A Dynamical Model for Surface Adsorption / Bulk Penetration of Acetic Acid on / into Ice Surfaces in Coated Wall Flow Reactors

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The interaction of acetic acid with ice surfaces at temperatures between 180 – 220 K has been studied using a coated wall flow tube reactor (CWFT) with mass spectroscopic detection of the gas phase acid concentration. With the gas injection probe of the CWFT moved forward and backward we observe consecutive absorption and desorption profiles from which we can extract Langmuir constants and dynamical quantities such as k_{ads} and k_{des} under conditions of fully reversible absorption. The numerical model that we used in this analysis has previously been described (Behr et al., 2004) and applied in studies of the reversible adsorption of acetone (Behr et al., 2006).

In the case of the interaction of acetic acid with ice surfaces we observe more complicated adsorption/desorption profiles, particularly at lower temperatures and for higher gas phase concentrations. Such profiles are characterized by an additional steady state loss of acetic acid at time scales of a few hundred seconds where the simple surface adsorption has long come to equilibrium. This indicates that not only adsorption but also penetration into the bulk phase of the ice film is likely to be operative. In order to extract additional physical information we have hence extended the existing numerical model to include Henry solution and bulk diffusion. In this extended model we assume that the concentration of acetic acid in the sub-surface layer corresponds to the Henry equilibrium concentration with the dynamical constants k_{sol} and k_{seg} accounting for solvation and segregation. The concentrations of acetic acid in the bulk at different depths are then calculated using a numerical solution of Fick`s second law.

The results obtained are consistent with the observations and with approximate values for the Henry constant and diffusion constant of acetic acid in ice as extrapolated from their room temperature values (Sander, 2011; Varotsos and Zellner, 2009).

References

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