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Discussions

Interactive comment on "Gas-Chromatography using ice coated fused silica-columns: Study of adsorption of sulfur dioxide on water-ice" *by* Stefan Langenberg and Ulrich Schurath

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We thank the referee for reviewing and commenting our discussion paper. The remarks of the reviewer are marked like *this*. To the comments and questions we answer as follows:

Reply to specific comments and questions

- The slow and inexorable "Degradation" of the ice film owing to the carrier gas decompression (pg. 3, lines 19 and 20, and equation (1)) should be explained in a bit more detail. Is this a temperature effect owing to adiabatic decompression across the length

of the capillary? If one has a flow with an equilibrium amount of humidity in the carrier gas one loses this same amount at the exit to first order: What goes must come out at the end of the capillary. What you lose by sublimation is redeposited downstream, provided we are at steady-state and have a uniform temperature profile. What else is implied or important beyond that? Any unaccounted loss processes? Please explain the scientific basis or complications.

The flow through the column is described by Poiseuille's equation for compressible fluids. It is assumed that the temperature of the carrier is permitted to equilibrate with the column wall. Due to the decompression of the carrier gas along the column at constant temperature, the mixing water vapor in equilibrium with the ice surface increases along the flow tube. Therefore, while the mass flow rate of the carrier gas $\dot{n}$ is constant, the mass flow rate of water vapor increases along the ice-coated column.

It is assumed that the water vapor pressure $p(H_2O)$ is in equilibrium with the ice surface. The mass flow of water leaving the column is given by

$$\dot{n}_o(H_2O) = \frac{p(H_2O)\dot{V}_o}{RT}$$

where $\dot{V}_o$ is the volume flow rate of the carrier gas at column exit. It is calculated from the carrier gas mass flow rate $\dot{n}$ and the carrier gas pressure at column exit p_o:

$$\dot{V}_o = \frac{\dot{n}RT}{p_o}.$$

Since the carrier gas entering the column is pre-humidified, the water mass flow entering the column is given by

$$\dot{n}_i(H_2O) = \frac{p(H_2O)\dot{V}_i}{RT}.$$

Due to carrier gas decompression $\dot{V}_i < \dot{V}_o$. Therefore, less water is entering the column

than leaving. Hence, the net rate of water leaving the column is given by

$$\dot{n}(\text{H}_2\text{O}) = \dot{n}_o(\text{H}_2\text{O}) - \dot{n}_i(\text{H}_2\text{O}) = \dot{n}p(\text{H}_2\text{O})\left(\frac{1}{p_o} - \frac{1}{p_i}\right).$$

After calculating $\dot{h}$ from $\dot{n}(\text{H}_2\text{O})$, Eq. (2) is obtained.

We conclude that our adsorption experiments were performed under desublimation conditions with respect to H_2O.

- I strongly suggest the addition of a qualitative explanation for the concentration dependence of the SO_2 retention time displayed in Figure 2. As far as I understand this effect it comes from the (partial) saturation of the SO_2 uptake (at equilibrium): The higher the SO_2 concentration the earlier the breakthrough because of vanishing interaction with the ice owing to surface saturation of the uptake following equation (11) (Langmuir dissociation, strong interaction) and (3) (Henry isotherm, weak interaction).

An explanation has been added to the introduction (p3, l5).

- The Temkin isotherm (equation (5)) seems to be a parametric treatment of the above behavior according to the derivation in the S1 section: Is there any scientifically rooted explanation to simply add algebraically both contributions (Henry + each of the stronger interactions) in all three models displayed in Table 1 as an "interpolation" or superposition scheme of two extremes? The molecular view (saturation to a variable degree depending on the SO_2 partial pressure) naturally arrives at the same result for purely kinetic reasons. Diffusion tube experiments under molecular flow conditions (T. Koch et al., JPCA 1998; C. Alcala-Jornod et al., PCCP 2000; C. Alcala-Jornod et al., JPCA 2004) arrived at the identical saturation behavior of salt and ice interfaces (without the presence of a carrier gas).

As we describe, the modified Temkin and Langmuir isotherms pass over to Henry's law of adsorption at very low concentration. But this type of adsorption must be a stronger chemisorption like adsorption process in contrast to the weaker physisorp-

C3

tion process. Both adsorption processes occur in parallel over the whole concentration range. Therefore, at very low concentration, the effective Henry's adsorption isotherm constant would be $K_H + K_T$. Even in case of dissociative adsorption, a linear adsorption behavior would be expected when $q(\text{H}_3\text{O}^+) > q(\text{HSO}_3^-)$.

- What is the rationale for using "deactivated" (alkyl-silylated) Pyrex as a Substrate to grow the ice sample in the first place? I do not believe that a coating of several micrometers will let the SO_2 "feel" the underlying properties of the substrate. From our own studies of pure ice performing quartz crystal microbalance measurements on the evaporation rate of H_2O from pure ice films result in a value of 80 to 100 nm thick layer beyond which subsurface effects cease to be important. Beyond this thickness the kinetics of evaporation is unchanged up to several micrometer thickness of pure vapor-deposited ice which is believed to be less compact (lower density, more surface imperfections) than ice samples frozen from pure water. By the same token, an interference of the silylated glass interface with ice at several micrometers thickness is highly unlikely (pg. 13, lines 30 and 31, and pg. 15, lines 15 and 16) unless the authors have solid evidence to the contrary.

Due to experimental constraints, about 1 m of the column inside the box remained uncoated. In order to minimize interfering adsorption of SO_2 on the ice-free surface, we used a methylsilyl-deactivated column. This is explained in the revised manuscript (p4, l18). We agree that SO_2 adsorption on the ice coating is not likely to be affected by the properties of the underlying tube surface. It is more likely that certain ice film properties e.g. surface roughness depend on the substrate. Unfortunately the microphysical properties of the ice coatings in our capillary columns could not be probed by our experimental techniques.

- Regarding the strongly tailing peak shapes of the chromatograms for SO_2, and to a lesser extent for acetone: Is this a thermodynamic or kinetic effect? Is the equilibrium between adsorbed and gas phase SO_2 established at low concentrations of SO_2 at constant flow rate?

C4

The most likely cause of the tailing is nonlinear adsorption at low temperature. This is supported by the decreasing adjusted retention times tn with increasing amounts of acetone injected. Therefore, Eq. (18) was used to extrapolate our measurements to zero concentration. However, we cannot exclude additional tailing due to slow incorporation of acetone into the ice surface even at higher temperatures. We assume that adsorption equilibrium of SO_2 on ice is established with respect to physisorption and dissociative adsorption but not with respect to uptake into the ice surface under our experimental conditions.

- As a general remark the units of K_H , K_L and q should be clearly included, at least once when mentioned in the text for the first time. One has to be aware that Henry's adsorption isotherm (K_H) is different from Henry's law solubility constant (gas-bulk partition coefficient)!

K_H, K_T and K_L have the same unit. This makes them comparable between themselves. After first occurrence of the symbols in the text, the unit has been denoted now in the revised manuscript.

The term *Henry's law of adsorption* was adopted from Wikipedia, see https://en.wikipedia.org/wiki/Henry_adsorption_constant: "The Henry adsorption constant is the constant appearing in the linear adsorption isotherm, which formally resembles Henry's law; therefore, it is also called Henry's adsorption isotherm."
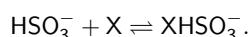
- Regarding the square root dependence of the surface coverage (equation (15) and pg. 8, line 16) the requirement is that the active sites must be NEIGHBORING sites in order to yield the square root dependence.

This is required for the steady state derivation of Eq. (15) given by Huthwelker et. al (2006). However, Eq. (15) is a thermodynamic relation. It can also be derived as follows on a pure thermodynamic base:

We assume that HSO_3^- is trapped by an unknown ice surface defect X. In addition to

<div align="center">C5</div>

equilibrium (R1) there is a second equilibrium

$$HSO_3^- + X \rightleftharpoons XHSO_3^-.$$

The total surface concentration of X is limited to q_S. This equilibrium corresponds to Langmuir adsorption of HSO_3^- on ice.

Reply to proposed technical corrections

- Pg. 2, line 30 and 31: sentence does not make sense!

Fixed.

- Pg. 3, line 20: "...ice film slowly but unavoidably..."

Fixed.

- Pg. 4, lines 15 and 16: Incomplete sentence.

Fixed.

- Pg. 8, line 5: I do not see a temperature effect in Figure 2b. It probably must be Figure 3b.

Fixed.

- Pg. 7, Figure 3: I do not see yellow data points, however there is a yellow (fitted) line.

Due to a strange software error, some points were not colored correctly. A workaround has been applied. A color palette better suited for printout has been chosen.

- Pg. 10, bottom: "miscible".

Fixed.

- Pg. 12, Table 2: units of K_H: $mol\,m^{-2}\,Pa^{-1}$.

<div align="center">C6</div>

$\ln K_H$ must be dimensionless, therefore K_H must be divided by $1 \, \mathrm{mol \, m^{-2} \, Pa^{-1}}$. To clarify this, two braces have been added.

The revised marked-up version of the discussion paper is attached as supplement.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2017-800/acp-2017-800-AC1-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-800, 2017.