SO3 dissociation;

[SO32-] - concentration of ions resulting from the second step of H2SO3 dissociation;

[H+] - hydrogen ion concentration;

[H2O] - water concentration.

The equilibrium of SO2 - H2O system may be appreciated using the equation [12]:

\[p_{\text{SO2}} = \text{H}^+ \left[\text{SO}_2\right] \left[\text{H}_2\text{SO}_3\right] \]

(5)

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where: \( p_{SO_2} \) represents the equilibrium pressure of sulfur dioxide, 
\( H \) - Henry constant.

The equation (5) can be transformed in a more explicit form:

\[
P_{SO_2} = H S = \frac{1 + K_1}{K_1} \left[ \frac{[H^+]^2}{[H_2O] + [H^+] + K_1} \right]
\]

(6)

where \( S \) represents the sum of chemisorbed species:

\[
S = [H_2SO_3] + [HSO_3^-] + [SO_3^2-]
\]

(7)

and

\[
K_1' = K_1 \cdot \frac{[H_2O]}{[SO_2]}
\]

(8)

Equation (2) highlights the equilibrium concentration of physically absorbed sulfur dioxide:

\[
[SO_2] = \frac{[H_2SO_3]}{K_1 \cdot [H_2O]} - \frac{[H_2SO_3]}{K_1}
\]

(9)

Combining equations (5) and (9) one obtain:

\[
P_{SO_2} = H \left\{ \frac{[H_2SO_3]}{K_1} + \frac{[H_2SO_3]}{K_1} \right\} - H \left\{ \frac{[H_2SO_3]}{K_1} \right\} \left(1 + \frac{1}{K_1} \right)
\]

(10)

The concentration of chemisorbed species [H\(_2\)SO\(_3\)] can be expressed, combining the relations (3), (4) and (7):

\[
[H_2SO_3] = S \frac{[H^+]}{[H^+] + K_1 [H^+] + K_2 [K_3]}
\]

(11)

By substituting the equation (11) in (10) we obtain the equation (6). The equilibrium constants \( K_1 = 1.7 \times 10^4 \) and \( K_2 = 6.2 \times 10^4 \) from equation (6) have the significance of ionization constants, indicating the H\(_2\)SO\(_3\) strength [11]. The low values of ionization constants \( K_1 \) and \( K_2 \) are indicating the weak character of sulfurous acid (H\(_2\)SO\(_3\)). Both constants can be used in calculating the proton concentration after the first and the second ionization step, according to equations:

\[
[H^+] = \sqrt{K_1 [C]}
\]

(12)

\[
[H^+] = \sqrt{K_2 [C]}
\]

(13)

where: \([H^+]\) represents the proton concentration after the first step of ionization; 
\([H^+]\) - the proton concentration after the second step of ionization; 
\([C]\) - the total sulfur dioxide concentration in water.

Considering the equation (6) one can see the correlation between SO\(_2\) equilibrium pressure, the solution pH and temperature (\( K_1 \) and \( K_2 \) are functions of temperature). This dependence can be put in evidence experimentally.

**Experimental part**

The absorption of SO\(_2\) in water was experimented in a device presented in figure 1 [16]. It contains a SO\(_2\) measurement vessel (1) having the volume \( V \) and an absorption vessel (2) whose volume is \( v \), a mercury manometer (3) and a water manometer (4). The mercury manometer is used for high SO\(_2\) concentrations and the water manometer for low SO\(_2\) concentrations. The order of operations is the following: by slowly opening the tap (8) a vacuum (\( \Delta h_1 \)) is made in the vessel (1). Then closing the tap (8) and opening the tap (5) pure SO\(_2\) is introduced, establishing the initial pressure. Closing the tap (5) and opening the tap (9) the communication between the vessel (1) and (2) is established, permitting the SO\(_2\) absorption in the absorbent contained in the vessel (2) till the equilibrium is attained. The SO\(_2\) absorption determines the creation of a vacuum (\( \Delta h_2 \)). Knowing \( \Delta h_1 \) and \( \Delta h_2 \) values and the amount of absorbent (g), a point on equilibrium diagram can be represented.

Let’s consider the following example. The volume \( V = 370 \, cm^3 \), \( v = 30 \, cm^3 \), \( \Delta h_1 = 300 \, mm \, Hg \), \( \Delta h_2 = 53 \, mm \, Hg \).

In these conditions the SO\(_2\) volume \( V_T \) introduced in the vessel (1) is:

\[
V_T = V \cdot \frac{\Delta h_1}{P_T} = 370 \cdot \frac{300}{760} = 146 \, cm^3
\]

where \( P_T \) is the total pressure (for example the atmospheric one).

The absorbed SO\(_2\) volume is \( V_{abs} \)

\[
V_{abs} = (V + v) \cdot \frac{\Delta h_2}{P_T} = \frac{370 + 30}{760} \cdot 53 = 27.9 \, cm^3
\]

The non-absorbed SO\(_2\) volume \( v \) is

\[
v = V_T - V_{abs} = 146 - 27.9 = 118.1 \, cm^3
\]

The equilibrium SO\(_2\) pressure \( \Delta h_e \) is:
Knowing the amount of absorbent \( g = 3 \text{g H}_2\text{O} \), the \( \text{SO}_2 \) concentration \( C_{\text{SO}_2} \) can be calculated (in \( \text{g SO}_2/1000 \text{ g H}_2\text{O} \)) as follows:

\[
C_{\text{SO}_2} = \frac{27.9 \text{g cm}^3}{22400 \text{cm}^3/\text{mol}} \times \frac{64 \text{g SO}_2}{\text{mol}} \times \frac{1000}{3} = 26.5 \text{g SO}_2/1000 \text{g H}_2\text{O}
\]

**Results and discussions**

The experimental method permits to determine the following equilibrium curves:

1) The dependence of sulfur dioxid concentration in liquid phase, \( C_{\text{SO}_2} \) [mol/L] on sulfur dioxid partial pressure, \( p_{\text{SO}_2} \) [mm Hg] at different water salinity \( S \) [g/L] (fig. 2) and

2) The dependence of sulfur dioxid concentration in liquid phase \( C_{\text{SO}_2} \) [mol/L] on water salinity \( S \) [g/L]. (fig. 3)

From the figure 2 one can see that the \( \text{SO}_2 \) concentration in liquid phase is decreasing when the salinity \( S \) is increasing. This dependence results also from the figure 2. The knowing of these dependences permits to establish the \( \text{SO}_2 \) pollution in different conditions.

The results obtained are presented in figure 3 as an equilibrium diagramme between the solubility of water \( S \) [g/L] and \( \text{SO}_2 \) concentration \( C_{\text{SO}_2} \) [mol/L]. The variation of marine solubility from 10 g/L to 40 g/L determines the variation of \( \text{SO}_2 \) concentration in water from 2.6 mol/L to about 3.2 mol/L. In consequence, the variation of water salinity in these limits can determine a quite big difference of water pollution.

**Conclusions**

The study reveals a big influence of salinity of water on \( \text{SO}_2 \) concentration in water, showing that even at big salinity (40 g/L) the concentration is big enough to create the conditions for natural waters acidification. The \( \text{SO}_2 \) concentration determined by \( \text{SO}_2 \) absorption from polluting gases can attain 26.5 g/1000 g water. This concentration is quite low for water acidification because of weak character of \( \text{H}_2\text{SO}_3 \), resulting from \( \text{SO}_2 \) absorption. Unfortunately in natural waters there are favorable conditions for \( \text{SO}_2 \) oxidation, conducting finally to \( \text{H}_2\text{SO}_4 \) formation. Only 0.5 \( \text{H}_2\text{SO}_4 \) g/1000gH\(_2\text{O}\) can determin the value of water pH about 3, damaging the fauna and flora. In order to put in evidence the influence of \( \text{SO}_2 \) partial pressure and temperature on \( \text{SO}_2 \) concentration in water, equilibrium diagrams have been determined. These diagrams can be also used to design \( \text{SO}_2 \) absorption devices.

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