Diffusion Coefficient of H2SO4 in Air Laboratory Measurements Using Laminar Flow Technique

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DIFFUSION COEFFICIENT OF H_2SO_4 IN AIR LABORATORY MEASUREMENTS USING LAMINAR FLOW TECHNIQUE

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INTRODUCTION

Sulphate aerosols play an important role in atmospheric chemistry. They have indispensable impact on climate, radiation balance, and human health. In the atmosphere sulphate aerosols are formed due to secondary particle production (gas to particle conversion) from sulphuric acid and water, and participation of trace species like ammonia, amines or other condensable organics. The sulphuric acid diffusion coefficient data have wide application in atmospheric and aerosol mass transfer models.

METHODS

The diffusion coefficient was estimated from the first-order rate coefficients for the wall loss of H_2SO_4. The wall losses were measured as a function of relative humidity (RH) in the range from 2 to 70 % in a laminar flow tube. The chemical ionization mass spectrometer (CIMS) was used to detect the H_2SO_4 concentration in gas phase (Petäjä et al. 2009). The H_2SO_4 loss measurements were carried out at three temperatures 5, 15 and 25°C and atmospheric pressure in a vertically positioned thermostated cylindrical tube with I.D. = 6 cm and length of 200 cm. The sulphuric acid vapour was generated by passing purified dry air through a temperature controlled saturator filled with 95-97 % w. t. H_2SO_4 (Baker) and subsequently mixed with humidified air in a mixer. The vapour gas mixture was then introduced to a laminar flow tube where the H_2SO_4 concentration was measured with CIMS at six different positions along the reactor, see Fig. 1. The wall losses were determined from the slopes of the fits to experimental data in the plot H_2SO_4 concentration as a function of position in the tube, see Fig 2 and 3. To ensure the independence of wall losses on H_2SO_4 concentration the measurements were carried out at different initial H_2SO_4 concentrations (from 10^6 to 10^8 molec cm^{-3}) and different total flow rates (8 - 11 l min^{-1}).

RESULTS AND CONCLUSIONS

In this study the first-order wall losses of sulfuric acid in the laminar flow tube were assumed. To test this presumption we applied the computational fluid dynamics (FLUENTInc., version 6.2) model (Herrmann et al., 2010) . The model is using the infinite sink boundary condition on the wall together with all other parameters (initial $[H_2SO_4]$, T, RH, total flow) used in our experiment. No particle production was assumed in the model. The modelled sulphuric acid losses in the flow tube are compared with experimental values for two relative humidities (RH = 5% and 44%) in Fig 2 and 3. The linear fits to experimental data represent the loss rate coefficients (k_w, cm^{-1}). In both cases the model describes behaviour of sulfuric acid in the flow tube very well. The model predicts in average about 5 % lower values of loss rate coeficient (k_w) than the experiment. Figure 4 shows the measured diffusion coefficients of H_2SO_4 in air as a function of RH and at three temperatures 5, 15 and 25 °C. The measured points are accompanied with the fit to H_2SO_4 - N_2 data at 25 °C published by Hanson and Eisele (2000). The diffusion coefficient values decreased as the RH was increased and the diffusion coefficient dependency on RH flattens in the range of RH = 20-70 %. These results show lower wall losses and slower diffusion to the wall due to strong hydration of H_2SO_4 molecules (Jaecker-Voirol and Mirabel, 1988). The temperature dependency was found to be the power of 5.8 (from theory this should be 1.5) to measured diffusion coefficient when data for the whole range of RH are considered. This discrepancy is possibly due to higher order losses of H_2SO_4 to bigger clusters at lower temperatures and/or presence of impurities like ammonia with subsequent ammoniu-sulfate or -bisulfate creation. The calculated values of diffusion coefficient of H_2SO_4 and ammonium-sulfate in dry air at 25 °C using the Fuller method (Reid et al, 1987) are 0.11 and 0.091 cm^2 s^{-1}, respectively.

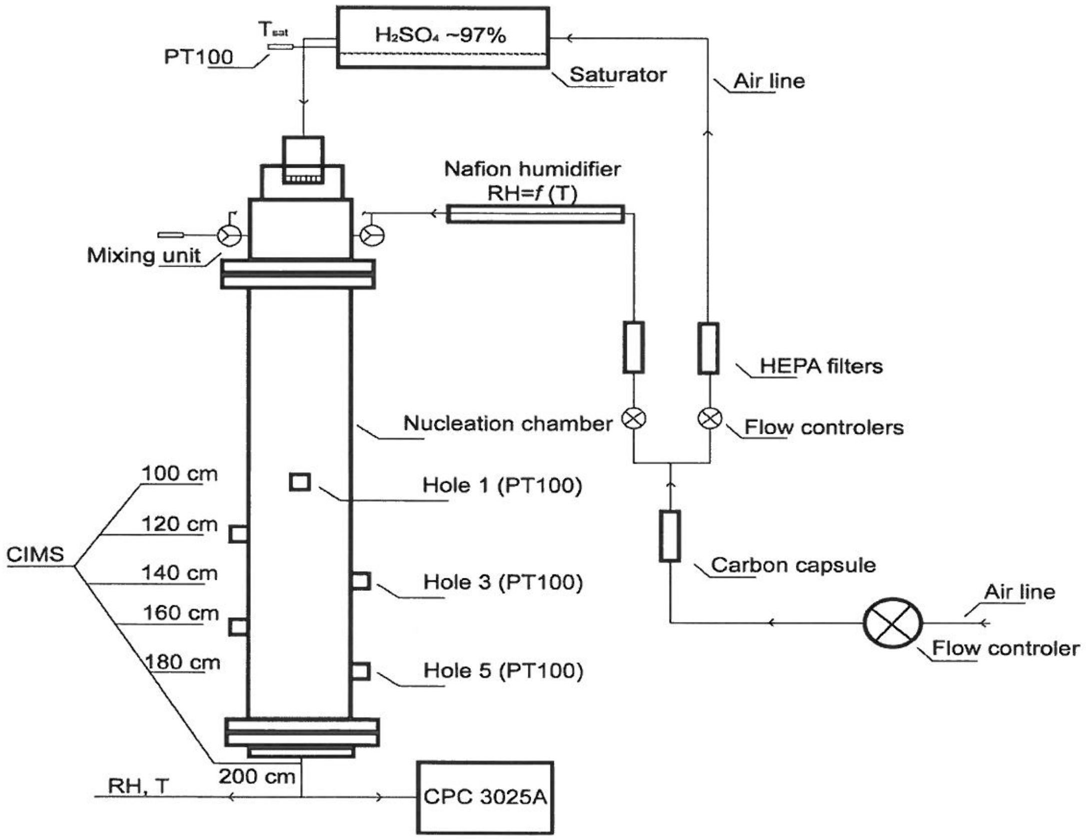

Fig. 1: Schematic figure of the FMI flow tube

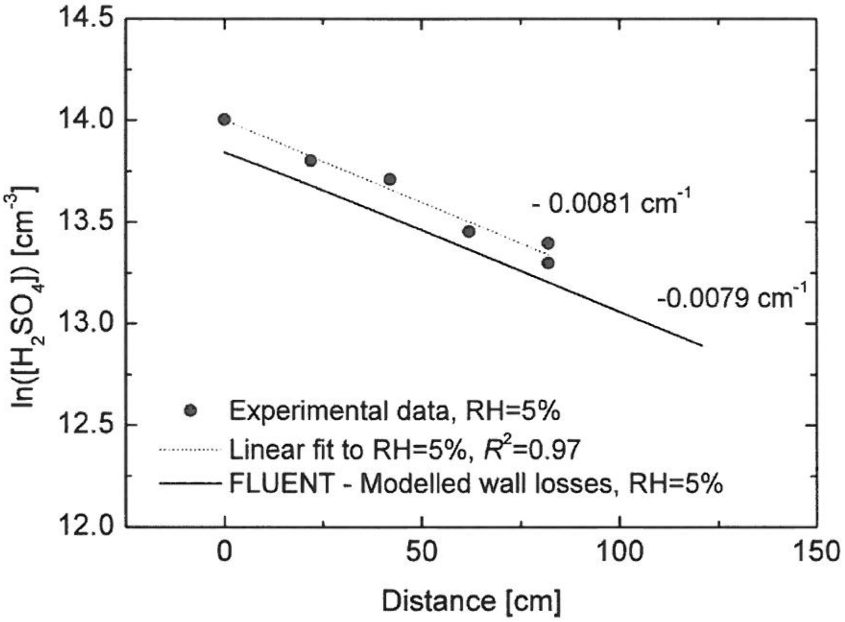

Fig. 2: Losses of sulphuric acid as a function of distance in the flow tube at relative humidity 5% at T 25°C. The wall loss rate coefficients obtained experimentally and with FLUENT modelling are indicated in figures.

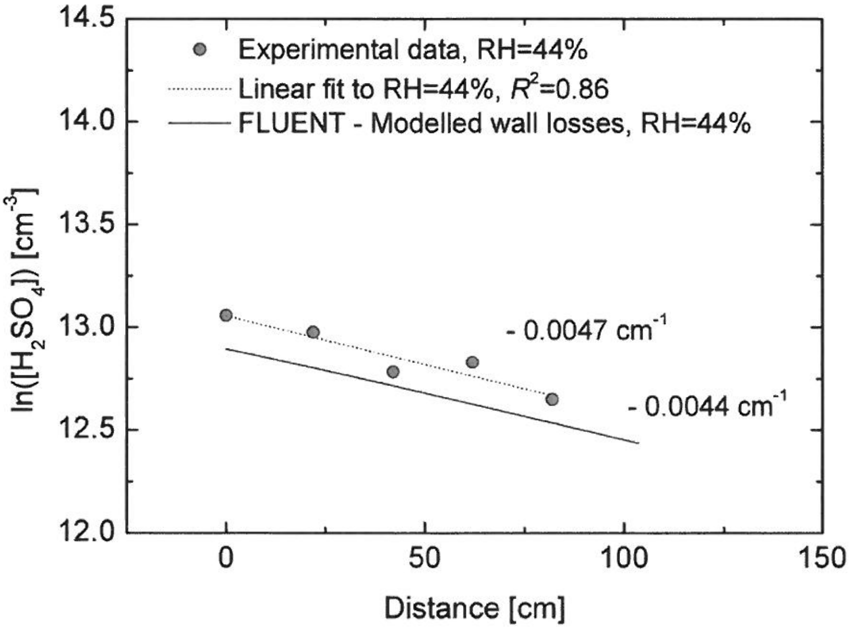

Fig. 3: Losses of sulphuric acid as a function of distance in the flow tube at relative humidity 44% at T 25°C. The wall loss rate coefficients obtained experimentally and with FLUENT modelling are indicated in figures.

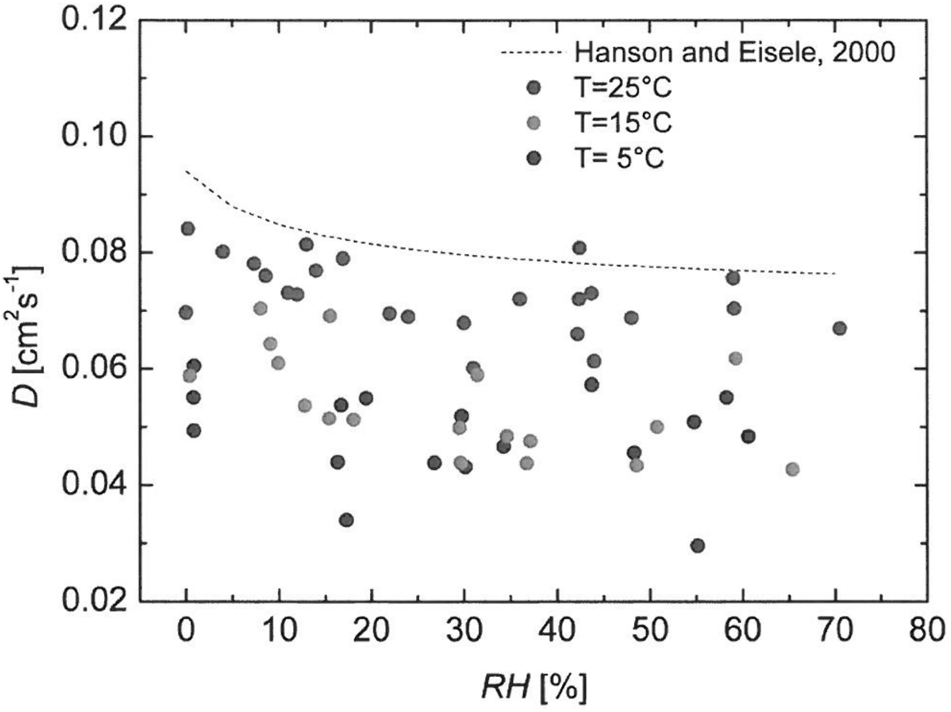

Fig. 4: Diffusion coefficient data of H_2SO_4 in air as a function of relative humidity compared with fit to H_2SO_4 in N_2 data of Hanson and Eisele (2000).

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