



**Treatment of non-ideality in the multiphase model SPACCIM**

A. J. Rusumdar et al.

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# Treatment of non-ideality in the multiphase model SPACCIM – Part 1: Model development

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Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	



## Abstract

Ambient tropospheric deliquesced particles generally comprise a complex mixture of electrolytes, organic compounds, and water. Dynamic modeling of physical and chemical processes in this complex matrix is challenging. Thus, up-to-date multiphase chemistry models do generally not consider non-ideal solution effects. Therefore, the present study was aimed at the further development of the SPACCIM model to treat both complex multiphase chemistry and phase transfer processes considering newly non-ideality properties of concentrated aerosol solutions. The present paper describes firstly, the performed model development including (i) the kinetic implementation of the non-ideality in the SPACCIM framework, (ii) the advancements in the coupling scheme of microphysics and multiphase chemistry and (iii) the required adjustments of the numerical schemes, especially in the sparse linear solver and the calculation of the Jacobian. Secondly, results of performed sensitivity investigations are outlined aiming at the evaluation of different activity coefficient modules and the examination of the contributions of different intermolecular forces to the overall activity coefficients. Finally, first results obtained with the new model framework are presented.

The main product of the performed model development is the new kinetic model approach SPACCIM-SpactMod, which utilizes activities in reaction terms instead of aqueous concentrations. Based on an intercomparison of different activity coefficient models and the comparison with experimental data, AIOMFAC was selected as base model and extended by additional interaction parameters from literature for mixed organic-inorganic systems. Moreover, the performance and the capability of the applied activity coefficient module were evaluated by means of water activity measurements, literature data and results of other thermodynamic equilibrium models. Comprehensive comparison studies showed that the SpactMod (SPACCIM activity coefficient module) is valuable to predict the thermodynamic behavior of complex mixtures of multicomponent atmospheric aerosol particles. First simulations with a detailed chemical mechanism have demonstrated the applicability of SPACCIM-SpactMod. The simulations have im-

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### Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



plied that the treatment of non-ideality should be mandatory for modeling multiphase chemistry processes in deliquesced particles. The modeled activity coefficients implicate that turnovers of chemical processes in deliquesced particles can be both decreased and increased depending on the particular species involved in the reactions.

5 For key ions, activity coefficients on the order of 0.1–0.8 and a strong dependency on the charge state as well as the RH conditions are modeled implicating a lowered chemical ion processing in concentrated solutions. In contrast, modeled activity coefficients of organic compounds are partly  $> 1$  and suggest the possibility of an increased organic processing. Moreover, the model runs have shown noticeable differences in the  
10 pH values calculated with and without consideration of non-ideality. On average, the predicted pH values of the simulations considering non-ideality are  $-0.27$  and  $-0.44$  pH units lower under 90 and 70 % RH conditions, respectively. More comprehensive results of detailed SPACCIM-SpactMod studies on the multiphase processing in organic–inorganic mixtures of deliquesced particles are described in a companion paper.

## 1 Introduction

15 The troposphere is a complex multiphase and multicomponent environment with simultaneous occurrence of heterogeneous chemical transformations, which potentially can alter the composition of tropospheric aerosols (Ravishankara, 1997). In order to access the impact of physico-chemical and dynamical processes associated with aerosol particles, a variety of multiphase chemistry mechanisms have been developed and coupled  
20 with atmospheric models (Binkowski and Roselle, 2003; Fast et al., 2006; Seinfeld and Pandis, 2006). During the last decade, some progress was made evaluating the role of chemical aqueous phase processes in deliquesced particles and cloud droplets (see e.g., Hallquist et al., 2009; Tilgner and Herrmann, 2010; Ervens et al., 2011; Tilgner et al., 2013; Guo et al., 2014). Beside the multiphase chemistry developments and findings, the inclusion of reliable thermodynamic modules in multiphase models is required in order to adequately calculate the particle deliquescence, associated water



instead of concentrations and the appropriate calculation methods have to be applied in multiphase chemistry models. Attempts at realistic estimation of activity coefficients can be traced back to extensive literature for inorganic, organic and mixed inorganic-organic solutions (e.g., Clegg et al., 2008; Erdakos et al., 2006; Li et al., 1994; Ming and Russell, 2002; Pitzer, 1991; Prausnitz et al., 1986; Raatikainen and Laaksonen, 2005; Topping et al., 2005a, b; Yan et al., 1999; Zaveri et al., 2005; Zuend et al., 2008, 2011).

Considerable effort has been devoted formerly to develop a number of thermodynamic models with reliable accuracy and efficiency to simulate aerosol thermodynamic equilibrium (e.g. AIM, Clegg et al., 1998b, a, GFEMIN, Ansari and Pandis, 1999, ISORROPIA and ISORROPIA II, Fountoukis and Nenes, 2007; Nenes et al., 1998, EQSAM3, Metzger and Lelieveld, 2007; Metzger et al., 2006, EQUISOLV II, Jacobson, 1997; Jacobson et al., 1996; MARS-A, Binkowski and Roselle, 2003; Saxena et al., 1986, MESA, Zaveri et al., 2005, UHAERO, Amundson et al., 2007, 2006). Various numerical techniques were developed based on direct minimization of Gibbs free energy, which is highly accurate, yet computationally expensive (Ansari and Pandis, 1999; Wexler and Clegg, 2002). Most of these models assume that particles are in thermodynamic equilibrium with the corresponding gas phase, i.e. the mass transfer between the phases is instantaneously. However, this assumption must not be necessarily valid for every compound and condition, for example in case of coarse particles. Therefore, the mass transfer has to be described dynamically (e.g., MADM by Pilinis et al., 2000). Only very few model approaches exist so far, that treat dynamically gas-particle partitioning of inorganic and organic gases coupled to an efficient and accurate thermodynamics module (e.g., MOSAIC by Zaveri et al., 2008, ADCHAM by Roldin et al., 2014). While the interactions between inorganic compounds are relatively well-known, interactions between organic components as well as organic-electrolyte mixtures comprised in complex multiphase systems have remained elusive, due to the large number of organic species with highly variable properties available in the gas phase and ambient particles. Hence, the development of kinetic model frameworks for modeling of processes

**Treatment of non-ideality in the multiphase model SPACCIM**

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



in multicomponent atmospheric particles, which include both a detailed description of organic and inorganic multiphase chemistry, as well as detailed thermodynamic comprehensions of its non-ideal behavior, is an object of intense research all along the last years (see e.g., Ervens et al., 2011; Shrivastava et al., 2011). However, such a kinetic model framework is needed to more precisely examine the role of concentrated aerosol solutions for the chemical processing of aerosol constitutes and the overall secondary mass formation as well as related atmospheric issues.

Therefore, the present study was aimed at the implementation of a combined approach for activity coefficient calculation of mixed solvent electrolyte systems into the Spectral Aerosol Cloud Chemistry Interaction Model (SPACCIM, Wolke et al., 2005). The parcel model SPACCIM was originally developed for the dynamical description of chemical and microphysical cloud processes. SPACCIM was successfully applied in several process studies using the complex multiphase mechanism CAPRAM (Bräuer et al., 2013; Herrmann et al., 2005; Tilgner et al., 2013; Tilgner and Herrmann, 2010).

In this paper, we present an extended model approach for the kinetic description of phase transfer and complex multiphase chemistry considering the non-ideality of solutions by means of activity coefficient models. The outline of this paper is as follows: the kinetic description of non-ideality in SPACCIM is elaborated in the beginning of Sect. 2. Afterwards, the coupling scheme and, particularly, the feedback of multiphase chemistry on microphysics are specified. The necessary adjustments of numerical schemes are outlined and discussed afterwards. In Sect. 2.3, the activity coefficient module is introduced, that is specifically designed to treat multicomponent mixed organic–inorganic aerosol particles. Section 3 presents an evaluation of the currently implemented activity coefficient module in SPACCIM. In order to validate the model performance and the capability, the model results were compared with available measurements and other thermodynamic equilibrium models such as mod. LIFAC (Kiepe et al., 2006), E-AIM (Clegg et al., 1998b, a), and AIOMFAC (Zuend et al., 2011, 2008; <http://www.aiomfac.caltech.edu/>). Furthermore, Sect. 3 presents sensitivity studies on

## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the importance of the different interactions and first model results obtained with the new model framework.

## 2 Methodology and model development

### 2.1 Multiphase model SPACCIM (original code)

In this section, a brief summary is provided for the methods used in SPACCIM original code and the current limitations are outlined. The air parcel model SPACCIM was developed for the description of simultaneously occurring chemical and physical processes in cloud droplets and deliquesced particles. Thus, SPACCIM combines a complex multiphase chemistry model with a detailed cloud microphysics for a size-resolved particle/droplet spectrum in a box model framework (Wolke et al., 2005). Depending on the used microphysical model, external and internal mixing of aerosol can be taken into account. The activation of droplets is explicitly described. Either the movement of the air parcel can follow a predefined trajectory (e.g., simulated by a 3-D atmospheric model) or the vertical velocity is calculated based on the parcel updraft compared to prescribed environmental conditions. Entrainment and detrainment processes are considered in a parameterized form. The model allows a detailed description of the processing of gases and particles shortly before cloud formation, during the cloud life time and shortly after cloud evaporation (Sehili et al., 2005).

All microphysical parameters needed by the multiphase chemistry are taken over from the microphysical model. For this purpose, an advanced coupling scheme between microphysical and multiphase chemical models is implemented. The coupling scheme provides time-interpolated values of the microphysical parameters (temperature, water vapor, liquid water content) and time-averaged mass fluxes between different droplet classes caused by microphysical processes (e.g., by aggregation, break up, condensation). Changes of the chemical aerosol composition by gas scavenging and chemical reactions feed back on the microphysical processes (e.g., water con-

## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



densation growth rates via changes in the Raoult term). The multiphase chemistry is performed for ideal solutions assuming well-mixed droplets. Activity coefficients and the diffusion inside of the droplets are not considered. Dissociations are described dynamically as forward and backward reactions. The used chemical mechanism (including phase transfer data and kinetic reaction constants) is given as an input file. Therefore, a high flexibility concerning changes in the chemical mechanism or the replacement of the entire reaction system is guaranteed. For further details, the reader is referred to the original publication by (Wolke et al., 2005). The performance of the model was shown for both simple chemical mechanisms considering inorganic chemistry only and for very complex mechanisms of the CAPRAM family, which contain a detailed description of the inorganic and organic chemistry (Bräuer et al., 2013; Herrmann et al., 2005; Tilgner et al., 2013; Tilgner and Herrmann, 2010).

In the published version of SPACCIM (Wolke et al., 2005), the influence of non-ideality on multiphase processing was not considered. In fact, the assumption of an ideal solution is not valid particularly for deliquescent particles, where highly concentrated solutions are typical present. Accordingly, the chemical reaction terms in the aqueous phase chemistry have to be modified by using the activities and therefore an activity coefficient module has to be added. Furthermore, the feedback approach is enhanced by using the calculated water activity for the Raoult term and by the consideration of surface tension effects. The changes in the model code are given in the following subsection.

## 2.2 Further development of SPACCIM

### 2.2.1 Mass balance equations

For the consideration of non-ideality effects in SPACCIM, it is required that rate expressions have to be written in terms of species activities, rather than mole fractions or concentrations. The activity  $a_i$  of species  $i$  can be expressed by  $a_i = \gamma_i \cdot m_i = \gamma_i \cdot c_i / L$  where  $\gamma_i$  denotes the molality based activity coefficient,  $m_i$  the molality and  $c_i$  the mass



concentration of an aqueous phase species  $i$ . The liquid water content  $L$  is given as the water volume fraction in the corresponding box volume. In the proposed approach, the non-ideal behavior is taken into account by means of activity coefficients. It should be emphasized that the activity coefficient  $\gamma_i$  depends usually on the concentrations of all species dissolved in the solution.

In Eqs. (1) and (2), the mass balance equations of the modified version of SPACCIM extended by the treatment of non-ideality are presented. Mainly, the aqueous concentrations in the original mass balance equations of the SPACCIM (see Eqs. 1 and 2 in Wolke et al., 2005) are replaced by corresponding activities.

The description of both microphysical and multiphase chemical processes is performed for a size-resolved particle/cloud droplet spectrum, which is subdivided into several classes  $k = 1, \dots, M$ . In each particle/droplet class,  $N_A$  aqueous phase species are treated, which are not necessarily identical to the number of gas phase species  $N_G$ . In the parcel model SPACCIM, the prognostic equations for the mass concentrations of a gas phase chemical species  $c_{j^*}^G$  and an aqueous phase chemical species  $c_l^k$  in the  $k$ th class have to take into account the chemical productions and degradations, phase transfers, mass transport between different classes caused by microphysical processes, and ent-/detrainment. These processes can be described by the following mass balance equations:

$$\frac{d(c_{j^*}^G)}{dt} = \underbrace{R_{j^*}^G(t, c_1^G, \dots, c_{N_G}^G)}_{\text{gas phase chemistry}} - \underbrace{\kappa_l \sum_k L_k k_t^{k/l} \left[ c_{j^*}^G - \frac{a_l^k}{H_l} \right]}_{\text{phase transfer}} + \underbrace{\mu [c_{j^*}^G - c^{G_{\text{ent}}}]}_{\text{entrainment/outflow}}, \quad (2)$$

**Treatment of non-ideality in the multiphase model SPACCIM**

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



$$\frac{d(c_l^k)}{dt} = \underbrace{L_k R_l^A(t, a_1^k, \dots, a_{N_A}^k)}_{\text{aqueous phase chemistry}} + \underbrace{\kappa_l L_k k_t^{k/l} \left[ c_{l^*}^G - \frac{a_l^k}{H_l} \right]}_{\text{phase transfer}} + \underbrace{F(c_l^1, \dots, c_l^M)}_{\text{mass transfer by microphysics}} + \underbrace{\mu [c_l^k - c_l^{k_{\text{ent}}}]}_{\text{entrainment/outflow}}, \quad (3)$$

with  $l^* = 1, \dots, N_G; l = 1, \dots, N_A; k = 1, \dots, M$ .

In the above formulation,  $L_k$  denotes the volume fraction [ $V_k/V_{\text{box}}$ ] of the  $k$ th droplet class inside the box volume. The values  $a_l^k, k = 1, \dots, M$ , represent the activities of species  $l$  in the  $k$ th liquid water fraction. The vector  $c^G$  stands for the concentrations of the gas phase species and  $k_t^{k/l}$  is the mass transfer coefficient. The chemical reaction terms of the corresponding species are denoted by  $R_{l^*}^G$  and  $R_l^A$ . The second term on the right-hand side of the aforementioned equations describe the change of mass concentration of the soluble species due to phase transfer between the gas phase and particle/cloud droplet classes. Hence, this term will be referred to as the Henry term in the following. The value  $H_l$  denotes here the dimensionless Henry's law coefficient for the species  $l$ . The prefactor  $\kappa_l$  of the Henry term is a solubility index and defined to be equal to 1 as well as 0 for soluble and insoluble species, respectively (see Wolke et al., 2005). The term  $F(c_l^1, \dots, c_l^M)$  in Eq. (3) stands for the mass transfer between different droplet classes by microphysical exchange processes (e.g. by aggregation, break up, condensation). The time-dependent natural and anthropogenic emissions as well as dry and wet deposition are parameterized in the last terms of the right hand sides using a time dependent entrainment/detrainment rate  $\mu$ . One should note that, above-mentioned mass balance equations are not only limited to "non-ideal" approach. Whenever, the activity coefficients are defined as unity then this numerical model formulation will reduce to the original version of SPACCIM.

**Treatment of non-ideality in the multiphase model SPACCIM**

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 2.2.2 Reaction kinetics

The first terms  $R_j^G$  and  $R_j^A$  in the right hand sides of the mass balance Eqs. (2) and (3) comprise the chemical transformations (production and degradation fluxes). However, the reaction term included in Eq. (2) is only a function of concentrations of gas phase species. Since, the gas phase mixture is assumed to be behaving as an ideal gas phase mixture, the non-ideality is not considered in this term.

Suppose, for an irreversible reaction  $A+B \rightarrow C+D$  in the aqueous phase, the reaction rate  $r_A$  can be written while considering the non-ideality as follows:

$$r_A = -k_A \cdot [a_A] \cdot [a_B] = -k_A \cdot \gamma_A [A] \cdot \gamma_B [B]. \quad (4)$$

Here, the activities of  $A$ ,  $B$ ,  $C$ , and  $D$  are used instead of the concentrations. The activity of  $A$  ( $a_A$ ) is proportional to its molar concentration (either molality based or mole fraction based)  $[A]$ , where the proportional constant is the activity coefficient  $\gamma_A$  of that particular species. The treatment of non-ideality was also considered for equilibrium reaction types, which should be explained with the generic example shown as:



The relative quantities (i.e. thermodynamic activities) of reactants and products in an equilibrium reaction are determined from the equilibrium relation,

$$\sum_i \{a_i\}^{\lambda_i \nu_i} = \frac{\{A\}^{\nu_A} \cdot \{B\}^{\nu_B}}{\{C\}^{\nu_C} \cdot \{D\}^{\nu_D}} = \frac{(\gamma_A^{\nu_A} \cdot [A]^{\nu_A}) \cdot (\gamma_B^{\nu_B} \cdot [B]^{\nu_B})}{(\gamma_C^{\nu_C} \cdot [C]^{\nu_C}) \cdot (\gamma_D^{\nu_D} \cdot [D]^{\nu_D})} = K_{\text{eq}}, \quad (6)$$

where  $K_{\text{eq}}$  called as equilibrium coefficient,  $\{a_i\}$  is the thermodynamic activity of species  $i$ ,  $\{A\}$ , etc., are individual thermodynamic activities,  $\lambda_i = +1$  for products, and  $\lambda_i = -1$  for reactants. As mentioned earlier, activity of a species  $A$  is its molality  $m_A$  multiplied by its activity coefficient  $\gamma_A$ . A solute activity coefficient represents the deviation from ideal behavior of the solute in solution. Hence, the concentration dependent

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



activity coefficients are estimated for all soluble species. Note, that the activity coefficients for neutral inorganic species (such as  $O_{2(aq)}$ ) are defined as unity. At the same time, the activity coefficients of radicals are also defined as unity, since their reactivity is quite fast and lifetime is rather small. The consideration of activities in the SPACCIM framework for different types of species is summarized in Table 1.

### 2.2.3 Phase transfer processes

The dynamical description of phase transfer processes between the gas and liquid phases in SPACCIM is specified according to the Schwartz approach (Schwartz, 1986). During dissolution, the saturation vapor pressure of gas  $A$  can be determined from the equilibrium relationship  $A_{(g)} \leftrightarrow A_{(aq)}$ . Thus, in terms of an arbitrary gas  $i$  the Henry's law is defined as:

$$p_{i,k}^s = \frac{m_i^k}{K_i^H} \quad (7)$$

where  $p_{i,k}^s$  is the saturation vapor pressure (atm) of gas phase species  $i$  over a particle in size bin  $k$ ,  $m_i^k$  ( $\text{mol kg}^{-1}$ ) is the molality of dissolved gas phase species  $i$  in particle class  $k$ , and  $K_i^H$  ( $\text{mol kg}^{-1} \text{ atm}^{-1}$ ) is the corresponding Henry constant. On the other hand, the saturation vapor pressure is related to the saturation vapor mole concentration  $c_{i,k}^s$  ( $\text{mol m}^{-3}$ ) by

$$p_{i,k}^s = c_{i,k}^s RT \quad (8)$$

where  $R$  denotes the universal gas constant in ( $\text{atm m}^3 \text{ mol}^{-1} \text{ K}^{-1}$ ) and  $T$  (K) the temperature. Then, Eq. (7) can be expressed in terms of concentrations rather than molalities and partial pressures as:

$$c_{i,k}^s = \frac{p_{i,k}^s}{RT} = \frac{m_i^k}{K_i^H RT} = \frac{m_i^k}{H_i} \quad (9)$$

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Here  $H_i = K_i^H RT$  stands for the dimensionless Henry constant. Considering the non-ideality in the aqueous phase, the molalities  $m_i^k$  are replaced by the activities  $a_i^k = \gamma_i^k m_i^k$ . Considering  $M$  classes of particles associated, we state the appropriate expression for gas-phase loss while neglecting the Kelvin effect (following Jacobson, 1997):

$$5 \quad \frac{dc_i^G}{dt} = - \sum_k k_t^{ki} L_k \left( c_i^G - \frac{a_i^k}{H_i} \right). \quad (10)$$

Equation (10) pertains to the case of a single gas phase species equilibrating between the gas and aqueous aerosol phases, with the mass transfer coefficient  $k_t^{ki}$  defined by

$$k_t^{ki} = \left( \frac{r_k^2}{3D_i^G} + \frac{4r_k}{3v_i\alpha_i} \right), \quad (11)$$

10 which depends on the droplet size  $r_k$ , the gas diffusion coefficient  $D_i^G$ , the molecular speed  $v_i$  and the mass accommodation coefficient  $\alpha_i$  of the  $i$ th species. These quantities play a decisive role in determining the rate of uptake of gaseous species by, and evaporation from aerosol particles, respectively, governing the timescale for a droplet to attain an equilibrium (Schwartz, 1986).

### 2.2.4 Coupling scheme

15 The coupling between microphysics and multiphase chemistry models in SPACCIM follows the so-called “operator splitting” technique. As described in Sehili et al. (2005), the coupling scheme provides time-interpolated values of the meteorological variables (temperature, water vapor, liquid water content) and generates the time-averaged mass fluxes  $F$  over the coupling time interval. The changes in the chemical aerosol composition by gas scavenging and the chemical reactions have a continuous feedback on the microphysical processes (e.g. water condensation growth rates via changes in surface tension and the Raoult term/water activity).

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## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



For the “non-ideal” approach in SPACCIM, the coupling scheme is modified, since activity coefficients have to be considered in both models. At the same time, the activity coefficients are repeatedly required to compute the chemical transformations and the phase transfer terms (see Sects. 2.2.2 and 2.2.3). Furthermore, the modified activity coefficients as well as the parameterized surface tension are delivered back to the microphysical model. Figure 1 illustrates this coupling strategy between microphysical and multiphase chemistry model as well as their interexchange while considering non-ideal solutions and surface tension effects (see Sect. 2.2.6). The coupling strategy enables a continuous feedback of the multiphase chemistry on the microphysical processes such as water condensational growth. The two models run separately and exchange information at every coupling time step (see Fig. 2). Moreover, both widely separated operating models use its individual time-step control. This is necessary in order to ensure a high flexibility regarding the usage of models with different complexities and numerical efficiency. The coupling between both models and the activity coefficient module utilize well-defined interfaces for the intercommunication of codes while considering the aqueous phase chemistry in non-ideal solutions. Furthermore, the interpolation and averaging of the required meteorological variables and parameters are arranged and implemented in the same way as described in Wolke et al. (2005).

### 2.2.5 Feedback of non-ideal aqueous phase chemistry on microphysics

Microphysical processes described in SPACCIM include equilibrium growth of aerosol particles and condensational growth of the droplets (Simmel and Wurzler, 2006). The Köhler equation (see e.g., Köhler, 1936; Pruppacher and Klett, 1997) gives the saturation ratio of water vapor at particle/air interface, which depends on the chemical composition, the droplet diameter and the surface tension of the particle. In SPACCIM, the non-linear relationship Eq. (1) is used to determine the equilibration of water between the liquid and surrounding vapor phase. The water saturation pressure in Eq. (1) is affected by the curvature of the particle (also known as Kelvin effect) and the water activity, which is determined by the solutes (Raoult effect). Previously, Wolke et al. (2005)

calculated the Raoult term in the condensation rate using osmotic coefficient, according to Pruppacher and Klett (1997). While, the intention was to allow the feedback of chemical particle composition onto microphysics, the Raoult term was replaced by the sum of molar ratios of all soluble species included in the multiphase system:

$$5 \text{ Raoult}_{\text{chem}}^k = \frac{\sum_i^{N_A} \text{mol}_{\text{sol}_i}^k}{\text{mol}_w^k}. \quad (12)$$

Here, the quantities  $\text{mol}_{\text{sol}_i}^k$  of soluble material are obtained from the multiphase chemistry. The molar water fraction  $\text{mol}_w^k$  varies and is taken directly from the microphysics. The Raoult term in Eq. (12) depends on all soluble species. In the non-ideal approach of SPACCIM, the water activity  $a_w^k$  estimated from activity coefficient module (see Sect. 2.3), is used directly for the Raoult term in microphysics. On the other hand, the description of change in droplet curvature (Kelvin effect) is precisely treated with surface tension approaches (see Sect. 2.2.6).

Both effects are primarily appointed by the particle composition, which is continuously changed by phase transfer and multiphase processes. However, the mass concentrations of all species are kept fixed for the microphysics over a coupling time step (see Fig. 1). But the molalities and, therefore, the Kelvin and Raoult terms are changed caused by the adjustment of the LWCs. Equation (1) has to be fulfilled simultaneously for all non-activated particle classes. The droplet activation is described explicitly and takes place for all particles, which grow over the critical radius. The condensation and evaporation of the activated droplet classes are described dynamically. The predicted saturation vapor pressure is used as input into the droplet growth equation. The coupled system for all classes has to be solved simultaneously, whereas the total amount of water (liquid or gaseous) is prescribed. This leads to a nonlinear system, which has to be solved iteratively at each microphysical time step. A more detailed description of the iterative procedure is given in Simmel and Wurzlner (2006). A new solution of the system is obtained, and defines the equilibrium saturation ratio and the correspond-

## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

ing particle/droplet diameters. This implies changes in the corresponding LWCs and, hence, in the molalities. Consequently, the water activity and the surface tension have to be recalculated at each microphysical time step. A description of the equilibration algorithm is presented schematically in Fig. 2. Based on this, SPACCIM allows an ongoing feedback of the chemical particle composition onto microphysics. Conversely, the microphysical model provides all microphysical variables for integrating the multiphase chemical system, such as LWC,  $T$  and the mass fluxes  $F$  at the coupling time step (see Fig. 1).

### 2.2.6 Surface tension

The calculation of droplet solution surface tension  $\sigma_{w,s}$  with simultaneous changes in solute concentration  $c_{sol}$  is almost a linear approximation:

$$\sigma_{w,s} = \sigma_w + \frac{\Delta\sigma_{w,s}}{\Delta c_{sol}} c_{sol} \quad (13)$$

where  $\sigma_w$  is the surface tension of pure water and  $\Delta\sigma_{w,s}/\Delta c_{sol}$  represents the linear rate of change in  $\sigma_{w,s}$  with solute concentration  $c_{sol}$ . However, a substantial approach is not available considering the influence of the separate inorganic/organic fractions.

Usually, anions dissolved in ionic solutions are enriched at the surface (Jungwirth and Tobias, 2001). Furthermore, due to the strong interactions of the anions with the cations in the bulk, the droplet surface tension is slightly higher than the pure water (Pruppacher and Klett, 1997). On the other hand, organic compounds dissolved in aqueous solution often reduce the droplet surface tension since their hydrophobic parts are oriented towards the surface. However, due to the mounting interest, as organic compounds lower the surface tension of droplet, the relationship between concentrations of organic aerosol constituents and surface tension, given by Facchini et al. (1999), was implemented in SPACCIM:

$$\sigma_{w,s}^k = \sigma_w^k - 0.01877 \cdot T \cdot \ln(1 + 628.14 \cdot [C^k]) \quad (14)$$

4170

## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





where  $T$  is the temperature in K and  $[C^k]$  represents the concentration of WSOC (Water Soluble Organic Carbon, molCL<sup>-1</sup>) in particle class  $k$ . A combined approach for accounting for a simultaneous change in  $\sigma_{w,s}^k$  and the mean molar mass of solute  $M_s$  derived by Ervens et al. (2004) was also implemented in the present work:

$$\sigma_{w,s}^k = \sigma_w^k - 0.01877 \cdot T \cdot \ln \left( 1 + 628.14 n_c c_{sol}^k \right) \quad (15)$$

where  $c_{sol}^k$  is the solute concentration in (molL<sup>-1</sup>) and  $n_c$  represents the number of carbon atoms defined by

$$n_c = \frac{M_s}{2.2 M_c} \quad (16)$$

with  $M_c = 12 \text{ g mol}^{-1}$ .

## 2.2.7 Adjustment of numerical schemes

In order to treat aqueous phase chemistry considering newly non-ideality effects, the numerical schemes used in Wolke et al. (2005) are required to adjust, mainly, (i) the time integration scheme, (ii) the computation of Jacobian matrix and (iii) the sparse linear solver. The system of mass balance equations (Eqs. 2 and 3) is integrated in an implicit and coupled manner by higher order backward differential formula (BDF) schemes (e.g., Hairer et al., 1993). In any implicit multistep method, the main computational task is the solution of a non-linear equation of the form:

$$F(\mathbf{c}^{n+1}) = \mathbf{c}^{n+1} - \mathbf{X}^n - \beta \Delta t_n \mathbf{f}(t_{n+1}, \mathbf{c}^{n+1}) = 0, \quad (17)$$

where  $\beta > 0$  is a parameter of the integration method and  $\mathbf{X}^n$  is a linear combination of previous values. If Eq. (17) is solved by a Newton-like method, the main burden is the approximate solution of linear systems of the form:

$$(\mathbf{I} - \beta \Delta t \mathbf{J}) \Delta \mathbf{c} = \mathbf{b} \quad (18)$$

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



where  $\mathbf{I}$  denotes the identity matrix and  $\Delta t$  represents the time step size. The matrix  $\mathbf{J}$  stands for an approximation of the Jacobian  $\partial f(t, c)/\partial c$  of the right hand side of the ordinary differential equation (ODE) system. The vector  $\mathbf{b}$  is given as:

$$\mathbf{b} = \mathbf{c}^n - \mathbf{X}^n - \beta \Delta t_n \mathbf{f}(t_n, \mathbf{c}^n). \quad (19)$$

Usually, the dimension of the linear system Eq. (18) is rather high. Large systems can be solved with reasonable effort by iterative or direct sparse solvers, which utilize the special structure of the system (sparsity, block structure, different types of coupling). Such efficient solvers are already developed and applied in the former version of SPACCIM for the “ideal” approach (see Wolke and Knoth, 2002; Wolke et al., 2005, for further details).

In this case, the Jacobian structure of the right-hand side of the multiphase system (Eqs. 2 and 3) for two droplet classes is shown in Fig. 3. As can be seen, the dots are usually non-zero entries means that the species in the row depends on the species in the column. The diagonal elements of the Jacobian describe the dependence from the species itself. These entries can be caused by chemical reactions and phase transfer, but also by the terms from microphysical fluxes and entrainment.

The block structure shown in Fig. 3 can be explained as follows: the blocks in the diagonal correspond to the Jacobian of the gas phase and aqueous phase reaction terms, respectively. The upper left block (light blue) represents the gas phase. The other two diagonal blocks (blue) are related to the aqueous phase chemistry attained to have the same sparse structure. The left and upper boundary blocks (green) represent the phase interchange between gas phase species and corresponding aqueous phase species in each class, according to Schwartz (1986). The orange diagonal matrices include the coupling terms resulting from the mass transfer between liquid species and the corresponding species in the other classes. These sparse block matrices are generated explicitly and stored in sparse form. The linear system (see Eq. 19) is solved by a sparse LU decomposition with diagonal pivoting. An optimal order of the pivot elements to avoid fill-in is determined by an adjusted Meis–Markowitz strategy (Wolke and

## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Knoth, 2002). In fact, only an appropriate approximation of the Jacobian is required to ensure the convergence of the Newton-like method for the corrector iteration (Eq. 18). Therefore, the sparse factorization is stored and has to be performed only when the Jacobian  $\mathbf{J}$  is recomputed.

The adjusted numerical scheme works robust and very efficient for the “ideal” case. But these effective approaches can only be used in the “non-ideal” case, if the special sparse and block structure can be largely preserved. The calculation of the Jacobian has to be performed by applying the “chain rule” for the aqueous phase reaction and mass transfer terms in the model equations Eqs. (2) and (3). These terms depend on the activities instead of the molalities in difference to the ideal case. While the “outer” derivatives are unchanged, the “inner” derivatives have to be modified. In case that  $\mathbf{c}^k$  is the vector of all concentrations and  $L^k$  the liquid water content in the  $k$ th droplet class, the gradient with respect to vector  $\mathbf{c}^k$  is denoted as

$$\nabla_{\mathbf{c}^k} = \left( \frac{\partial}{\partial c_1^k}, \dots, \frac{\partial}{\partial c_{N_A}^k} \right). \quad (20)$$

In the ideal approach the molalities depend only on the corresponding species itself. Then the gradient of the molalities is given as follows:

$$\nabla_{\mathbf{c}^k} m_j^k(\mathbf{c}_j^k) = \frac{1}{L^k} (0, \dots, 0, 1, 0, \dots, 0). \quad (21)$$

In the above formulation, the gradient has only one entry in the  $j$ th position, which conserves the structure of the “outer” Jacobian. Contrary, while applying the chain rule, the gradient for non-ideal solutions would be:

$$\nabla_{\mathbf{c}^k} a_j^k(\mathbf{c}^k) = \frac{c_j^k}{L_k} \cdot \left( \nabla_{\mathbf{c}^k} \gamma_j^k(\mathbf{c}^k) \right) + \frac{1}{L_k} \cdot (0, \dots, 0, \gamma_j^k, 0, \dots, 0) \quad (22)$$

where the gradient  $\nabla_{\mathbf{c}^k} \left( \gamma_j^k(\mathbf{c}^k) \right)$  of activity coefficients depends usually on all concentrations of the vector  $\mathbf{c}^k$  considered in the activity calculations.

The first term in Eq. (22) is a vector with entries in several positions depending on the activity coefficient module. This leads to “fill-in” in the corresponding lines of the Jacobian from aqueous phase chemistry (blue blocks) and the phase transfer terms (green blocks). Consequently, the efficient direct sparse solvers are used in SPACCIM for the linear system cannot be utilized. However, since only a “good” approximation for the Jacobian is needed, the first term shown in Eq. (22) is omitted assuming that the dependency of the activity coefficients from the concentrations can be neglected over the time step. The second term involves the activity coefficient  $\gamma_j^k$  that yields from the derivative of the activity with respect to molality of that particular species  $m_j$ . Although, the derivative of activity coefficients is omitted, the same data structures are obtained as in ideal case. The second term on the right hand side of Eq. (22) has the same structure as on the right hand side of Eq. (21). Only the non-zero entry in the  $j$ th position changes from 1 to  $\gamma_j^k$ . This leads to modifications of the non-zero entries in the Jacobians of the chemistry (blue blocks) and the phase transfer (green blocks) terms. However, the sparse structure of the systems is conserved effectively.

### 2.3 SPACCIM’s activity coefficient module

In this section, we present the mixed-solvent electrolyte model that is designed to predict the activity coefficients, based mainly on AIOMFAC (Zuend et al., 2008), which is valid for systems over a wide concentration range. The AIOMFAC was originally developed for systems composed of organic compounds with  $-\text{CH}_n$  ( $n = 0, 1, 2, 3$ ) and  $-\text{OH}$  as functional groups. On the other hand, several authors (e.g., Gilardoni et al., 2009; Liu et al., 2009; Russell et al., 2009; Takahama et al., 2011) reported that other individual organic compounds and compound classes have also a strong impact on multiphase chemical processing on ambient aerosols for instance, aldehydes, ketones, carboxylic acids, and multifunctional organic compounds. Moreover, the aforementioned organic

## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



compound classes are almost omnipresent in tropospheric aerosol particles and, therefore, explicitly treated in complex multiphase chemistry mechanism such as CAPRAM (see e.g., Herrmann et al., 2005; Tilgner et al., 2013). Hence, the prediction of the activity coefficients for complex multi-component aerosols, composed of various organic functional groups and electrolytes dissolved in water is the primary purpose of SpactMod. In order to treat various aerosol constituents, the model interaction parameters were extended based on the activity coefficient model of mod. LIFAC (Kiepe et al., 2006), while using the mathematical model expressions according to Zuend et al. (2008). Thus, SpactMod allows a reliable prediction of activity coefficients of the considered organic–electrolyte mixture, flexibly, from these two approaches AIOMFAC (Zuend et al., 2008) and modified LIFAC (Kiepe et al., 2006), within a single model framework. The two different frameworks including the estimated interaction parameters are described in detail in Zuend et al. (2008) and Kiepe et al. (2006), therefore, only main features are discussed here.

### 2.3.1 Model treatment of non-ideality

The development of thermodynamic models for mixed-solvent electrolyte systems was an active area of research during the last three decades. In general, these models contain several contributions to describe the system non-ideality, that define the excess Gibbs energy  $G^{\text{ex}}(p, T, n_j)$ :

$$G^{\text{ex}}(p, T, n_j) = G_{\text{LR}}^{\text{ex}} + G_{\text{MR}}^{\text{ex}} + G_{\text{SR}}^{\text{ex}}, \quad (23)$$

where  $G_{\text{LR}}^{\text{ex}}$  represents the long-range (LR) electrostatic interactions,  $G_{\text{SR}}^{\text{ex}}$  is the short-range (SR) contribution resulting from dipole ↔ dipole and dipole ↔ induced dipole interactions, and an additional term (middle-range, MR)  $G_{\text{MR}}^{\text{ex}}$ , which accounts for ionic interactions (e.g., ion ↔ ion, ion ↔ dipole, ion ↔ induced dipole interactions),  $p$  is the total pressure,  $T$  the absolute temperature, and  $n_j (j = 1, \dots, N)$  the number of moles of component  $j$  in a system. Accordingly, the corresponding activity coefficient  $\gamma_j^k$  of

Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



a species  $j$  with amount of moles  $n_j$  in the mixture are derived from expressions for the different parts of  $G^{\text{ex}}$  using the relation:

$$\ln \gamma_j = \left( \frac{\partial G^{\text{ex}} / RT}{\partial n_j} \right)_{p, T, n_{j' \neq j}} \quad (24)$$

where  $R$  is the universal gas constant. Correspondingly, the activity coefficients are calculated from the aforementioned three different contributions:

$$\ln \gamma_j = \ln \gamma_j^{\text{LR}} + \ln \gamma_j^{\text{MR}} + \ln \gamma_j^{\text{SR}}. \quad (25)$$

### 2.3.2 The long-range contribution

The LR interactions are described same as original AIOMFAC, based on the Debye-Hückel theory (Debye and Hückel, 1923). In contrast to other works (Chang and Pankow, 2006; Li et al., 1994; Yan et al., 1999), AIOMFAC uses the water properties for all solvent components for density and dielectric constant of the solvent mixture, instead of using mixing rules. With this assumption, the corresponding LR activity coefficient expressions for the solvents and ions are defined according to Zuend et al. (2008) as

$$\ln \gamma_s^{\text{LR},(x)} = \frac{2AM_s}{b^3} \left( 1 + b\sqrt{I} - \frac{1}{1 + b\sqrt{I}} - 2 \ln \left( 1 + b\sqrt{I} \right) \right), \quad (26)$$

$$\ln \gamma_i^{\text{LR},(x),\infty} = \frac{-z_i^2 A \sqrt{I}}{1 + b\sqrt{I}}. \quad (27)$$

Equation (27) gives the activity coefficient of ion  $i$  in the mole fraction basis ( $x$ ) with the reference state of infinite dilution in water, indicated by super script  $\infty$ .  $M_s$  represents the molar mass of solvent  $s$  and  $z_i$  is the number of elementary charges of ion  $i$ . The

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ionic strength  $I$  ( $\text{mol kg}^{-1}$ ) is given as

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (28)$$

with the Debye–Hückel parameters:

$$A = 1.327757 \times 10^5 \cdot \frac{\sqrt{\rho_w}}{(\epsilon_w T)^{3/2}}, \quad (29)$$

$$b = 6.359696 \cdot \sqrt{\frac{\rho_w}{\epsilon_w T}}. \quad (30)$$

The Debye–Hückel parameters  $A$  ( $\text{kg}^{1/2} \text{mol}^{-1/2}$ ) and  $b$  ( $\text{kg}^{1/2} \text{mol}^{-1/2}$ ) depend on temperature  $T$  (K), density  $\rho_w$  ( $\text{kg m}^{-3}$ ) and static permittivity  $\epsilon_w$  ( $\text{C}^2 \text{J}^{-1} \text{m}^{-1}$ ) of water, calculated based on a distance of closest approach of between ions (see Antypov and Holm, 2007; Demaret and Gueron, 1993).

Moreover, this simplification to a water-property based expression for LR activity coefficients are favorable, due to the uncertainties to estimate unknown dielectric constants of certain organic compounds and maintaining the thermodynamic consistency regarding the selection of reference states (see Raatikainen and Laaksonen, 2005; Zuend et al., 2008). In a real mixture, solvents have densities and dielectric properties different from those of pure water. For this reason, these simplifications of the LR part were made in other mixed solvent models in chemical engineering and technical chemistry applications (see Iliuta et al., 2000). Compensation of these inaccuracies is controlled by this simplification, in the semi-empirical MR part as performed in original AIOMFAC (Zuend et al., 2008).

### 2.3.3 The middle-range contribution

The  $G_{\text{MR}}^{\text{ex}}$  term is the contribution of the indirect effects of the ionic interactions such as ion  $\leftrightarrow$  dipole interactions and ion  $\leftrightarrow$  induced dipole interactions to the excess Gibbs

## GMDD

8, 4155–4219, 2015

### Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



energy. For any mixture containing  $n_k$ , ( $k = 1, \dots, s$ ) moles of solvent  $k$  (main groups of organics and water) and  $n_i$  moles of ion  $i$ ,  $G_{MR}^{ex}$  can be expressed as described by Zuend et al. (2008):

$$\begin{aligned}
 \frac{G_{MR}^{ex}}{RT} = & \frac{1}{\sum_k n_k M_k} \sum_k \sum_i B_{k,i}(I) n_k n_i \\
 5 & + \frac{1}{\sum_k n_k M_k} \sum_c \sum_a B_{c,a}(I) n_c n_a \\
 & + \frac{1}{\sum_k n_k M_k} \sum_c \sum_a C_{c,a}(I) n_c n_a \sum_i \frac{n_i |z_i|}{\sum_k n_k M_k} \\
 & + \frac{1}{\sum_k n_k M_k} \sum_c \sum_{c' \geq c} R_{c,c'}(I) n_c n_{c'} \\
 & + \frac{1}{\left(\sum_k n_k M_k\right)^2} \sum_c \sum_{c' \geq c} \sum_a Q_{c,c',a} n_c n_{c'} n_a \quad (31)
 \end{aligned}$$

where  $n_c$  and  $n_{c'}$  are the moles of cations,  $n_a$  are the moles of anions, and  $I$  is the ionic strength as defined in Eq. (28).  $B_{k,i}(I)$  ( $\text{kg mol}^{-1}$ ) and  $B_{c,a}(I)$  ( $\text{kg mol}^{-1}$ ) are ionic strength dependent binary interaction coefficients between solvent main groups and ions, and between cations and anions, respectively.  $C_{c,a}(I)$  ( $\text{kg}^2 \text{mol}^{-2}$ ) are interaction coefficients between cation  $\leftrightarrow$  anion pairs with respect to the total charge concentration. The coefficients  $R_{c,c'}(I)$  ( $\text{kg mol}^{-1}$ ) and  $Q_{c,c',a}(I)$  ( $\text{kg}^2 \text{mol}^{-2}$ ) are defined as binary and ternary interactions involving two different cations. These binary and ternary interaction coefficients have been introduced in AIOMFAC to improve the description of various ion combinations, specifically at high ionic strength. Hence, these two terms

## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





in Eq. (31) can be vanished or neglected in other cases, i.e. for low to moderate ionic strengths.

In the current approach, the MR terms of activity coefficients for the species and organic functional groups described in AIOMFAC are estimated using Eq. (31). As mentioned earlier, the first three interaction coefficients in Eq. (31) are parameterized as functions of ionic strength  $I$ , which are similar to the ones used for the Pitzer model of Knopf et al. (2003):

$$B_{k,i}(I) = b_{k,i}^{(1)} + b_{k,i}^{(2)} \exp\left(-b_{k,i}^{(3)} \sqrt{I}\right), \quad (32)$$

$$B_{c,a}(I) = b_{c,a}^{(1)} + b_{c,a}^{(2)} \exp\left(-b_{c,a}^{(3)} \sqrt{I}\right), \quad (33)$$

$$C_{c,a}(I) = c_{c,a}^{(1)} \exp\left(-c_{c,a}^{(2)} \sqrt{I}\right), \quad (34)$$

where  $b_{k,i}^{(1)}$ ,  $b_{k,i}^{(2)}$ ,  $b_{c,a}^{(1)}$ ,  $b_{c,a}^{(2)}$ ,  $c_{c,a}^{(1)}$  and  $c_{c,a}^{(2)}$  are adjustable parameters, which are determined by fitting AIOMFAC activity coefficients to experimental data sets (see Zuend et al. (2008) for further details). The parameter  $b_{c,a}^{(3)}$  was used mostly to describe aqueous salt solutions assuming a fixed value of  $0.8 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ . Similarly, we have considered the same value for the ions when the activity coefficients are estimated from AIOMFAC. Furthermore, Zuend et al. (2008) argued that for such cases, where this value did not result in a satisfactory data fit,  $b_{c,a}^{(3)}$  allow to vary. On the other hand, the parameter  $b_{k,i}^{(3)}$  was fixed for all mixed organic–inorganic solutions assuming a value of  $1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ . All interaction coefficients in the MR part are symmetric  $B_{c,a}(I) = B_{a,c}(I)$ . Subsequently, water is defined as the reference solvent for inorganic ions, no explicit ion  $\leftrightarrow$  water interactions are determined, i.e.,  $B_{k=\text{H}_2\text{O},i}(I)$  is prescribed as zero for all inorganic ions. However, the effects of non-ideality from cations and anions interacting with water molecules are indirectly accounted for via the cation  $\leftrightarrow$  anion interaction coefficients,  $B_{c,a}(I)$ ,  $C_{c,a}(I)$ ,  $R_{c,c'}$  and  $Q_{c,c',a}$  as the corresponding interaction

## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



parameters, that were determined on the basis of (organic-free) aqueous electrolyte solutions.

As depicted earlier, the MR interaction parameters in AIOMFAC were fitted for limited organic compounds (i.e. alkyl and hydroxyl) and ions. Contrary, interaction parameters were not evenly available for over all systems of current interest, i.e. to treat the organic compounds and ions involved in multiphase mechanism such as CAPRAM. Hence, in this study, the ion ↔ ion and organic main group ↔ ion interaction parameter database is extended by incorporating parameters of the modified LIFAC approach of Kiepe et al. (2006). The complete procedure of the extension of model interaction parameters is explained in Appendix A1.

### 2.3.4 The short-range contribution

The SR contribution  $\ln \gamma_{SR}^{ex}$  to the total Gibbs excess energy in SpactMod is represented by the modified group-contribution method UNIFAC (Fredenslund et al., 1975), as performed by Zuend et al. (2008). AIOMFAC incorporates the revised parameter set of Hansen et al. (1991) (standard UNIFAC) for most of the functional group interactions. Besides, these modifications include the insertion of further inorganic ions to account for their effects on the thermodynamic properties such as entropy and enthalpy of mixing apart from their charge-related interactions (Li et al., 1994; Yan et al., 1999; Zuend et al., 2008). AIOMFAC utilizes the specific UNIFAC parameterizations of Marcolli and Peter (2005) for hydroxyl and alkyl functional groups.

Similar to the addition of interaction parameters derived for MR part, the same functional groups are also comprised in the SR part, while maintaining the compatibility with the standard UNIFAC parameter set, when the same mathematical model expressions are used. The influence of estimated activity coefficients when merging specific parameters from the distinctive UNIFAC parameterizations within SPACCIM has been tested. It was found that the model produce relatively better results in most of the cases in comparison with the parameters from standard UNIFAC only. The interaction parameters for these organic functional groups are shown in Appendix A1.

GMDD

8, 4155–4219, 2015

## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



In UNIFAC, the activity coefficient  $\gamma_j$  of a molecular component  $j$  ( $j$  can be used for solute or solvent) in a multicomponent mixture is in general expressed as the summation of contributions of (i) a combinatorial part ( $C$ ) accounting for the geometrical properties of the molecule and (ii) a residual part ( $R$ ), which results from inter-molecular interactions:

$$\ln \gamma_j^{\text{SR}} = \ln \gamma_j^{\text{C}} + \ln \gamma_j^{\text{R}}. \quad (35)$$

Since ions are treated such as solvent components in the SR terms, resulting activity coefficients in Eq. (35) are with respect to the symmetrical convention on mole fraction basis. For ions, the unsymmetrical normalized activity coefficient is determined from:

$$\ln \gamma_i^{\text{SR},(x),\infty} = \ln \gamma_i^{\text{SR},(x)} + \ln \gamma_i^{\text{SR},(x),\text{ref}}. \quad (36)$$

The symmetrically normalized value at the reference state is computed from the combinatorial and residual parts, by introducing the reference state conditions of the ions (setting  $x_w = 1$ ,  $\sum_s x_s = 0$  for  $s \neq w$  and  $\sum_i x_i = 0$ ):

$$\ln \gamma_i^{\text{SR},(x),\text{ref}} = \ln \frac{r_i}{r_w} + 1 - \frac{r_i}{r_w} + \frac{z}{2} q_i \left[ \ln \left( \frac{r_w q_i}{r_i q_w} \right) - 1 + \frac{r_w q_i}{r_i q_w} \right] + q_i (1 - \ln \psi_{w,i} - \psi_{i,w}), \quad (37)$$

where subscript  $w$  stands for the reference solvent (water). The parameters  $q_i$  and  $r_i$  represent the surface area and the volume, respectively, of component  $i$ . The last term on the right-hand side of Eq. (37) reflects the residual part reference contribution and becomes zero as we defined the SR ion  $\leftrightarrow$  solvent interactions to be zero. Figure 4 shows the binary species combinations, for which the specific parameters have been used in this study. Mean interactions between ions and water are indirectly represented by the parameters of the cation  $\leftrightarrow$  anion interaction pairs according to (Zuend et al., 2008), since the aqueous solution is defined as the reference system similar to the assumption used in conventional Pitzer models (Pitzer, 1991). The relative van der Waals subgroup volume and surface area parameters,  $R_t$  and  $Q_t$ , account for pure

component properties. At the same time,  $R_t$  and  $Q_t$  values for the ions can be estimated from the ionic radii. In order to maintain the compatibility with the model equations of AIOMFAC, the hydrated group volume and surface area parameters  $R_t^H$  and  $Q_t^H$  are calculated using an empirical parameterization given by Achard et al. (1994). For those ions, the activity coefficients are estimated using the mod. LIFAC approach. Likewise, the database is extended for other ions in order to estimate the activity coefficients from the SR part. The measured apparent dynamic hydration numbers ( $N_t^{ADH}$ ) data are adopted from Kiriukhin and Collins (2002) to estimate the final values  $R_t^H$  and  $Q_t^H$  instead of  $R_t$  and  $Q_t$ .  $R_t^H$  and  $Q_t^H$  are computed consistently in the model equations (see Table A1) by:

$$R_t^H = R_t + N_t^{ADH} \cdot R_w, \quad (38)$$

$$Q_t^H = Q_t + N_t^{ADH} \cdot Q_w, \quad (39)$$

where  $R_w$  and  $Q_w$  refer to the values of the water molecule and  $N_t^{ADH}$  are measured apparent dynamic hydration numbers at 303.15 K (Kiriukhin and Collins, 2002). As shown in Fig. 4, the interactions of the ions  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $F^-$ ,  $I^-$ ,  $OH^-$ ,  $NO_2^-$ ,  $CO_3^-$  and  $CH_3COO^-$  are implemented from Kiepe et al. (2006). Due to the increasing interest on remaining ions included in the multiphase mechanism CAPRAM (e.g.  $Fe^{2+}$ , succinate, and malonate) the activity coefficients are computed while prescribing the corresponding interaction parameters as zero.

### 2.3.5 Total activity coefficients

Finally, SPACCIM's activity coefficient module (SpactMod) estimates the total activity coefficients for each species according to the Gibbs energy (cp. Eqs. 23 and 25). Then, the activity coefficient of a solvent species  $s$  is determined by Kiepe et al. (2006), Li et al. (1994), Yan et al. (1999) and Zuend et al. (2008).

$$\ln \gamma_s^{(x)} = \ln \gamma_s^{LR,(x)} + \ln \gamma_s^{MR,(x)} + \ln \gamma_s^{SR,(x)} \quad (40)$$

## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Accordingly, the complete expression for the ions, with regard to the unsymmetrical convention on molality basis at which the standard state is the hypothetical ideal solution of unit molality at system pressure and temperature, can be written as follows:

$$\ln \gamma_i^{(m)} = \left[ \ln \gamma_i^{\text{LR},(x),\infty} + \ln \gamma_i^{\text{MR},(x),\infty} + \ln \gamma_i^{\text{SR},(x),\infty} \right] - \ln \left[ \frac{M_w}{\sum_s X_s^* M_s} \right] + M_w \sum_{i'} m_{i'} \quad (41)$$

5 where  $M_s$  is the molar mass of solvent component  $s$ ,  $X_s^*$  its salt-free mole fraction, and  $m_{i'}$ , is the molality of ion  $i'$ . The last term on the right-hand side of Eq. (41) converts the activity coefficient  $\ln \gamma_s^{(x)}$  (infinitely diluted reference state on the mole fraction basis) to the activity coefficient on molality basis and infinitely diluted (in water) reference state. One can derive this term based on convention-independence of the chemical potentials ( $\mu_i^{(m)}(p, T, n_j) = \mu_i^{(x)}(p, T, n_j)$ ) and the definitions of the chosen reference states (Zuend et al., 2008).

10 The extension of database by the combination of AIOMFAC and modified LIFAC makes SPACCIM a versatile tool to study the influence of the treatment of non-ideality on multiphase aerosol chemistry. SpactMod is highly flexible to extension and further inclusion of organic functional groups and ions, whenever the required data become available. During the implementation of the code, the activity coefficients responsible for LR and SR contribution terms are computed for all the ions (either cation or anion) included in the considered chemical system. For those species, where the interaction parameters are not available to compute MR contribution terms; they are prescribed as unity (i.e.,  $\gamma_i^{\text{MR},(x),\infty} = 1$ ) due to the lack of extensive database.

### 3 Model evaluation and applications

In this section we will examine the model extensions described above. Especially, the activity coefficient module SpactMod is evaluated and compared with literature data.

## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The reliability of the extended SPACCIM code is shown in the last subsection. Furthermore, the deviation of the activity coefficients from ideality and, consequently, the impact on the chemical behavior are demonstrated for a test scenario. A more detailed analysis of the impact of the non-ideality approach on the multiphase will be published in a separate paper.

### 3.1 Evaluation of the activity coefficient module

Considerable effort has been devoted by several authors (see e.g., Raatikainen and Laaksonen, 2005; Tong et al., 2008; Zuend et al., 2008) to compare different established activity coefficient models that could be potentially suitable for modeling of hygroscopic properties of organic–electrolyte particles as well as the prediction of activity coefficients of aqueous species. The investigations summarized here were aimed to evaluate the robustness of the implemented module SpactMod and to check the reproducibility towards original model results. However, the interaction parameters in the applied models were fitted against measurements. Hence, this comparison can be considered as indirect comparison with measurements. Furthermore, results are also compared with direct also water activity measurements and the AIM model (Aerosol Inorganic Model) of Clegg et al. (1998b, a). The model comparisons cover a scale, ranging from very simple to complex simulations. Initially, the comparison is performed for selected binary aqueous electrolyte solutions, then aqueous organic solutions, followed by mixtures of aqueous organic–electrolyte solutions. However, here we present the results of selected examples only.

#### 3.1.1 Comparison between activity coefficient models for inorganic systems

Naturally, the reproducibility of the original AIOMFAC results in Zuend et al. (2008) was verified in a first step but is described here. Note that the graphs of the newly implemented module SpactMod depicted in Figs. 5 and 6 correspond to the original results given in Zuend et al. (2008). Figure 5 shows the comparison between calculated water

## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



activities predicted by the selected four models and experimental data. The differences for the electrolyte mixture of NaCl + NH<sub>4</sub>NO<sub>3</sub> are in good agreement up to moderate salt concentrations ( $x_w \geq 0.5$ ). The values for high concentrations ( $x_w \leq 0.4$ ) indicate the formation of a solid salt (or hydrate), when the solution becomes supersaturated as well as the deliquescent point of the particular salt. The models do not reproduce this, since the formation of solids was not incorporated in the present model calculations. As can be seen from Figs. 5 and 6, the modeled water activities agree well with each other at low concentrations. Contrary at high salt concentrations, mod. LIFAC strongly deviates from SpactMod as shown in Fig. 5, by a steep increase in  $a_w$  and in Fig. 6 by an increase followed by a sharp decrease, as shown by Zuend et al. (2008). Note that the Ca(NO<sub>3</sub>)<sub>2</sub> parameterization of mod. LIFAC (see Fig. 6) results only from water activity data of bulk measurements as the approach of Ming and Russell (2002) model, behaves similar to SpactMod at medium concentrations and proceed to formation of solids. The interaction coefficients of AIOMFAC applied in SpactMod were fitted from vapor–liquid as well as liquid–liquid equilibrium data, salt solubilities and electromotive force measurements covering also high solution concentrations and ternary mixtures (Zuend et al., 2008). Hence, the slope of the curve enables much better descriptions and predictions up to high concentrations, even very low water concentration available and at high ionic strength. It is noted that Ca(NO<sub>3</sub>)<sub>2</sub> is not available in the AIM, thus Fig. 6 includes only results of the other activity coefficient approaches.

Apart from the predicted water activities, the calculated mean activity coefficients also have differences with each other. Therefore, a comparison of mean activity coefficients is presented additionally in Fig. 6. The mean activity coefficient ( $\gamma_{\pm}$ ) is related to single ion-activity coefficients by

$$\gamma_{\pm} = \left( \gamma_{+}^{V_{+}} \cdot \gamma_{-}^{V_{-}} \right)^{1/(V_{+}+V_{-})} \quad (42)$$

where  $\gamma_{+}$  and  $\gamma_{-}$  are the activity coefficients of a cation and anion, respectively.  $V_{+}$  and  $V_{-}$  are the corresponding stoichiometric coefficients. The mean activity coefficients predicted by AIOMFAC and the approach of Ming and Russell (2002) show a similar

## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion







**Treatment of non-ideality in the multiphase model SPACCIM**

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the strange behavior does not appear for the pure organic and pure electrolyte mixture predictions. The MR interaction term in the model is responsible for this atypical shape in the predictions. Moreover, Raatikainen and Laaksonen (2005) argued that, in the MR part, the logarithms of activity coefficients are calculated as sums of terms, which are proportional to the fitting parameters, ion molalities and ionic strength. Because these terms have quite large numerical values, and a small change in the interaction parameters or molality can cause a very big change to activity coefficients. The MR part and modification of SR part given in SpactMod could be the main reason, since this model can predict the water activities at high salt concentrations as well. Consequently, as can be seen from Fig. 8, mod. LIFAC have an increase followed by a sharp decrease, features that have to be rated as artifacts of the mod. LIFAC parameterization, whereas the Ming and Russell (2002) model has also a strong increase after the water fraction is about ( $x_w \approx 0.3$ ). As mentioned earlier, these artifacts indicate the formation of a solid salt (or hydrate), when the solution becomes supersaturated, since the formation of solids was not enabled in the model calculations.

However, the consideration here is only a limited set of mixtures of organic–electrolyte compounds. Hence, the presented results should be viewed as a first assessment. The scarcity of experimental data for mixtures of atmospheric relevance remains a limitation for testing activity coefficient models. When experimental data become available in the future, the models can be validated against measurements, while comparing the water activity and species activity coefficients against water fraction  $x_w$ . All in all, despite the difficulties in determining the ion  $\leftrightarrow$  organic mixture parameters, it should be noted that the ion  $\leftrightarrow$  organic interaction parameters have improved the model performance, a fact which was already noted in previous studies (Clegg and Seinfeld, 2006b, a; Clegg et al., 2001; Tong et al., 2008).

### 3.2 Sensitivity studies on the importance of the different interactions

Tong et al. (2008) studied the importance of inclusion of a treatment of ion  $\leftrightarrow$  organic interactions and states that these interactions would substantially improve the

**Treatment of non-ideality in the multiphase model SPACCIM**

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



performance of the coupled models over that of the decoupled models. It has been concluded that, decoupled approaches, such as those in CSB (Clegg et al., 2001), ADDEM (Topping et al., 2005a, b), performs well, and in some cases better than the coupled models (Ming and Russell, 2002; Erdakos et al., 2006a, b). Additionally in such cases, the ion  $\leftrightarrow$  organic terms do not necessarily lead to improved model predictions. At the same time, models are prerequisite, composed of an aqueous electrolyte term, an (aqueous) organic term, and an organic  $\leftrightarrow$  ion mixing term in order to treat the organic–inorganic mixtures. In contrast to the study of Tong et al. (2008), the present study aims at the evaluation of the importance of different interaction terms in the model approach Eq. (25) for the computation of water activities and the activity coefficients.

Intermolecular forces or interactions are essential in the deliquesced particle phase, where high solute concentrations and low water fractions are available. They are important because they are responsible for many of the physical properties of solids, liquids, and gases. Moreover, these interaction forces become significant at the molecular range of about 1 nm or less, but are much weaker than the forces associated with chemical bonding. The characteristic contribution of different interaction forces from the model development point of view in the solution can be computed using Eq. (25). Utilizing this conceptual idea in the computation of activity coefficients, here we address the question, which intermolecular forces of attraction are important and need be considered for the treatment of non-ideality for organic–electrolyte mixtures. In order to answer this question, the SpactMod is used for sensitivity studies. Overall, the studies have revealed that middle-range (MR) interactions are important to compute the total activity coefficients.

Figure 9 shows the contribution of different interaction forces in the solution for the mixture of NaCl + (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> + Ethanol + Malonic acid [1 : 1 : 1 : 1 (mole ratio)] as an example. However, the deviations regarding the different interactions depend on the considered mixture. As can be seen in Fig. 9, the water activity strongly deviates in absence of MR interaction forces, mainly caused from ion  $\leftrightarrow$  ion, ion  $\leftrightarrow$  dipole and ion  $\leftrightarrow$  induced dipole forces. Thus, the MR interactions were found important. Similar

**Treatment of  
non-ideality in the  
multiphase model  
SPACCIM**

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



to the findings of Tong et al. (2008), it is expected that ion ↔ organic interactions be of most importance in solutions with high solute concentrations, for which inclusion of ion ↔ organic parameters would be beneficial. However, the absence of each interaction terms can be seen in Fig. 9. The short-range interactions also influence in the total contribution of computation of water activity, where the deviations are about 10 %. In the case of considered the MR and SR interactions, the deviations are about 25 %. It should be noted that the ion ↔ organic interactions are the dominant interaction forces in the solution, however the further interaction forces need to be considered. The deviations from the total contribution of interaction forces is significant in all ranges of relative humidity as well as in the full range of concentration. Nevertheless, the deviations are increasing from lower salt/acid concentration to higher. During the low salt/acid concentration ( $x_w \approx 0.9$ ) the contribution of the considered interactions were found similar.

### 3.3 First application of the advanced SPACCIM model

To demonstrate the functioning of the whole advanced SPACCIM model framework including the newly considered activity coefficient module SpactMod and a complex multiphase aerosol chemistry mechanism, first air parcel simulations have been performed with a simple model scenario. In the two following subsections, the applied model scenario and chemical mechanism is briefly outlined, and subsequently selected model results are presented. However, it is noted that the presented simulations are not aimed at the detailed examination of non-ideal solution effects on multiphase chemistry processes. The detailed investigation of this complex issue will be given in a companion paper (Rusumdar et al., 2015).

#### 3.3.1 Model scenario and chemical mechanism

In the applied meteorological scenario, an air parcel moves along a predefined 3 h model trajectory that involves three cloud passages and non-cloud periods in which the aerosol particles are deliquesced. Simulations were performed with and without consid-

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## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

eration of non-ideal solutions. Furthermore, the simulations have been performed with two different relative humidity levels (90 and 70 % RH) during the non-cloud periods. In total, simulations have been performed for four cases: with and without consideration of non-ideal solutions and both with a 90 and 70 % relative humidity level during the non-cloud periods, respectively. For the two cases without treatment of non-ideal effects, the aqueous phase chemistry is treated as ideal. For the modeling, mono-disperse aerosol particles with a radius of 200 nm and a number concentration of  $1.0 \times 10^{+8} \text{ cm}^{-3}$  were used.

For the test simulations, a complex multiphase chemistry mechanism has been applied. The applied mechanism consists of the gas phase mechanism RACM-MIM2ext (Tilgner and Herrmann, 2010) and an extended version of the aqueous phase mechanism CAPRAM2.4 (CAPRAM2.4 + organicExt). The employed aqueous phase mechanism consists of the CAPRAM2.4 mechanism (Ervens et al., 2003) combined with the reduced organic extension of CAPRAM3.0i-red (Deguillaume et al., 2010) along with the condensed oxidation scheme of malonic acid and succinic acid based on the CAPRAM3.0i-red (see Deguillaume et al., 2010, for further details). Thus, the aqueous phase mechanism contains a detailed oxidation scheme of inorganic as well as organic compounds with 204 species and 477 reactions. In the considered organic reaction scheme describes the chemistry of organic compounds with up to 4 carbon atoms and different functional groups. All model simulations have been performed for continental remote environmental conditions (see Ervens et al., 2003, for further details).

### 3.3.2 Model results

#### Modeled activity coefficients of key inorganic ions

Figure 10 depicts the time evolution of the activity coefficients of main inorganic ions and key transition metal ions (TMIs) modeled for the two different relative humidity cases. The plots show, expectedly, a strong dependency on the microphysical conditions. During cloud conditions, the modeled activity coefficients are almost equal to

**Treatment of  
non-ideality in the  
multiphase model  
SPACCIM**

A. J. Rusumdar et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

unity for the depicted ions. The in-cloud activity coefficients of ions with charge state 3+ deviate a bit more from the one than less charged ions. Under concentrated deliquesced particle conditions, the activity coefficients of ions are much lower and show a strong dependence on the relative humidity level. In the 90 % RH case, the activity coefficients of singly charged ions are in the range of 0.6–0.7, whereas the modeled coefficients for the doubly and triply charged ions are 0.3–0.35 and 0.1, respectively. Additionally, Fig. 10 reveals that the deviations from ideal behavior strongly depend on the species regarded but mainly on the charge state. The comparison with the 70 % RH case shows clearly that the activity coefficients do not change linearly with relative humidity. This fact is caused by a non-linear change of activity coefficients in terms of the molality due to the different types of interactions in the solution. From Fig. 10 it can be seen that the activity coefficients of singly or doubly charged ions are significantly lowered in the 70 % RH case compared to the 90 % RH case. However, no substantial decrease is simulated for triply charged ions such as  $\text{Fe}^{3+}$ , which are still in the range of 0.1. Interestingly, the activity coefficient of  $\text{H}^+$  show only a drop of 0.1 between the two cases, while the activity coefficients of other singly charged ions are lowered by approximately 0.2.

In total, the simulated activity coefficients of inorganic ions with values below 1 implicate that the turnover of chemical processes in deliquesced particles involving those ions are most likely decreased leading thus to a different chemical regime than present under ideal cloud conditions. For example, the partly quite huge differences in the activity coefficients of the TMIs can lead to substantial differences in the redox cycling.

**Modeled activity coefficients of important organic compounds**

Figure 11 illustrates the modeled time evolution of the activity coefficients of important organic carbonyl compounds and organic acids (both free acid and anions) for the two different relative humidity cases. For organic carbonyl compounds, the depiction reveals quite uneven pattern. For hydrated glyoxal and glycolaldehyde, the predicted activity coefficient are larger than 1 in both model cases. In contrast, activity coefficients

**Treatment of non-ideality in the multiphase model SPACCIM**

A. J. Rusumdar et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

below 1 are predicted for the other unhydrated organic carbonyls and the hydrated formaldehyde. As shown for the organic ions, there is a strong dependence of the non-ideal behavior on the species and their specific forms (i.e., functional groups included) as well as additionally the relative humidity conditions. For the hydrated glyoxal and glycolaldehyde with more than 3 OH functionalities included, activity coefficient values of about 1.2 and 1.6, respectively, are modeled in the 90 % RH case. Many times higher activity coefficients are calculated for the 70 % RH case.

The predicted activity coefficients of the organic acid anions behave similarly to the inorganic ions. Differences can be observed for the 2 free acids plotted in Fig. 11. While the activity coefficient of formic and acetic acid corresponds mainly to the present supersaturation of 0.9 in the 90 % RH case, the activity coefficient of acetic acid are higher during the more concentrated case at 70 % RH. This behavior is caused by the additional methyl group. In summary, the predicted activity coefficients of organic compounds imply that the organic chemical processing can be either increased or decreased under deliquesced particle conditions depending on the particular compound.

### Modeled acidity

The modeled pH-values for the four different simulations are plotted in Fig. 12. The pH values simulated with and without consideration of non-ideal solution effects reveal no difference during the cloud periods but substantial deviations during the non-cloud periods. During the cloud periods under almost ideal conditions, an decrease of the pH value is modeled due to occurring acidifying reactions such as the S(IV) to S(VI) conversion. The acidification is strongest during the first cloud passage and lower during the two following clouds. From the two plots, it can be seen that the difference between the ideal and non-ideal case is somewhat larger for the 70 % case. On average, the pH values of the simulations considering non-ideality are  $-0.27$  and  $-0.44$  pH units lower under 90 and 70 % RH conditions, respectively. This, lower acidity in the non-ideal case is able to affect both aqueous phase chemical reactions (i.e., acid catalyzed reactions)

and all dissociations. Further implications of this difference for the chemical processing are not discussed here, but outlined in a companion paper (Rusumdar et al., 2015).

Overall, the performed simulations demonstrated that the further developed SPACCIM model including the considered non-ideality approach performs well and the simulation results emphasize the consideration of non-ideality in multiphase chemistry models especially for an adequate description of the chemical aerosol processing in deliquesced particles.

## 4 Summary

In the present work, a robust and comprehensive model framework is developed and implemented in order to treat the aqueous phase chemistry considering non-ideal solution effects in the context of the multiphase model SPACCIM. The implemented group-contribution concept enables the reliable estimation of activity coefficients for organic–inorganic mixtures composed of various ions and functional groups. Treatment of non-ideality for mixed-solvent systems requires a careful combination of standard-state properties with activity coefficient models. This was achieved in practice by ensuring the correct representation of Gibbs excess energy by three contributions to the excess Gibbs energy. Surface tension depreciation due to the organic compounds is effectively accounted and included in the model framework. Interaction parameters accounts for various contributions of interactions. Mixed organic–inorganic systems from the literature are critically assessed and a new database is created. For all tested types of systems and data, the designed model SpactMod has been shown to reproduce both the original model results and experimental results with good accuracy. Sensitivity studies have shown that the inclusion of middle-range interaction contributions are necessary. This inclusion enhances the robustness of the model. The current developed framework is open to extension to further organic functional groups, and ions, when thermodynamic data on such systems become available. Indeed, compound specific parameter, such as charge, organic functional groups and interaction parameters, re-

### Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion







fraction basis can be written as:

$$\begin{aligned}
 \ln \gamma_{c^*}^{\text{MR},(x),\infty} &= \frac{1}{M_{\text{av}}} \sum_k B_{k,c^*}(l) x'_k + \frac{z_{c^*}^2}{2M_{\text{av}}} \sum_k \sum_i B'_{k,i}(l) x'_k m_i + \sum_a B_{c^*,a}(l) m_a \\
 &+ \frac{z_{c^*}^2}{2} \sum_c \sum_a B'_{c,a}(l) m_c m_a + \sum_a C_{c^*,a}(l) m_a \sum_i m_i |z_i| \\
 &+ \sum_c \sum_a \left[ C_{c,a}(l) |z_{c^*}| + C'_{c,a}(l) \frac{z_{c^*}^2}{2} \sum_i m_i |z_i| \right] m_c m_a \\
 &+ \sum_c R_{c^*,c} m_c + \sum_c \sum_a Q_{c,c^*,a} m_c m_a
 \end{aligned} \tag{A1}$$

For a better understanding, Eq. (A1) can be divided into different terms:

$$\ln \gamma_i^{\text{MR}} = T_i^{\text{solvent}} + T_i^{\text{ion-solvent}} + T_i^{\text{ion}} + T_i^{\text{ion-ion}} + T_i^{\text{ternary}} \tag{A2}$$

with

$$T_i^{\text{solvent}} = \frac{1}{M_{\text{av}}} \sum_k B_{k,c^*}(l) x'_k, \tag{A3}$$

$$T_i^{\text{ion-solvent}} = \frac{z_{c^*}^2}{2M_{\text{av}}} \sum_k \sum_i B'_{k,i}(l) x'_k m_i, \tag{A4}$$

$$T_i^{\text{ion}} = \sum_a B_{c^*,a}(l) m_a + \sum_c R_{c^*,c} m_c + \sum_a C_{c^*,a}(l) m_a \sum_i m_i |z_i|, \tag{A5}$$

$$\begin{aligned}
 T_i^{\text{ion-ion}} &= \frac{z_{c^*}^2}{2} \sum_c \sum_a B'_{c,a}(l) m_c m_a \\
 &+ \sum_c \sum_a \left[ C_{c,a}(l) |z_{c^*}| + C'_{c,a}(l) \frac{z_{c^*}^2}{2} \sum_i m_i |z_i| \right] m_c m_a
 \end{aligned} \tag{A6}$$

**Treatment of non-ideality in the multiphase model SPACCIM**

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



$$T_i^{\text{ternary}} = \sum_c \sum_a Q_{c^*,c,a} m_c m_a. \quad (\text{A7})$$

The term  $T^{\text{ternary}}$  stands for the ternary terms in Eq. (31) which was incorporated by Zuend et al. (2008) to improve the treatment of systems at high ionic strength.

As mentioned in Sect. 3, the activity coefficient module SpactMod is substantially based on AIOMFAC (Zuend et al., 2008). But it has been extended by including the new interaction parameters for the species shown in Fig. 4, based on the mod. LIFAC (Kiepe et al., 2006). A sufficient evaluation was performed using the actual experimental database, which has been significantly enlarged within the last years (see Raatikainen and Laaksonen, 2005; Tong et al., 2008).

The general concentration dependence of the interaction parameters can be written as analogous to Eq. (32):

$$B_{i,j} = b_{i,j} + c_{i,j} \exp(a_1 \sqrt{I}) \quad (\text{A8})$$

where,  $b_{i,j}$ ,  $c_{i,j}$  and  $a_1$  are adjustable interaction parameters. However, according to mod. LIFAC (Kiepe et al., 2006), the second virial coefficient  $B_{i,j}$  is the interaction coefficient between the species  $i$  and  $j$ . The relations of the ion  $\leftrightarrow$  ion interaction parameter  $B_{c,a}$  and the ion  $\leftrightarrow$  solvent group interaction parameter  $B_{k,\text{ion}}$  to the ionic strength are described by Kiepe et al. (2006).

$$B_{c,a} = b_{c,a} + c_{c,a} \exp(-\sqrt{I} + 0.125I), \quad (\text{A9})$$

$$B_{k,i} = b_{k,i} + c_{k,i} \exp(-1.2\sqrt{I} + 0.25I). \quad (\text{A10})$$

The equation for interaction parameters shown in the two versions (Eqs. 32–34, A9 and A10) was compared and the final model equations are derived. As a result, Eq. (A9) can be written as similar to Eq. (33):

$$B_{c,a}(I) = b_{c,a} + c_{c,a} \exp\left(-\left(1.0 - 0.125\sqrt{I}\right)\sqrt{I}\right). \quad (\text{A11})$$

Based on this, while using the similar model equations, the database was utilized with the ion ↔ ion interaction parameters as:

$$b_{c,a}^{(1)} = b_{c,a}, \quad b_{c,a}^{(2)} = c_{c,a}, \quad b_{c,a}^{(3)} = \left(1.0 - 0.125\sqrt{I}\right). \quad (\text{A12})$$

Since ion ↔ ion ↔ ion interaction parameters (ternary interactions) were not available with mod. LIFAC, the interaction parameters for  $c_{c,a}^{(1)}$  and  $c_{c,a}^{(2)}$  were assigned to zero. Similar to ion ↔ ion interaction parameters, the model equations to compute the solvent ↔ ion interaction parameters were also modified. Compared to Eqs. (32) and (A10), the parameters are assigned as:

$$b_{k,i}^{(1)} = b_{k,i}, \quad b_{k,i}^{(2)} = c_{k,i}, \quad b_{k,i}^{(3)} = \left(1.2 - 0.25\sqrt{I}\right). \quad (\text{A13})$$

Afterwards without altering the model equations given in AIOMFAC, computation of activity coefficients for all species is performed. Even, the ternary and quaternary interactions were also assigned to zero during the computation of activity coefficients for solvent groups. Hence, the model equations reduced to original model equations as described in Kiepe et al. (2006) and Yan et al. (1999). Similarly, for the ions, the ternary interactions (Eq. A6) are not considered to compute the activity coefficients, which are not explicitly described in the original AIOMFAC. So this term leads to zero, and hence the Eqs. (3.19) and (3.20) given in Zuend et al. (2008) leads to the original model equations (see Eq. 12 in Kiepe et al., 2006). The chemical species included in the multiphase mechanism are categorized by different classes in the input files. While using these input files, this algorithm performs a search, and gathers the information, whether the computation of interaction parameters needs to perform according to AIOMFAC or the modified equations specified according to Kiepe et al. (2006). Thus, the adjustable interaction parameters are used to compute and finally utilized by the activity coefficients responsible for MR interactions.

## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**GMDD**

8, 4155–4219, 2015

## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Treatment of  
non-ideality in the  
multiphase model  
SPACCIM**

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Treatment of  
non-ideality in the  
multiphase model  
SPACCIM**

A. J. Rusumdar et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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30



**Treatment of  
non-ideality in the  
multiphase model  
SPACCIM**

A. J. Rusumdar et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Treatment of non-ideality in the multiphase model SPACCIM**

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


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**Treatment of  
non-ideality in the  
multiphase model  
SPACCIM**

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



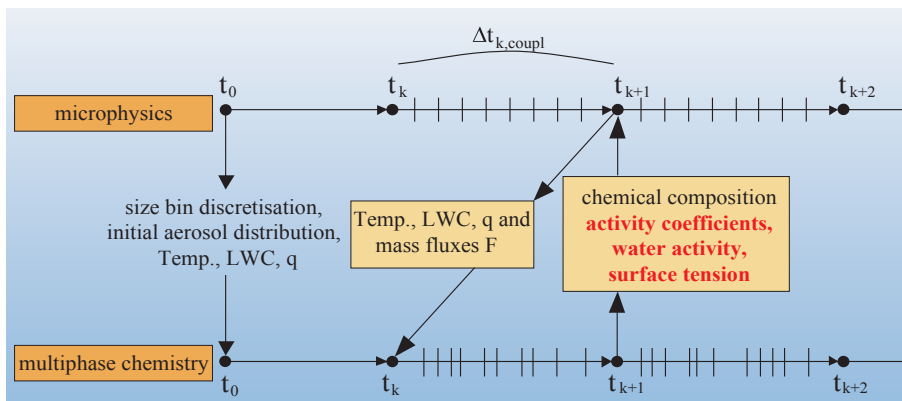
**Table 1.** Description of activities implemented in SPACCIM.

Activities	Description
Activity of a gas over a particle surface	$\{A_{(g)}\} = p_{A,s}$
Activity of an un-dissociated compound	$\{A_{(aq)}\} = m_A \gamma_A$
Activity of an ion in solution	$\{A^+\} = m_{A^+} \gamma_{A^+}$
Activity of liquid water in a particle	$\{H_2O_{(aq)}\} = a_w$
Activity of a solid	$\{A_{(s)}\} = m_s$



## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.



**Figure 1.** Schematic of the model coupling strategy and its implementation considering the treatment of non-ideality and surface tension effects in SPACCIM.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

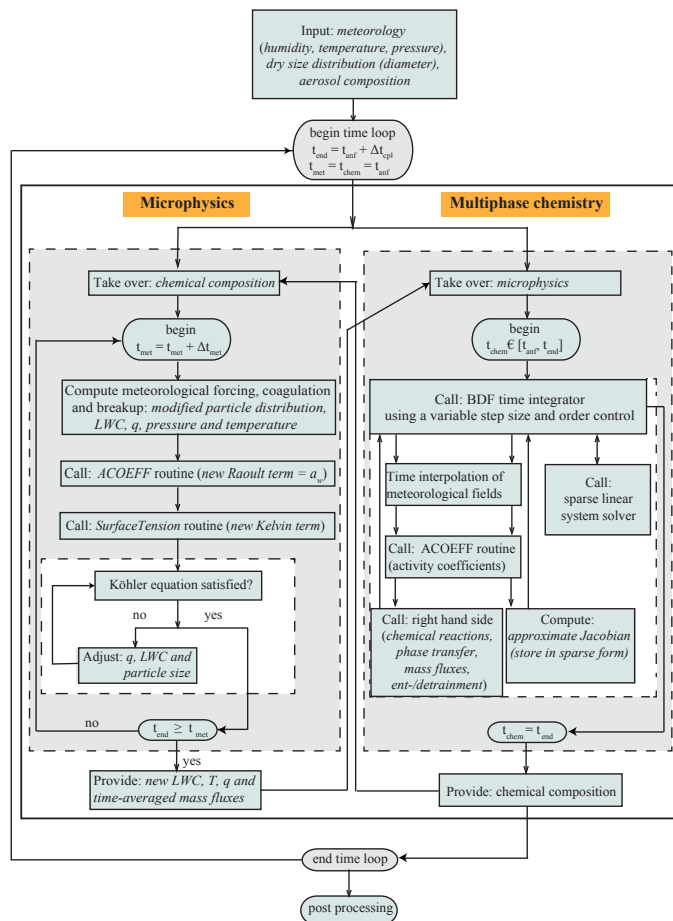
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Interactive Discussion



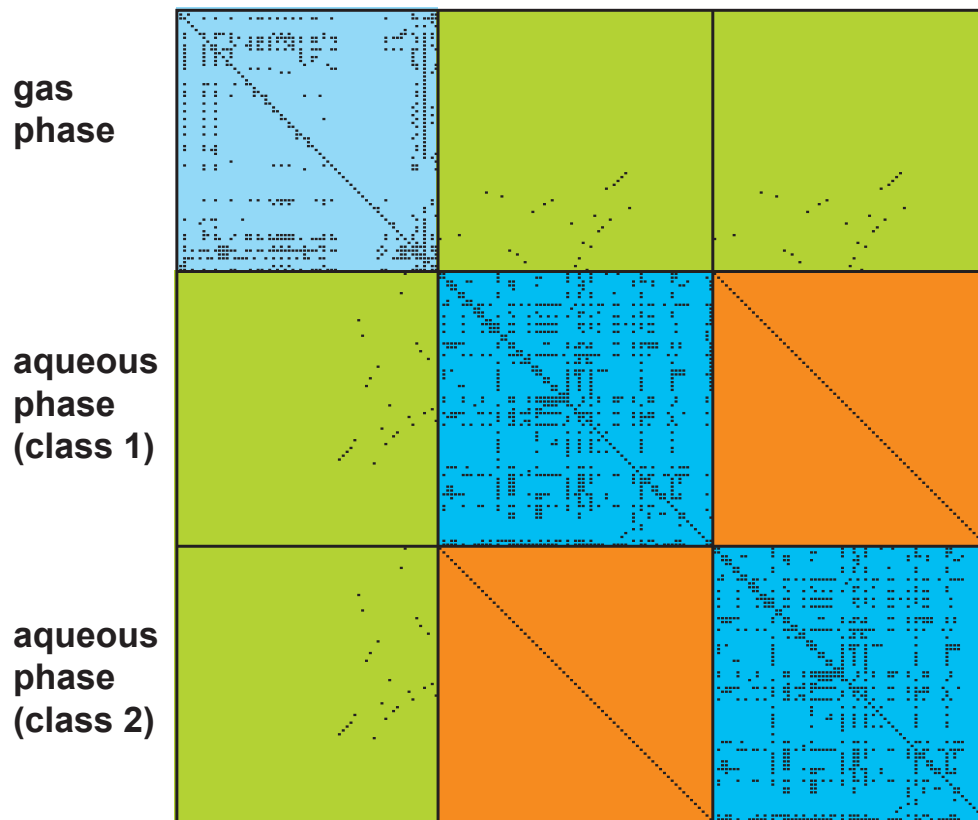
## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.



**Figure 2.** Scheme of activity coefficients and surface tension used in the microphysics and multiphase chemistry models.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[⏪](#)
[⏩](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

**Figure 3.** Sparse structure of Jacobian and two droplet classes (adapted from Wolke et al, 2005).

## GMDD

8, 4155–4219, 2015

### Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

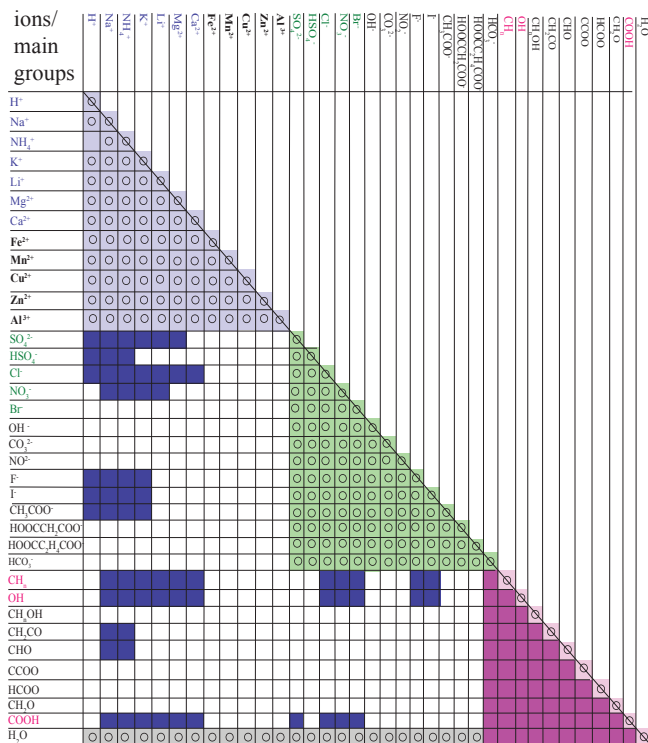
Interactive Discussion





## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.



- cation ↔ anion, ion ↔ funct. main group: parametrised in MR
- cation ↔ cation: no MR parameters with the exception of  $\text{NH}_4^+ \leftrightarrow \text{H}^+$
- anion ↔ anion: no MR parameters
- funct. subgroup ↔ funct. subgroup: parametrised in SR (UNIFAC) already
- same funct. group: no interaction
- water as the reference solvent for ions: no direct MR parameters

**Figure 4.** Scheme of the currently used interactions in the MR and SR part. Parameters for ion ↔ ion and ion ↔ organic main group interactions are all incorporated in the MR part and set to zero in the SR (UNIFAC) part.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

Full Screen / Esc

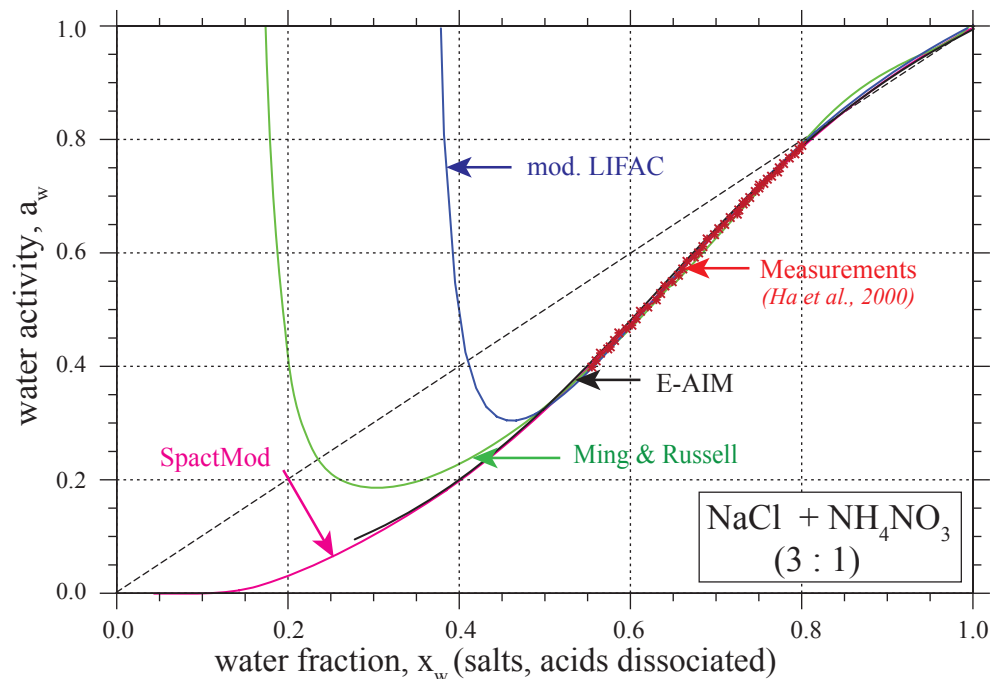
Printer-friendly Version

Interactive Discussion



## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.



**Figure 5.** Comparison with measurements of aqueous electrolyte solutions (symbols) and corresponding calculations of the models AIM III (Clegg et al., 1998b), mod. LIFAC (Kiepe et al., 2006), Ming and Russell (2002) and AIOMFAC (Zuend et al., 2008) at 298 K for the salt  $\text{NaCl} + \text{NH}_4\text{NO}_3$  at a molar salt mixing ratio of (3 : 1).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

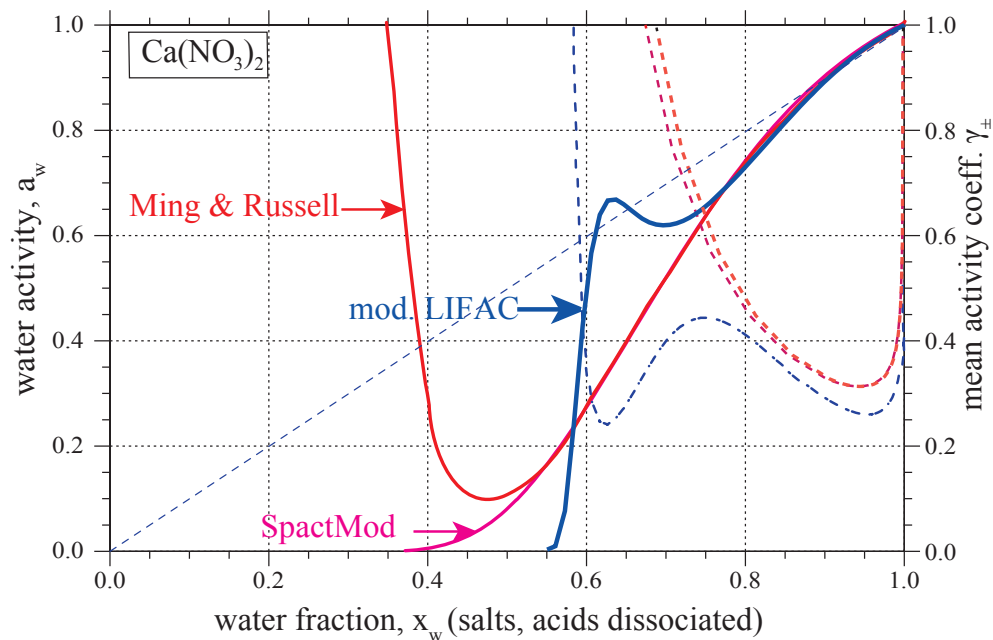
Printer-friendly Version

Interactive Discussion



## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.



**Figure 6.** Intercomparison between selected models for  $\text{Ca}(\text{NO}_3)_2$  salt: water activities (solid lines) and mean activity coefficients (dashed lines).

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

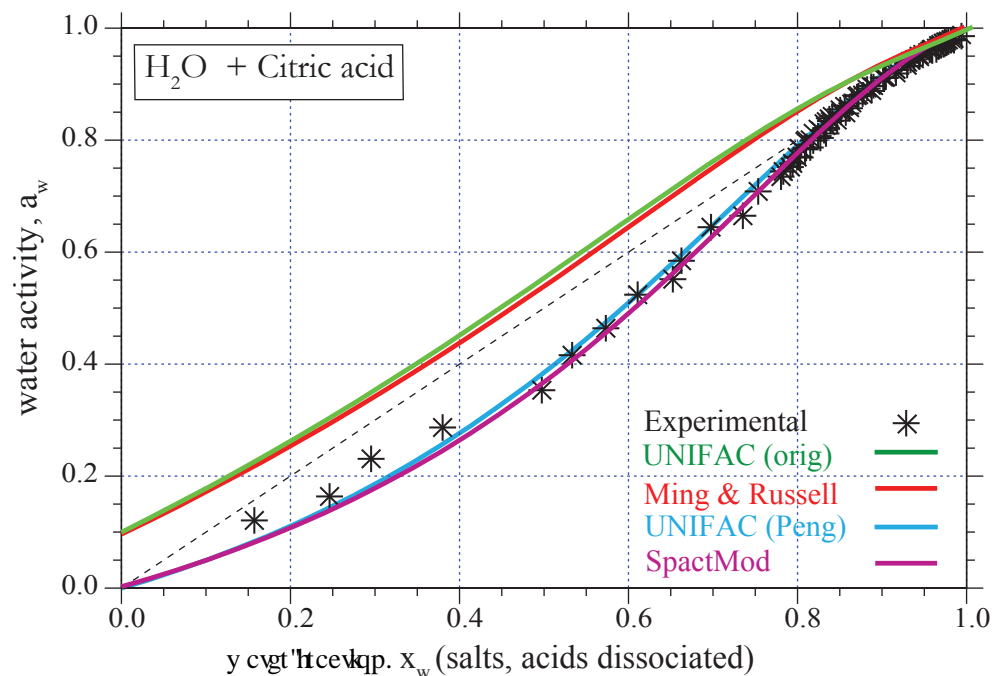
Printer-friendly Version

Interactive Discussion



## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.



**Figure 7.** Comparison between experimental and calculated water activities ( $a_w$ ) in aqueous citric acid solutions as a function of water fraction ( $x_w$ ) at 298.15 K. Experimental data from Maffia and Meirelles (2001).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

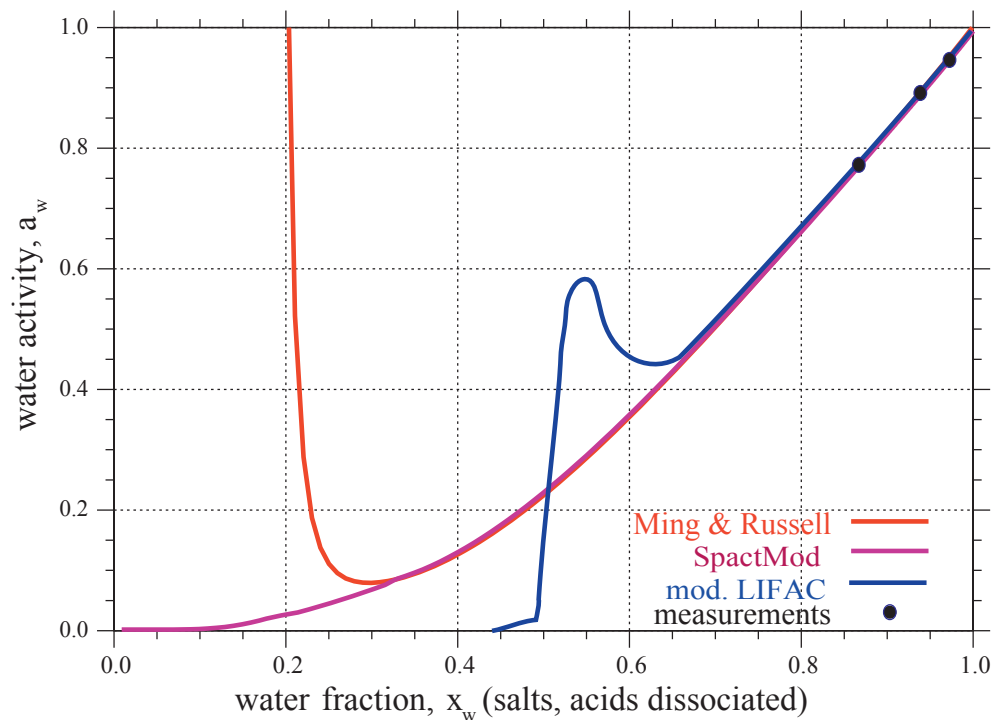
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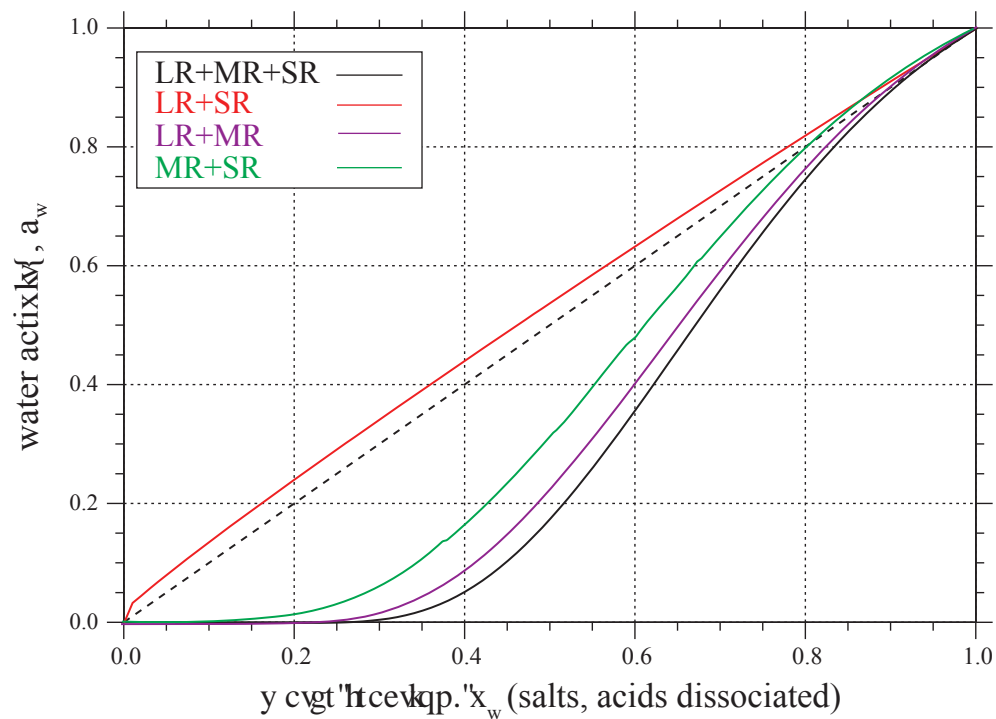
A. J. Rusumdar et al.



**Figure 8.** Comparison between measured and modeled water activities for the aqueous solution composed of organic–electrolyte mixture:  $(\text{NH}_4)_2\text{SO}_4$  + Ethanol + Acetic acid ((2 : 1 : 1) mole ratio).

## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.



**Figure 9.** Importance of different interactions in the aqueous solution composed of NaCl +  $(\text{NH}_4)_2\text{SO}_4$  + Ethanol + Malonic acid (1 : 1 : 1 : 1 (mole ratio)).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

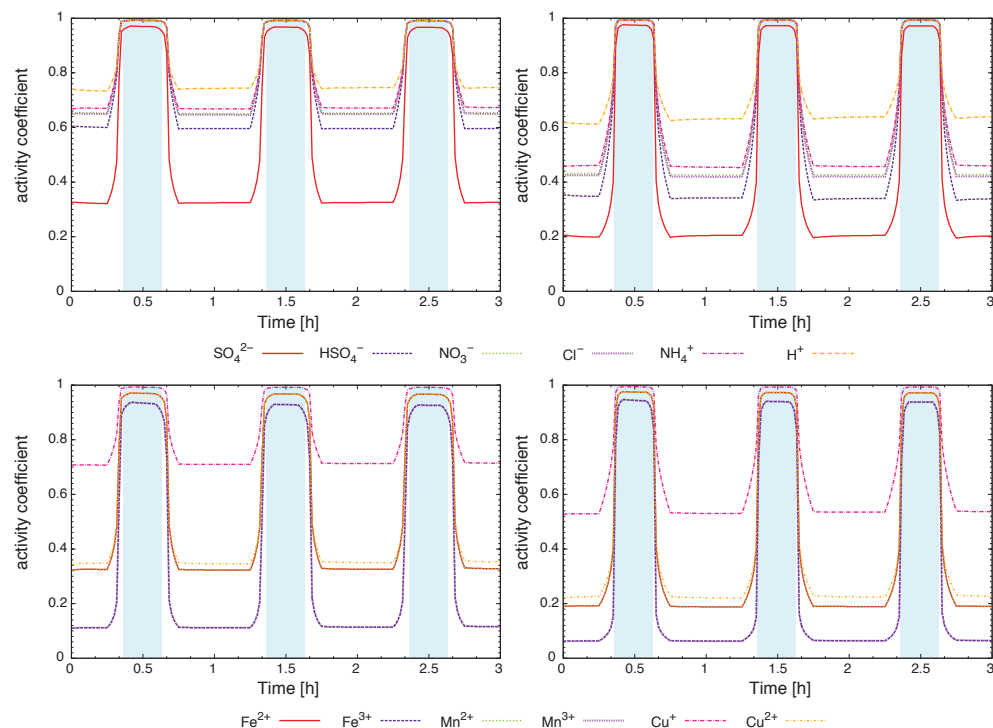
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A. J. Rusumdar et al.

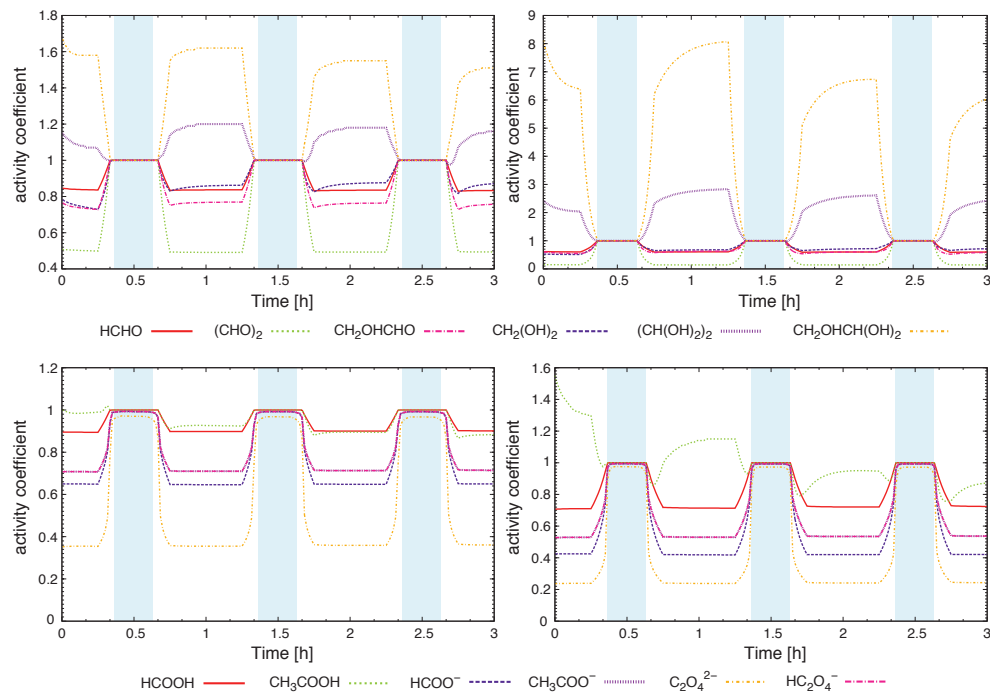


**Figure 10.** Modeled activity coefficients of main inorganic particle phase constituents (top) and important transition metal ions (TMIs, down) as the function of the simulation time for the two different relative humidity cases (left: 90 % RH, right: 70 % RH). The blue bars mark the in-cloud time periods during the simulation time.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[⏪](#)
[⏩](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


## Treatment of non-ideality in the multiphase model SPACCIM

A. J. Rusumdar et al.



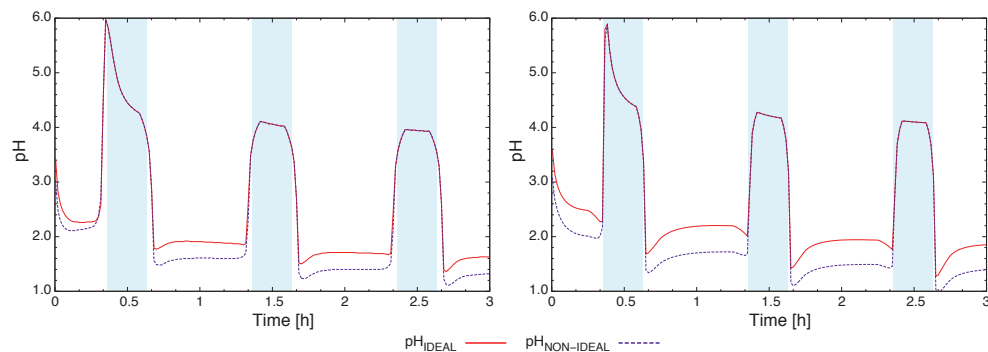
**Figure 11.** Modeled activity coefficients of organic carbonyl compounds (top) and organic acids/anions (TMs, down) as the function of the simulation time for the two different relative humidity cases (left: 90 % RH, right: 70 % RH). The blue bars mark the in-cloud time periods during the simulation time.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[⏪](#)
[⏩](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)




**Treatment of non-ideality in the multiphase model SPACCIM**

A. J. Rusumdar et al.



**Figure 12.** Modeled pH values as the function of the simulation time for the two different relative humidity cases (left: 90 % RH, right: 70 % RH) considering ideal (red line) and non-ideal (blue line) solutions, respectively. The blue bars mark the in-cloud time periods during the simulation time.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)