Effect of Temperature and Sulfur Dioxide Pressure on Natural Water Pollution

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This study presents an investigation concerning the influence of temperature and sulfur dioxide partial pressure on natural water pollution. In order to put in evidence this influence equilibrium diagrams have been determined in a wide range of temperature (10-60°C) covering a sulfur dioxide pressure interval between 50-800 mm Hg. A thermostated vacuum installation has been used permitting the direct pressure measurement at equilibrium. The results show a big influence of temperature on water acidification, especially in the presence of some cations having a catalytic action on sulfur dioxide oxidation.

Keywords: sulfur dioxide absorption, water pollution, water acidification, absorption equilibrium

Sulfur dioxide emissions generated as a result of combustion of fossil fuel, especially in thermal power plants, represent one of the most important atmosphere pollutant. It is estimated that almost 65 million tons of sulfur per year enter the atmosphere, polluting the vegetation and water sources [1, 2]. Big quantities of sulfur dioxide enter the lakes poisoning the flora and the living beings [3].

Sulfur dioxide affects the environmental in different ways like acid rains, corrosion of plants and health damages. The concentration of sulfur dioxide in residual gases emitted by thermal power plants is low (0.15-0.25%). In some industrial plants the sulfur dioxide concentration can attain much bigger values, like in metallurgical ones (1-2%). In such cases the residual gases must be purified using different methods especially alkaline solutions [4-6].

In the present paper the influence of SO_2 partial pressure and temperature on water acidification are studied, showing the influence of these parameters on SO_2 absorption process in equilibrium conditions.

Theoretical approach

The absorption of sulfur dioxide in water is a physicochemical process, developing according to [7], in the equation (1) the proton H^+ represents the strongly hidrated ion H_3O^+.

$$SO_2 + H_2O \overset{K_1}{\leftrightarrow} H_2SO_3 \overset{K_2}{\leftrightarrow} H^+ + HSO_3^- \overset{K_3}{\leftrightarrow} H^+ + SO_3^{2-} \quad (1)$$

K_1, K_2 and K_3 representing the equilibrium constants:

$$K_1 = \frac{[H_2SO_3]}{[SO_2][H_2O]} \quad (2)$$

$$K_2 = \frac{[H^+][HSO_3^-]}{[H_2SO_3]} \quad (3)$$

$$K_3 = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} \quad (4)$$

where:

$[SO_2]$ is the physically absorbed sulfur dioxide concentration;

$[H_2SO_3]$ - the chemically absorbed sulfur dioxide concentration;

$[HSO_3^-]$ - concentration of ions resulting from the first step of H_2SO_3 dissociation;

$[SO_3^{2-}]$ - concentration of ions resulting from the second step of H_2SO_3 dissociation;

$[H^+]$ – hydrogen ion concentration;

$[H_2O]$ - water concentration.

The equilibrium of SO_2 - H_2O system may be appreciated using the equation [8]:

$$p_{SO_2(e)} = H\{[SO_2] + [H_2SO_3]\} \quad (5)$$

where:

$p_{SO_2(e)}$ represents the equilibrium pressure of sulfur dioxide,

H - Henry constant.

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

$$p_{SO_2(e)} = HS\frac{1+K_1^{'}}{K_1^{'}}\frac{[H^+]^2}{[H^+]^2 + K_2[H^+] + K_2K_3} \quad (6)$$

where S represents the sum of chemisorbed species:

$$S = [H_2SO_3] + [HSO_3^-] + [SO_2^{2-}] \quad (7)$$

and $K_1^{'}$ is the ratio between chemically and physically absorbed species:

$$K_1^{'} = K_1[H_2O] = \frac{[H_2SO_3]}{[SO_2]} \quad (8)$$

Equation (2) put in evidence the equilibrium concentration of physically absorbed sulfur dioxide:

$$[SO_2] = \frac{[H_2SO_3]}{K_1[H_2O]} = \frac{[H_2SO_3]}{K_1^{'}} \quad (9)$$

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

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$$p_{SO_2} = H\{\frac{[H_2SO_3]}{K_1^{'}} + [H_2SO_3]\} = H\{[H_2SO_3]\frac{1+K_1^{'}}{K_1^{'}}\} \quad (10)$$

The concentration of chemisorbed species *[H_2SO_3]* can be expressed, combining the relations (3), (4) and (7):

$$[H_2SO_3] = S\frac{[H^+]}{[H^+]^2 + K_2[H^+] + K_2K_3} \quad (11)$$

By substituting the equations (11) in (10) one obtain the equation (6).

The equilibrium constants $K_2 = 1.7 \times 10^{-2}$ and $K_3 = 6.2 \times 10^{-8}$ from equation (6) have the significance of ionization constants, indicating the H_2SO_3 strength [7].

The low values of ionization constants K_2 and K_3 are indicating the weak character of sulfurous acid (H_2SO_3). Both constants can be used in calculating the proton concentration after the first and the second ionization step, according to equations:

$$[H^+]_1 = \sqrt{[C]K_2} \quad (12)$$

$$[H^+]_2 = \sqrt{[C]K_3} \quad (13)$$

where:

[H^+]$_1$ represents the proton concentration after the first step of ionization;

[H^+]$_2$ - 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_2 and K_3 are functions of temperature).

This dependence can be put in evidence experimentally.

Experimental part

The adopted equipment for water-SO_2 equilibrium study (fig.1) contains a SO_2 measurement vessel (1) having the volume V, 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 (Δh_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 (Δh_2). Knowing Δh_1 and Δh_2 values and the amount of absorbent (g), a point on equilibrium diagram can be represented.

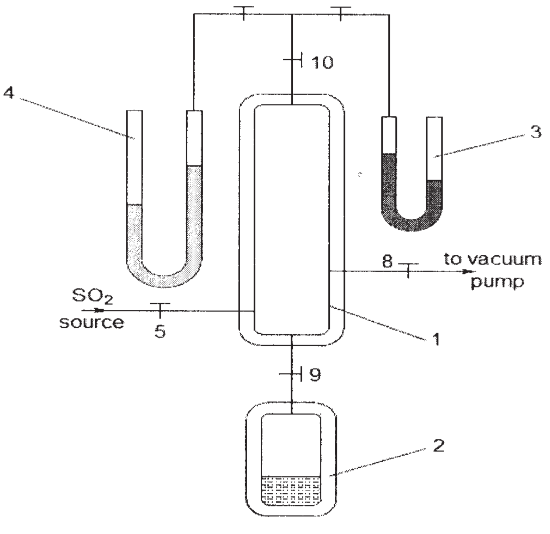

Fig. 1. Experimental device for water-SO_2 equilibrium study
1 – thermostated vessel; 2 – thermostated absorption vessel;
3 – mercury manometer; 4 – water manometer;
5, 6, 7, 8, 9, 10 – taps

Let's consider the following example. The volume V = 370 cm^3, v = 30 cm^3, Δh_1=300 mm Hg, Δh_2=53 mm Hg. In these conditions the SO_2 volume V_T introduced in the vessel (1) is:

$$V_T = V\frac{\Delta h_1}{P_T} = 370\frac{300}{760} = 146 \text{ cm}^3$$

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

The absorbed SO_2 volume is: v_{abs}

$$v_{abs} = (V+v)\frac{\Delta h_2}{P_T} = (370+30)\frac{53}{760} = 27.9 \text{ cm}^3$$

The non-absorbed SO_2 volume v_r is

$$v_r = V_T - v_{abs} = 146 - 27.9 = 118.1 \text{ cm}^3$$

The equilibrium SO_2 pressure Δh_e is:

$$\Delta h_e = p_e = \Delta h_1\frac{V}{V+v} - \Delta h_2 = 300\frac{370}{370+30} - 53 = 225 \text{ mm Hg}$$

Knowing the amount of absorbent *g* = 3g H_2O, the SO_2 concentration C_{SO2} can be calculated (in g SO_2/1000 g H_2O) as follows:

$$C_{SO_2} = \frac{27.9[cm^3]}{22400[cm^3/mol]}64\left[\frac{gSO_2}{mol}\right]\frac{1000}{3} = \\ = 26.5[gSO_2/1000gH_2O]$$

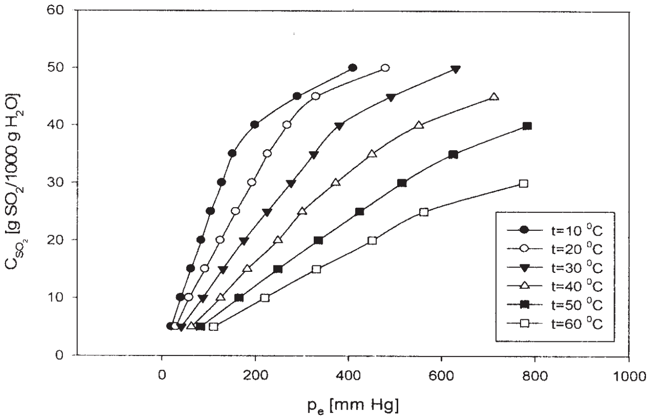

Fig. 2. Correlation between sulfur dioxide concentration in liquid phase C_{SO2} and partial SO_2 pressure p_e at equilibrium

The obtained point on the equilibrium diagram in coordinates C_{SO2} [g/L]-p_e [mm Hg] is (26.5; 225).

In the same manner can be calculated the other points on the equilibrium diagram (fig. 2).

Results and discussions

The equilibrium diagrams of water-SO_2 system, obtained using the installation described in figure 1, are presented in figure 2. One can notice the big influence of temperature and SO_2 pressure on SO_2 concentration in water. This influence can be put better in evidence examining the diagrams presented in figure 3. At low temperatures the water pollution can be important even at low pressure. For instance, at 10°C and 20 mm Hg, the SO_2 concentration in

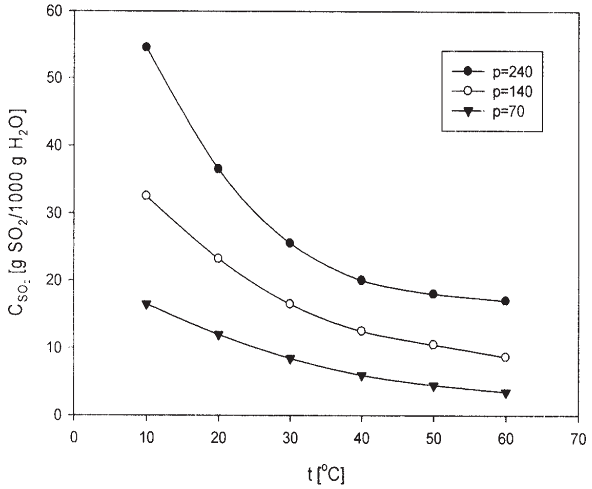

Fig. 3. Dependence of C_{SO2} on temperature at different SO_2 equilibrium pressures

water can attain 5g/1000g H_2O. The SO_2 concentration in air corresponding to 20 mm Hg is about 2.6%.

The concentration of SO_2 emitted by thermal power plants is low (0.2-0.25%), rarely surpassing 0.4%. The partial SO_2 pressure corresponding to this concentration is about 1.5 mm Hg and 3 mm Hg for 0.2% and 0.4% SO_2 respectively. Experimentally has been shown that using gases containing 0.2% SO_2 the equilibrium concentration of SO_2 in water can attain 0.32g SO_2/1000g H_2O at 10°C. In such conditions the water acidification is insignificant. For instance if the initial water pH is 7, after SO_2 absorption the pH decreases to 6.7. Unfortunately, in atmospheric conditions the water pH in similar conditions can attain values between 2.5—3.0. In Finland, for instance, the major part of lakes has became “dead” due to the atmospheric conditions, the polluting gases emitted by North England power plants being directed to Scandinavian lands.

The explanation of this phenomenon is the following. The presence in water, even in traces, of some metals like Zn^{2+} and Fe^{2+} can determine the catalytic reactions, [9, 10]:

$$Zn+O_2 \xrightarrow{H_2O} H_2 O_2 +Zn(OH)_2 \quad (14)$$

$$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+HO^{-}+HO^{*} \quad (15)$$

$$Fe^{3+}+H_2O_2 \rightarrow [Fe(OOH)]^{2+}+H^{+} \quad (16)$$

$$[Fe(OOH)]^{2+} \rightarrow Fe^{2+}+HO_2^{*} \quad (17)$$

The reaction (15) determines the formation of HO^* radicals (Fenton effect), [11, 12] having a strong oxidation character. The same oxidative character have the HO_2^* radicals, formed according to reaction (17).

The oxidative character of HO^* and HO_2^* radicals determines the SO_2 oxidation to SO_3, [13]:

$$SO_2 +2\ HO^{*} \rightarrow SO_3 +H_2O \quad (18)$$

producing the water acidification [14,15].

Theoretically the oxidation degree of SO_2 to SO_3 can attain 99.9% at equilibrium. Considering the example presented above, the absorbed SO_2 (0.32g SO_2/1000gH_2O) correspond to about 0.49g H_2SO_4/1000g H_2O. So, the pH value can decrease from 6.7 to 3. That’s why the water acidification can occur even at very low SO_2 concentrations, specific to power plants polluting gases.

Conclusions

The study reveals a big influence of sulfur partial pressure and temperature on SO_2 concentration in water, showing that even at low SO_2 partial pressure and increased temperatures the SO_2 concentration is big enough to create the conditions for natural waters acidification.

The SO_2 concentration determined by SO_2 absorption from polluting gases can attain 0.3-0.5 g/1000g H_2O. This concentration is quite low for water acidification because of weak character of H_2SO_3 resulting from SO_2 absorption. Unfortunately in natural waters there are favorable conditions for SO_2 oxidation, conducting finally to H_2SO_4 formation. Only 0.5 H_2SO_4 g/1000g H_2O can determine the value of water *p*H about 3, damaging the fauna and flora.

In order to put in evidence the influence of SO_2 partial pressure and temperature on SO_2 concentration in water, equilibrium diagrams have been determined. These diagrams can be also used to design SO_2 absorption devices.

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