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Short communication

Sulfur dioxide absorption and desorption by water drops

A. Saboni*, S. Alexandrova

Groupe Ecoulements Transferts de Matière et de Chaleur, LTP, Université de Caen, Dépt GTE, 120 rue de l'Exode 50000 Saint Lô, France

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Abstract

A new model is developed for the absorption and desorption of sulfur dioxide by drops falling through air containing a low concentration of it. The model predictions are compared with published experimental results. We observe that whatever the type of absorption or desorption experiments is, the present model fits the experimental results.

Keywords: Absorption; Sulfur dioxide; Modeling; Drops

1. Introduction

A knowledge of the mass transfer mechanism in the case of gas absorption (from/into) drops is necessary to understand the scavenging of trace gases in clouds, rain and wet scrubbers. Mass transfer between gas phase and water drops depends on the physical and chemical properties of the diffusing gas, the drop size and the hydrodynamics around and inside the moving drops.

The transport of trace gases from the air into the falling drop is controlled by molecular diffusion, as well as by the convective mass transfer outside and inside the falling drops. The internal circulation, generated by the aerodynamic drag on the drop surface, facilitates the redistribution of the absorbed gas [1–4]. For instance, the short residence time of some gases in the atmosphere is due to the fact that these gases are preferentially absorbed by cloud and rain droplets and removed in this way from the air. As a consequence the acidic precipitations are strongly affecting the aquatic deterioration and material degradation, resulting in agricultural productivity, forest growth and known or anticipated effect on human health.

A number of mathematical models has been proposed and many experimental investigations have been carried out in the area of air-pollution control in order to provide better understanding of the scavenging of trace gases in clouds, rain drops, and industrial wet scrubbers. For drops, falling in a well soluble gas medium (in this case the transfer resistance is located in the gas phase), the survey of the published studies [5–10] shows that a number of good numerical models exists, as well as experimental correlations for prediction of the mass transfer coefficients in the gas film. For liquid phase controlled resistance, Saboni [4] proposed a model based on local scales, interfacial liquid friction velocity and drop diameter. The model was validated experimentally by Amokrane et al. [11] who compared literature models with the experimental data of Walcek et al. [6], Kaji et al. [7], Altwicker and Lindhjem [8], and Garner and Lane [12]. They found considerable discrepancies between the experimental data and the published models. On the contrary, they observed that the Saboni model [4] fits the experimental data very well. The experimental study and model validation in the case of sulfur dioxide absorption by water drops falling through air containing high gas concentration (few %) has been described in details by Amokrane et al. [11]. The purpose of this article is to test a new model (an extension of our previous model) to predict the SO_2 absorption and desorption by falling drops in air containing low gas concentration of sulfur dioxide.

2. Model formulation

Starting from the expression for mass flux across the interface, we can write

$$V_l \frac{dC_l}{dt} = S_l k_l (C_{li} - C_l) \tag{1}$$

where S_l and V_l are the surface area and the droplet volume respectively, k_l is the local liquid mass transfer coefficient,

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* Corresponding author. Tel.: +33-2-33-77-11-72; fax: +33-2-33-77-11-78.
E-mail address: asaboni@aol.com (A. Saboni).

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Nomenclature

a	radius of drop
C_{D}	drag coefficient
C_{g}	bulk gas concentration
C_{gi}	interface gas concentration
C_{l}	concentration of drop
C_{li}	equilibrium concentration of drop
d	drop diameter
$D_{\mathrm{g,l}}$	molecular diffusivity gas/liquid phase
k_{l}	liquid mass transfer coefficient
k_{g}	gas mass transfer coefficient
Re	Reynolds number
r	radial coordinate
S	surface area
Sc	Schmidt number
Sh	Sherwood number
t	dimensional time
u^*	interfacial liquid friction velocity
U	terminal velocity
V	drop volume
$\rho_{\mathrm{g,l}}$	fluid density (gas/liquid)

C_{li} is the equilibrium concentration at the interface and C_{l} is the average concentration in the drop. Therefore, it is sufficient to know only S_{l}, V_{l} and k_{l} to compute the average concentration in the droplets. However, drops larger than 500 μm are not spherical: this is due to their shape deformation under the action of internal turbulence and oscillation. In this case the most reasonable analysis is to assume that water drop has the radius of a spherical drop of the same volume. So, regardless of the drop diameter, the integration of Eq. (1) leads to the following relation

$$\frac{C_{\mathrm{li}}-C_2}{C_{\mathrm{li}}-C_1} = \exp\left\lfloor -\frac{6k_l}{d}(t_2-t_1)\right\rfloor \tag{2}$$

where d is the drop diameter. According to Saboni [4] and Amokrane et al. [11], the liquid mass transfer coefficient is given as

$$k_{\mathrm{l}} = 0.8\sqrt{\frac{D_{\mathrm{l}}u^*}{d}} \tag{3}$$

with

$$u^* = U\sqrt{\frac{\rho_{\mathrm{g}}}{\rho_{\mathrm{l}}}\frac{C_{\mathrm{D}}}{2}}$$

where D_{l} is the liquid phase molecular diffusivity, u^* the interfacial liquid friction velocity, ρ_{g} the gas density and ρ_{l} the liquid density.

The total drag coefficient, C_{D} can be deduced from the equation proposed by Berry and Pranger [13]:

$$\begin{aligned}\ln(Re) &= -3.126 + 1.013\times\ln(C_{\mathrm{D}}\,Re^2)\\ &\quad -0.01912\times[\ln(C_{\mathrm{D}}\,Re^2)]^2\end{aligned} \tag{4}$$

In this relation, the Reynolds number (Re) ranges between 1 and 3550 and the term $C_{\mathrm{D}}\,Re^2$ between 2.4 and 10^7.

Local equilibrium is supposed at the interface between liquid and gas phase concentration. For this reason and supposing that the pH value does not exceed 5.5 we can write

$$C_{\mathrm{li}} = K_{\mathrm{H}}C_{\mathrm{gi}} + \sqrt{K_{\mathrm{H}}K_{\mathrm{l}}C_{\mathrm{gi}}} \tag{5}$$

where K_{H} and K_{l} are the equilibrium constants and C_{gi} is the gas concentration at the interface.

In addition to equilibrium, mass flux continuity across the interface give the gas concentration at the interface:

$$C_{\mathrm{gi}} = C_{\mathrm{g}\infty} - \frac{k_{\mathrm{l}}}{k_{\mathrm{g}}}(C_{\mathrm{li}}-C_{\mathrm{l}}) = C_{\mathrm{g}\infty} - \frac{k_{\mathrm{l}}\delta_{\mathrm{g}}}{D_{\mathrm{g}}}(C_{\mathrm{li}}-C_{\mathrm{l}}) \tag{6}$$

with

$$\delta_g = \frac{2a}{Sh} \tag{7}$$

where $C_{\mathrm{g}\infty}$ is the bulk gas concentration, k_{g} the local gas mass transfer coefficient D_{g} the gas phase molecular diffusivity.

The gas concentration boundary layer, δ_{g}, is calculated from the expression for the Sherwood number in the gas phase [14,15]:

$$Sh = 1.61 + 0.718\,Re^{0.5}Sc^{0.33} \tag{8}$$

where Sc is the Schmidt number.

Only results for the total sulfur concentration will be presented. $\mathrm{C}_1 = [\mathrm{H_2SO_3}] + [\mathrm{HSO_3}^-] + [\mathrm{SO_3}^{2-}]$, the concentrations of the individual species being obtained from the total concentrations by simple relations (Appendix A).

3. Results and discussion

In order to evaluate the model adequacy, we test the model for the case of low and intermediate gas concentration (the mass transfer resistance is located both in the gas and the aqueous phase). The comparison is made between the model and the experimental results for sulfur dioxide absorption by and desorption from individual large water drops. The model is compared to the Mitra et al. [9] and Mitra and Hannemann [10] experimental results concerning two broad categories of sulfur dioxide absorption. The experiments were carried out in a vertical wind tunnel which allows to freely suspend a single drop in the vertical air stream of the tunnel. In the first category (Mitra et al. [9]) a 2.88 mm radius drop was exposed to a sulfur dioxide–air mixture. Fig. 1 shows the evolution of the average total sulfur dioxide concentration versus the time exposure in the case of 1035 ppbv $\mathrm{SO_2}$ concentration in the gas phase. In Fig. 2 results are reported for the absorption in the case of 97 ppm $\mathrm{SO_2}$ concentration in the gas phase. From Figs. 1 and 2, we observe that the values predicted by the present model are in good agreement with the experimental results. Unfortunately in the case of 97 ppm SO_2 concentration in the gas phase the comparison is limited to a very small range of time, approaching saturation conditions (no experimental results are available at time short enough to test the model). In the second category of experiments (Mitra and Hannemann [10]), a drop initially containing S(IV) was exposed to sulfur-free air to determine the rate of sulfur dioxide desorption. Fig. 3 shows the evolution of the average total sulfur dioxide concentration versus the exposure time for a 3.39×10^{-3} mol/l drop initial concentration. The results obtained from the model agree well with those from experiments.

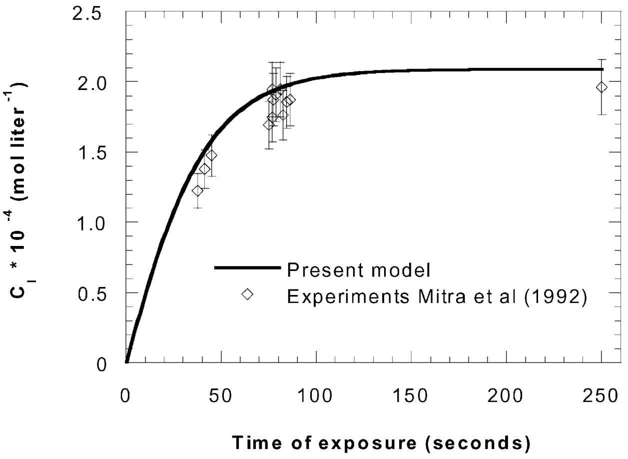

Fig. 1. Concentration within a drop as a function of time of exposure to SO_2 (for a 2.88 mm drop radius, drop temperature = 10°C, $[SO_2]_g = 1035$ ppbv).

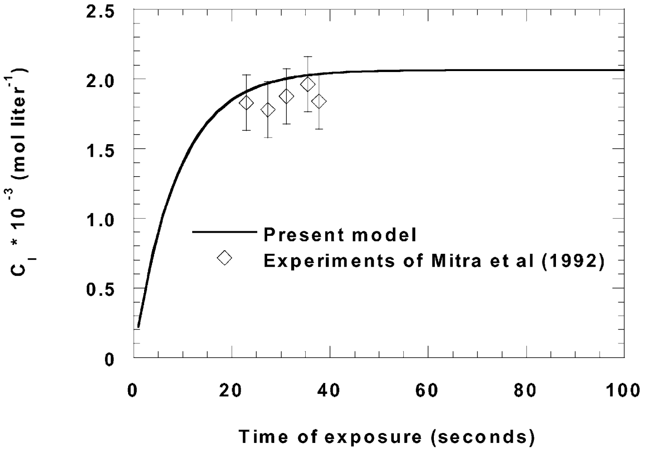

Fig. 2. Concentration within a drop as a function of time of exposure to SO_2 (for a 2.88 mm drop radius, drop temperature = 12.5°C, $[SO_2]_g = 97$ ppm).

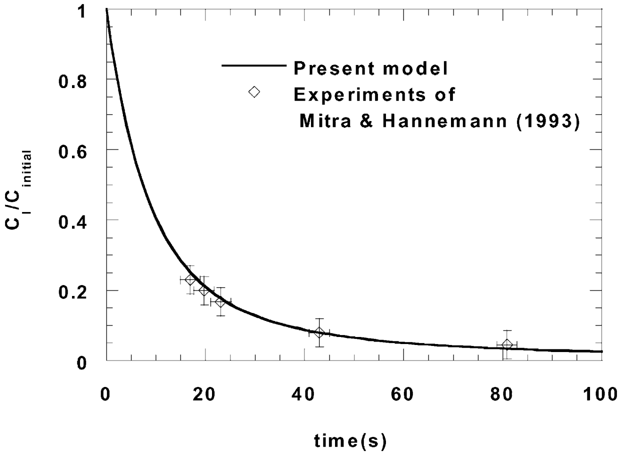

Fig. 3. The variation of the rate C_l/C_{initial} of S(IV) desorption with time exposure SO_2 (for a 2.88 mm drop radius, drop temperature = 15°C, $C_{\text{initial}} = 3.39 \times 10^{-3}$ mol/l).

4. Conclusion

The aim of this article was to present a simple model for prediction of the SO_2 absorption and desorption by falling drops through air with low concentration of sulfur dioxide. In the liquid phase, a model based on local scales, interfacial liquid friction velocity and drop size diameter is used. In the continuous gas phase the well known Beard and Pruppacher [14] model is applied. Data obtained by the modeling of the SO_2 absorption and desorption by a single water drop are compared to published experimental results and a fairly good correspondence was found.

Appendix A. Equilibrium relations for sulfur dioxide in water

When sulfur dioxide is absorbed into water, the resulting equilibrium relations (Walcek et al. [6], Amokrane et al. [11]) are written as

$$SO_2 + H_2O \Leftrightarrow H_2SO_3 \tag{A.1}$$

$$H_2SO_3 + H_2O \Leftrightarrow H_3O^+ + HSO_3{}^- \tag{A.2}$$

$$HSO_3{}^- + H_2O \Leftrightarrow H_3O^+ + SO_3{}^{2-} \tag{A.3}$$

The values of the equilibrium constants K_H (in mol/mol), K_1 and K_2 (in mol/l) of the reactions (A.1), (A.2) and (A.3) are respectively [10,16]

$$K_H = \frac{[H_2SO_3]}{[SO_2]} = 10^{\{(1376.1/T)-4.521\}}RT \tag{A.4}$$

$$K_1 = \frac{[HSO_3{}^-][H_3O^+]}{[H_2SO_3]} = 10^{\{(853/T)-4.74\}} \tag{A.5}$$

$$K_2 = \frac{[SO_3{}^{2-}][H_3O^+]}{[HSO_3{}^-]} = 10^{\{(621.91/T)-9.278\}} \tag{A.6}$$

where T is the temperature expressed in Kelvin.

The total sulfur concentration [S] is written as

$$[S] = [H_2SO_3] + [HSO_3^-] + [SO_3^{2-}] \qquad (A.7)$$

after several manipulations from Eqs. (A.4)–(A.6), together with the following conditions.

Condition of electroneutrality:

$$[H_3O^+] = [OH^-] + [HSO_3^-] + 2[SO_3^{2-}] \qquad (A.8)$$

Condition of water ionization

$$H_2O + H_2O \Leftrightarrow H_3O^+ + OH^- \qquad (A.9)$$

The equilibrium constant of the ionization of water is defined by

$$K_W = [H_3O^+][OH^-]\ (\text{that is } K_W = 10^{-14} \text{ at } 25^\circ\text{C}) \qquad (A.10)$$

The total sulfur concentration as function of pH of the solution is given by:

$$[S] = \left([H_3O^+] - \frac{K_W}{[H_3O^+]}\right) \times \frac{[H_3O^+]^2 + K_1[H_3O^+] + K_1K_2}{K_1[H_3O^+] + 2K_1K_2} \qquad (A.11)$$

For pH < 5.5, reaction (A.3) may be neglected. Thus, the total S concentration is then given by

$$[S] = [H_2SO_3] + [HSO_3^-] = \frac{[H_3O^+]^2 + K_1[H_3O^+]}{K_1} \qquad (A.12)$$

which may be written in this form

$$[S] = [H_2SO_3] + [HSO_3^-] = K_H[SO_2]_g + \sqrt{K_1K_H[SO_2]_g} \qquad (A.13)$$

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