Modelling the non-ideal multiphase chemical processing in aqueous aerosol particles with SPACCIM-SpactMod

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Motivation

Highly polluted urban regions are often characterized by high aerosol particle loadings impacting atmospheric chemistry and, hence, air quality. Tropospheric deliquesced particles including haze particles are in a complex multiphase and multi-component environment with simultaneously occurring multiphase chemical transformations. Such chemical processes are able to alter the chemical composition and the deduced physical aerosol properties. Deliquesced haze particles are characterized by concentrated non-ideal solutions that can affect the occurring multiphase chemical processing. The effects of such non-ideal solutions have generally not been adequately investigated by present complex multiphase chemistry models. Thus, the present study is aimed at accessing the impact of non-idealities on multiphase chemical processing.

Model Results & Discussion

- Modelled multiphase H2O
- Modelled multiphase CH2
- Modelled multiphase C2
- Modelled acidify and ionic strength
- Treatment of non-idealities leads to higher Fe2+ concs. (Fig.3) and reaction rate analysis reveals a factor of 2.8 lower Fe2+ cycling.
- Impact on HOx/HOy budget
- Factor of 3.1 larger aqueous concs. of H2O2 on average during the non-cloud periods (Fig.4).
- Fenton reaction with Fe2+ about 70% non-ideal.
- Substantially lower OH concs. in the non-ideal case under aerosol conditions and reaction kinetics analysis shows increased OH rates (Fig.6).
- Glyoxylic and glycolic acid show increased aqueous degradation rates due to the reduction of OH radical.
- Reactivity coefficients of dissociated and undissociated forms are lower leading to lowered reactions.
- Non-idealities significantly affect the chemical fluxes of oxalic acid as a consequence of the reduced activity coefficient effects of the non-ideal urban haze case.
- Reduced decay leads to higher oxalic acid concs.
- Non-ideal treatment enables more realistic predictions of high oxalic acid concentrations under high pollution conditions.

Summary and Outlook

In order to examine the effects of non-ideal solutions on the occurring multiphase chemistry, simulations with SPACCIM-SpactMod are performed [7]. The present study shows that activity coefficients of inorganic ions are often below unity, and that most uncharged organic compounds exhibit activity coefficient values around or even above unity under deliquesced aerosol conditions. The model studies demonstrate that the inclusion of non-idealities considerably affects the multiphase chemical processing of transition metal ions (TMs), key oxidants, and related chemical sub-systems, e.g. organic chemistry. In detail, both the chemical formation and oxidations of TMs are substantially lowered by a factor of 2.8 under polluted haze conditions compared to a case without non-ideal treatment. The reduced Fe2+ processing in the polluted base case, including lower chemical reactions of the Fenton reaction (70%), results in a reduced multiphase H2O2 distribution. Therefore, higher multiphase H2O2 concentrations (~factor of 3.1 larger) and lower aqueous-phase OH concentrations (~factor of 4 lower) are modelled during aerosol conditions. For H2O2, the consequence of non-idealities increases the oxidation fluxes under aqueous aerosol conditions by 40%. Moreover, the chemical fluxes of the OH radical are about 50% lower in the non-ideal urban haze case. Accordingly, the consideration of non-idealities affects the chemical processing and the concentrations of organic compounds in a compound-specific manner. For important organic carbon acids, e.g. glyoxylic acid and oxalic acid, the reduced radical oxidation budget under aqueous particle conditions leads to increased concentration levels. For oxalic acid, the present study demonstrates that the non-ideal treatment enables more realistic predictions of high oxalate concentrations obtained under ambient polluted conditions. Furthermore, the simulations show that lower humidity conditions, i.e. more concentrated solutions, might promote higher oxalic acid concentration levels in aqueous aerosols due to differently affected formation and degradation processes. Overall, the model studies demonstrate the important role of a detailed non-ideal treatment in multiphase models dealing with aqueous aerosol chemistry, and the needs to improve current model implementations.

References


Fig.1: Scheme of the meteorological scenario.

Fig.2: Modelled pH value (left) and ionic strength (right) as functions of the simulation time of the different urban simulation cases (90%-IDU/90%-NIDU and 70%-IDU/70%-NIDU).

Fig.3: Modelled Fe2+ concentrations in ng m^-3 for the different urban simulation cases (top left) and corresponding time evolution of activity coefficients (right).

Fig.4: Modelled aqueous-phase C2 chemistry in the different urban simulation cases (bottom left) and corresponding time evolution of activity coefficients (right).

Fig.5: Modelled CH2OHCOO- concentrations in ng m^-3 for the different urban simulation cases (top left) and corresponding activity coefficients (right).