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**THERMODYNAMIC MODELLING OF
MULTICOMPONENT AEROSOLS**

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Doctoral dissertation

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Helsinki, December 2009

Tomi Raatikainen

Thermodynamic modelling of multicomponent aerosols

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University of Kuopio, 2009

ABSTRACT

Aerosols are known to have a significant effect on climate change as they are both directly scattering and absorbing solar radiation and indirectly affecting cloud properties. Uncertainties of these aerosol effects are still quite large, at least compared with those of the common greenhouse gases such as carbon dioxide. Both aerosol effects depend on several factors including aerosol size and hygroscopicity, which describes the tendency of particles to absorb water vapour. As water is the most common condensable atmospheric vapour, aerosol size depends directly on hygroscopicity. Atmospheric aerosol is composed of roughly equal amounts of organic and inorganic species. When the inorganic fraction is composed of a few well known species, the organic fraction is composed of thousands of species having a wide range of different properties.

Aerosol processes such as hygroscopic growth and cloud droplet activation can be modelled based on thermodynamic relations. In addition to the pure component properties, mixture properties such as solution surface tension and activity coefficients describing solution non-ideal behaviour are needed. These are calculated from simple parameterizations and semi-empirical models fitted to experimental data from macroscopic solutions.

The first purpose of this thesis project was to develop surface tension and activity coefficient models for aqueous organic–electrolyte mixtures of atmospheric interest. It was seen that the biggest problem in model development is the lack of both experimental data and fundamental thermodynamic models for multicomponent particles.

The second purpose was to test the effect surface active agents (surfactants), which decrease surface tension by accumulating on the solution surface, on cloud formation. Surface tension decrease is often ignored, but partly by cancellation of errors, it seems to be a good approximation. On the other hand, surface partitioning can not be ignored when the surface tension decrease is taken into account.

The third purpose was to estimate hygroscopicity, volatility and origin of real atmospheric aerosols detected by an aerosol mass spectrometer at a boreal forest measurement site. Measured total organic mass was divided into two organic fractions by applying a numerical method. It was found that one fraction contains less oxidized, fresh, semi-volatile and non-hygroscopic species from local sources. The other fraction contains highly oxidized, aged, less volatile and hygroscopic species mainly from anthropogenic sources.

It was shown that the activity coefficient and surface tension models can increase the accuracy of aerosol hygroscopicity predictions. Furthermore, when significant surface tension decrease is expected, surface partitioning is important for cloud droplet activation. These models are suitable for a limited group of known substances, but ambient aerosol hygroscopicity can be predicted well by using the fitted hygroscopicity parameters of the inorganic species and the organic aerosol components.

Keywords: Thermodynamic modelling, activity coefficient, surface tension, hygroscopic growth, cloud droplet activation, aerosol mass spectrometry

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List of publications

This thesis consists of an introductory review, followed by five research articles. The papers are reproduced with the kind permission of the journals concerned.

I Raatikainen, T., and Laaksonen, A. (2005). Application of several activity coefficient models to water–organic–electrolyte aerosols of atmospheric interest. *Atmos. Chem. Phys.*, 5, 2475–2495.

II Raatikainen, T., Laaksonen, A., Hyvärinen, A.-P., Vanhanen, J., Hautio, K., Lihavainen, H., Viisanen, Y., and Napari, I. (2008). Surface tensions of multicomponent aqueous electrolyte solutions: predictive models based on binary limits. *J. Phys. Chem. C*, 112, 10428–10434.

III Prisle, N. L., Raatikainen, T., Sorjamaa, R., Svenningsson, B., Laaksonen, A., and Bilde, M. (2008). Surfactant partitioning in cloud droplet activation: a study of C8, C10, C12 and C14 normal fatty acid sodium salts. *Tellus B*, 60, 416–431.

IV Prisle, N. L., Raatikainen, T., Laaksonen, A., and Bilde, M. (2009). Surfactants in cloud droplet activation: mixed organic-inorganic particles. *Atmos. Chem. Phys. Discuss.*, 9, 24669–24715.

V Raatikainen, T., Vaattovaara, P., Tiitta, P., Miettinen, P., Rautiainen, J., Ehn, M., Kulmala, M., Laaksonen, A., and Worsnop, D.R. (2009). Physicochemical properties and origin of organic groups detected in boreal forest using an aerosol mass spectrometer. *Atmos. Chem. Phys. Discuss.*, 9, 21847–21889.

Author's contribution

I wrote the summary part of this thesis. I planned the calculations in **Paper I** and collected experimental data for the comparison of published models and for fitting of the new and updated models. With a contribution from the co-author, I also wrote the text. Modelling work in **Paper II** is made by me. Other researchers are responsible for the new experimental data, but it I did the parameterizations. Again, I did most of the writing work. Cloud droplet activation experiments described in **Papers III** and **IV** were conducted by the first author. For these papers, I did all the modelling work and also participated in the writing work, especially in the modelling sections. Although the cloud droplet activation modelling scheme is not completely new, it was coded from scratch by using computationally efficient routines. Experimental data in **Paper V** is measured by others, but most of the raw data, especially the most relevant AMS and VTDMA data, was processed and analysed by me. Furthermore, I did all the calculations shown in the paper. I also did most of the writing work.

Aerosol is defined as a suspension of solid particles and liquid droplets in a gas. Their sizes range from one nanometre (10^{-9} m) clusters containing a few molecules up to $100 \mu\text{m}$ (0.1 mm). Here we are focused on the fine fraction, which means sizes smaller than $2.5 \mu\text{m}$. Atmospheric aerosols are known to have an effect on the climate change, directly by scattering and absorbing incoming solar radiation and indirectly by affecting on cloud properties, but the magnitude of this effect is still uncertain (Solomon et al., 2007). Especially the indirect effects, which mean the effect of aerosols on cloud optical properties (Twomey, 1977) and lifetime (Albrecht, 1989), have high uncertainties (Solomon et al., 2007). Properties of the aerosols and clouds depend on several factors such as meteorological conditions, atmospheric water content, initial aerosol number size distributions and aerosol hygroscopicity, which describes tendency of aerosols to absorb water. For example, when dried non-hygroscopic soot particles remain dry at 99 % relative humidity (RH), hygroscopic sea salt particles absorb significant amounts of water vapour even at much lower RH. Hygroscopicity is an important factor for both the direct and indirect effects simply by affecting on aerosol size at $\text{RH} < 100\%$ and on cloud droplet properties at $\text{RH} > 100\%$ (Haywood & Boucher, 2000; McFiggans et al., 2006; Swietlicki et al., 2008; Solomon et al., 2007). For example, if aerosol hygroscopicity is suddenly increased, droplets shrink and the evaporated water condenses to smaller droplets. For clouds this means increased optical thickness (cooling effect) and cloud lifetime (less rain). In reality, the situation is not that simple due to several feedback mechanisms (Solomon et al., 2007; Harvey, 2000).

Total aerosol mass and composition have a great spatial and temporal variability, but on the average about half of the continental submicron particle mass is from organic species (e.g. Saxena & Hildemann, 1996; Zhang et al., 2007). The inorganic fraction is composed of a few common ions like ammonium, sodium, sulphate, nitrate and chloride (Seinfeld & Pandis, 2006), whose chemical and physical properties are well known. Organic fraction, on the other hand, is composed of thousands of species with different properties (e.g. Saxena & Hildemann, 1996; Atkinson & Arey, 2003). Inorganic species can be identified rather easily, but a large fraction of the organic species can remain unidentified simply due to low mass concentrations and sampling issues related to reactivity, volatility and solubility of the species (Turpin et al., 2000).

Because organics can not be ignored in the aerosol modelling (Kanakidou et al., 2005), it is important to develop thermodynamic models suitable for aqueous organic–electrolyte

mixtures. Of course, the real composition of atmospheric organic aerosol is far too complicated for direct modelling, but certain "model" substances or organic groups can be used in representing different organic aerosol types. For example, dicarboxylic acids are used in several laboratory experiments (e.g. Peng et al., 2001; Prenni et al., 2001) to represent oxidized organic aerosol. In addition to the pure component properties such as densities and molecular weights, some mixture properties are needed. Activity coefficients are needed to describe non-ideal behaviour and surface tension is needed for calculating vapour pressure increase due to droplet curvature (Seinfeld & Pandis, 2006). Both surface tension and activity coefficients are calculated from parameterizations or semi-empirical models fitted to experimental data from macroscopic solutions (e.g. Hyvärinen et al., 2004, 2005; Vanhanen et al., 2008; Li et al., 1994; Yan et al., 1999; Clegg & Pitzer, 1992). In addition to the common solid–liquid and vapour–liquid equilibria, models can include bulk–surface partitioning. It is important for surfactants (surface active agents), which decrease solution surface tension by accumulating on the surface (Li et al., 1998; Sorjamaa et al., 2004).

Significant simplifications are needed for modelling of real atmospheric mixtures, where even pure component properties, or corresponding hygroscopicity parameters (Stokes & Robinson, 1966; Petters & Kreidenweis, 2007; Kreidenweis et al., 2008), of the organics are often unknown. Ideally just pure component hygroscopicity parameters and particle composition data are needed for predicting hygroscopic behaviour of multicomponent aerosols. Hygroscopicity parameters are readily available for the common inorganic species, but not for the organic fraction. However, these can be fitted to experimental chemical composition and hygroscopicity data (e.g. Duplissy et al., 2008). Aerosol hygroscopicity can be measured by a hygroscopicity tandem differential mobility analyser (HTDMA) (Rader & McMurry, 1986; Hämeri et al., 2000; Ehn et al., 2007). Chemical composition can be detected e.g. by an Aerodyne Aerosol Mass Spectrometer (AMS), which can measure mass concentrations of non-refractory species including total organic mass from submicron particles (Jayne et al., 2000; Allan et al., 2003; Canagaratna et al., 2007). It is not possible to identify individual organic species by using this instrument, but so called factors can be extracted from the total organic mass by applying matrix factorization methods (Zhang et al., 2005, 2007; Lanz et al., 2007; Ulbrich et al., 2009). From the modelling point of view, it is better to have a few relevant factors instead of hundreds of species or just one total organic mass.

The purpose of this thesis is to increase understanding of the aerosol organic fraction by developing thermodynamic models for mixed organic–electrolyte particles. In addition to organic substances used mainly in laboratory studies, properties of real ambient organic particles are estimated. The specific points of the thesis are to:

- test and develop activity coefficient models for multicomponent aerosols [**Paper I**]
- test and develop surface tension parameterizations for multicomponent aerosols [**Paper II**]
- investigate the effect of surfactants, which decrease droplet surface tension by partitioning to the surface, on cloud droplet formation [**Papers III and IV**]
- estimate hygroscopicity, volatility and origin of real atmospheric particles [**Paper V**]

As water vapour is the prevailing condensable vapour in the atmosphere, aerosol properties and effects on e.g. climate change depend largely on the tendency of aerosols to absorb water vapour, i.e. hygroscopicity (Haywood & Boucher, 2000; McFiggans et al., 2006). Hygroscopicity depends on aerosol size, chemical composition and properties of the species. Aerosol processes including hygroscopic growth and cloud droplet activation can be modelled based on thermodynamic relations, but it requires knowledge of both mixture (e.g. solution surface tension and activity coefficients) and pure component properties (e.g. equilibrium constants, molecular weights and densities).

There are several classes of small-scale aerosol models starting from single particle thermodynamics up to particle population dynamics. Depending on modelling framework, some processes are clearly time-dependent and some are practically independent of time. For example, most atmospheric particles are in thermodynamic equilibrium with the ambient water vapour at low relative humidity, but not necessarily at high relative humidities. For example, gas–particle partitioning (e.g. condensation of water, trace gases including semi-volatile organic vapours), and most chemical reactions (e.g. oxidation of organics and gas phase chemistry in general) can be quite slow processes, at least compared with the time scales of the liquid phase processes. Even if a model contains time dependent calculations, equilibrium thermodynamics is often needed. For example, air parcel models can have an equilibrium part for calculating equilibrium in the droplets (e.g. salt solubility and equilibrium vapour pressures at the droplet surface) and a non-equilibrium part for time-dependent processes such as diffusion limited condensation of vapours (e.g. Kokkola, 2003). This thesis starts from the basic thermodynamic properties of macroscopic solutions and then calculations are extended for systems of one aerosol particle in equilibrium with water vapour. Time dependent processes or particle populations are not considered here.

Theoretically a droplet containing water and dissolved solutes is in equilibrium with ambient water vapour when droplet and gas phase partial vapour pressures are equal (Seinfeld & Pandis, 2006). According to the Köhler equation (Köhler, 1936), equilibrium relative humidity (RH) for water in a droplet is:

$$\frac{RH}{100\%} = \gamma_w x_w \exp\left(\frac{4\sigma\bar{v}_w}{RTD_{aq}}\right), \quad (2.1)$$

where γ_w , x_w and \bar{v}_w (m^3/mol) are water activity coefficient, mole fraction and partial molar

volume, respectively. σ (N/m) is droplet surface tension, R ($\text{J mol}^{-1} \text{K}^{-1}$) is the ideal gas constant, T (K) is temperature, and D_{aq} (m) is droplet diameter. Commonly water partial molar volume is approximated by that of pure water, v_w . The water activity or Raoult term ($\gamma_w x_w$) describes the effect of solutes on water vapour pressure. Activity coefficient γ is a correction factor needed for non-ideal solutions. The exponential or Kelvin term accounts for water vapour pressure increase due to droplet curvature and surface tension.

Usually Köhler equation (Eq. 2.1) is used in calculating equilibrium RH as a function of droplet size for a given temperature and fixed dry particle composition (size D_{dry} and dry particle volume fractions ξ_i). Then, by using the pure component molecular volumes (v_i), water mole fraction can be calculated:

$$x_w = \frac{D_{aq}^3 - D_{dry}^3}{D_{aq}^3 - D_{dry}^3 + D_{dry}^3 v_w \sum_i \xi_i \nu_i / v_i} \quad (2.2)$$

Dissociation fraction (ν_i) is zero for insoluble species, one for molecular solutes and two for univalent electrolytes. In principle, it could also include the effects of partial dissociation and limited solubility, but here these are ignored. For an ideal case, where activity coefficients are set to unity and surface tension is equal to that of pure water, only pure component properties (ν_i and v_i) are needed for calculations. These can be found from the literature for most chemical substances.

Figure 2.1 shows an example of the dependence of equilibrium RH and particle size based on the Köhler equation (Eq. 2.1) for an initially dry 40 nm salt particle. Solute properties were the same as those of sodium chloride, but water activity coefficient was set to unity and surface tension was the same as that of pure water. Also, the deliquescence (DRH) and efflorescence (ERH) relative humidities were selected arbitrarily. The dry particle does not absorb water before the deliquescence relative humidity, where the salt dissolves completely and forms saturated salt solution. When ambient RH is increased from the DRH, water vapour condenses until equilibrium is reached. The growth is quite smooth up to 99 % RH, but after that it becomes highly sensitive to the RH (note the different scales for the sub- and supersaturated conditions). Kelvin and Raoult terms are monotonically decreasing and increasing functions of the droplet size, respectively, but their product has a maximum value. In this case the maximum equilibrium supersaturation (SS=RH-100 %) of the droplet water is 0.41 %. When the ambient SS is higher than this, condensation of water can not lead to the equilibrium. Eventually this non-equilibrium growth, which depends on the availability of water vapour, leads to formation of a cloud droplet. The supersaturation where particles start to grow spontaneously is called critical supersaturation (SSc). When the ambient SS decreases below droplet equilibrium SS, the droplet shrinks spontaneously so that equilibrium is reached again. As an example shown in Fig. 2.1, initially 520 nm droplets shrink spontaneously to 268 nm, when ambient supersaturation decreases to 0.35 %. When ambient RH is further decreased, particle size follows the growth curve down to the DRH. After the DRH, droplets can become supersaturated, which means that the smooth size decrease continues. Eventually droplets get dry at the efflorescence relative humidity (ERH).

There are a few quite new instruments such as LACIS (Leipzig Aerosol Cloud Interaction Simulator) (Stratmann et al., 2004; Wex et al., 2005, 2006) that are applicable for

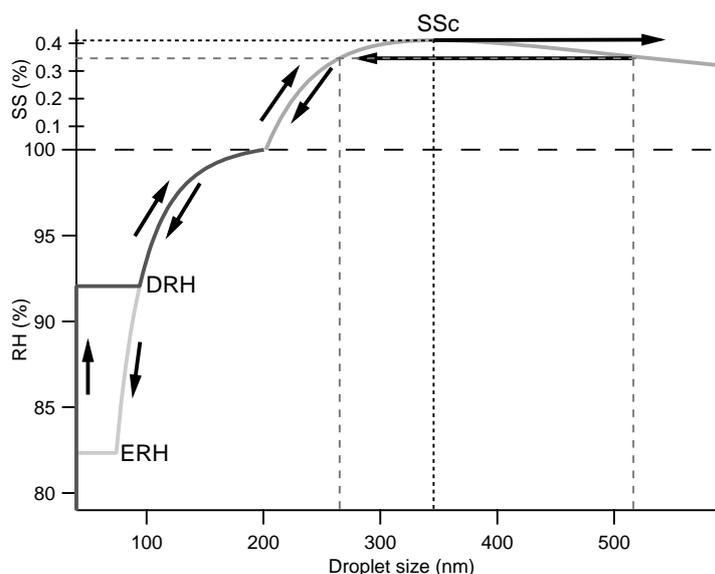


Figure 2.1: Droplet water equilibrium relative humidity (RH) and supersaturation (SS) as a function of droplet diameter. Calculations are for an initially dry 40 nm particle forming ideal solution. Note the different scales for the sub- and supersaturated conditions.

both low and high RH measurements. More commonly experiments as well as modelling studies are focused on either hygroscopic growth ($RH < 100\%$) or cloud droplet formation ($RH > 100\%$) regions, and this is the case in this thesis also. Cloud condensation nuclei (CCN) counters (e.g. Hudson, 1993; McMurry, 2000) measure critical supersaturation, and hygroscopicity tandem differential mobility analyzers (e.g. Swietlicki et al., 2008) measure particle growth factors (droplet size divided by the dry size) for $RH < 100\%$. Different variables of the Köhler equation are important for the high and low RH regions. Activity coefficients are especially important for predicting hygroscopic growth ($RH < 100\%$), because then the droplets are far from the ideal dilute solution limit. In addition, most solutes have the greatest effect on surface tension at high concentrations. Because droplets are dilute at the cloud droplet activation region ($RH > 100\%$), solute effects on both activity coefficients and surface tension are often ignored, i.e. activity coefficients are set to unity and constant surface tension of pure water is used. However, surfactants (surface active agents) can have significant effects on both surface tension and concentrations even in these dilute solutions (Li et al., 1998; Sorjamaa et al., 2004).

In general, water activity coefficient and surface tension are the most difficult variables of the Köhler equation (Eq. 2.1) simply, because they depend on mixture properties. Due to the absence of accurate theoretical models, these are calculated from semi-empirical models or just simple parameterizations fitted to experimental data from macroscopic solutions. It is clear that ambient aerosols contain far too many species to be considered separately, so some kind of simplification is definitely needed. For example, aerosol organic fraction can be described by a few organic groups so that one group contains chemically similar substances. When suitable experimental data (e.g. hygroscopic growth factors as a function aerosol composition) is available, at least average properties of groups containing different

chemical substances can be estimated. Much more data is needed for the fitting of surface tension and activity coefficient models. **Paper I** describes a comparison of previously published activity coefficient models and presents four new and modified activity coefficient models for atmospheric organic–electrolyte mixtures. Similarly, simple surface tension models are compared in **Paper II**. As a result, two simple predictive models are suggested for acid–base mixtures. **Papers III** and **IV** describe a comparison between measured and modelled cloud droplet activation of particles containing strong surfactants. **Paper V** is focused on atmospheric aerosols and especially on estimating hygroscopic properties of the organic fraction.

2.1 Activity coefficient models

Ideally water equilibrium RH over a flat solution surface depends on just water mole fraction in the solution. In reality dissolved solutes have different interactions with the water molecules, so the real equilibrium RH depends on both solute concentration and the types of the solutes. This solution non-ideality is described by the activity coefficient (γ), so that the effective concentration or activity (a) is the product of activity coefficient and concentration, e.g. $a_w = \gamma_w x_w$. In the absence of interacting solutes, pure solvents have unit activity coefficients. Usually solutes increase or decrease water activity coefficient, however, if the sum of interactions is the same as that in pure water, water activity coefficient is unity just as in the ideal solution.

Activity coefficients of the solution species (ions, molecular solutes and water) can be defined for different concentration scales and reference states. For example, mole fraction scale is common for solvents, but mole fraction, molal (mol/kg) and molar (mol/L) scales are all possible for solutes. Reference state, where the activity coefficient approaches unity, is commonly a pure component for the solvents and infinite dilution for the solutes. Reference state and concentration scale are related to the standard state defined as an ideal solution with unit concentration. Standard state thermodynamic constants such as free energy of formation and related equilibrium constants are used in calculating equilibrium between solid, liquid and gas phases (e.g. Ansari & Pandis, 1999).

Accurate activity coefficient models are available for thermodynamics of particles containing only inorganic components (e.g. Pitzer equations (Pitzer, 1973; Pitzer & Mayorga, 1973; Pitzer, 1991) and the Pitzer–Simonsen–Clegg model (Clegg & Pitzer, 1992; Clegg et al., 1992, 1998)), but those for predicting activity coefficients in mixed organic–electrolyte particles are more scarce. The main reason is that atmospheric particles contain thousands of organic species. The other reason is the lack of experimental activity coefficient data needed in model parameter fitting. In fact, most of the published experimental data as well as activity coefficient models are for mixtures used in the industrial processes.

From the model development point of view, solution species have different interactions. Electrolyte and non-electrolyte solutions have mainly long-range (LR) ion–ion and ion–water interactions and short-range (SR) dipole–dipole interactions, respectively. In addition to these, mixed solutions have middle-range (MR) interactions between ions and non-electrolytes. As a result, activity coefficients can be described as a sum of the different

contributions (Li et al., 1994; Yan et al., 1999):

$$\ln \gamma_i = \ln \gamma_i^{LR} + \ln \gamma_i^{MR} + \ln \gamma_i^{SR} \quad (2.3)$$

Usually long-range interactions are described by an electrolyte solution model such as ideal Debye-Hückel limiting law (Debye & Hückel, 1923). There are no fundamental models for the middle range interactions, but some kind of virial equations can be used (e.g. Li et al., 1994; Yan et al., 1999; Chang & Pankow, 2006). It is also quite common that the MR contribution is just ignored (Thomsen et al., 1996; Ming & Russell, 2002; Tong et al., 2008). Short range interactions can be described by a non-electrolyte model such as UNIQUAC (UNiversal QUAsiChemical) (Abrams & Prausnitz, 1975) or UNIFAC (UNiversal Functional Activity Coefficient) (Fredenslund et al., 1975) models. UNIFAC is based on so called group contribution concept, where all species are described by functional groups. For example, all organic acids can be described just by hydrocarbon chain (CH_n) and acid (COOH) groups. Thanks to that, the number of model parameters, which are related to the functional groups, is quite low and the model is predictive.

Paper I describes a comparison of experimental data and predictions from five previously published organic–electrolyte activity coefficient models: LIQUAC (Li et al., 1994), LIFAC (Yan et al., 1999), Extended UNIQUAC (Thomsen et al., 1996), Modified UNIFAC (Achar et al., 1994), and Ming and Russell model (Ming & Russell, 2002). Only the last model is designed for atmospheric aerosols; organics in the other models are mainly alcohols. Based on the model comparison, four activity coefficient models were selected for fitting of new parameters for atmospherically relevant mixtures. Experimental fitting data such as solubilities and activity coefficients were collected from the literature. When it was found useful, some modifications were made to the models. Organic species in the new model parameterizations are di-, poly- and hydroxycarboxylic acids, and inorganic species include common atmospheric salts and acids. All new models have the same UNIFAC parameterization for the SR interactions. The simplest new model contains just this UNIFAC part with additional parameters for the electrolytes. In addition to the UNIFAC part, Extended UNIFAC and re-parameterized LIFAC models have simple Debye–Hückel equations and re-parameterized Ming and Russell model has the Pitzer–Simonsen–Clegg model (Clegg et al., 1998). The re-parameterized LIFAC also accounts for the MR interactions by a virial equation. These models are all based on the group contribution concept, so in principle they are predictive. Model calculations showed that e.g. hygroscopic growth factors (defined as size of a droplet in equilibrium with water vapour divided by the dry size, $GF = D_{aq}/D_{dry}$) of mixed particles could be predicted accurately even with simple models. Solubility calculations, however, were inaccurate for most of the models.

The lack of experimental data for organic–electrolyte mixtures was the biggest problem in the parameter fitting. As a result, model predictions may be inaccurate for the highest concentrations as well as for the mixtures not used in the parameter fitting. Instead of one fundamental model, current models are just combinations of electrolyte and non-electrolyte models. A better model formulation could improve predictions, but the lack of experimental data is still a problem.

In general, these activity coefficient models are suitable for mixtures of a few known substances, e.g. used in some laboratory experiments. Composition of the ambient aerosol is both largely unknown and far too complicated for this kind of direct modelling.

2.2 Surface tension

Surface tension, σ (N/m or J/m²), can be defined as an energy needed to increase solution surface area. When a solution species is brought from interior to solution surface, energy is needed to break some intermolecular bonds as there are less interacting molecules in the surface. Because energy minimum is always preferred, solution surface area is minimized. As a result, spherical shape is preferred for small liquid volumes and liquids with curved surface experience increased pressure. Another consequence of the tendency towards energy minimum is that surfaces are arranged by an energetically favourable manner. This means that surface molecules can have a net orientation. For example, in the case of polar solvents such as water, species having both polar and non-polar ends are arranged so that the non-polar (hydrophobic) ends are towards gas phase and polar (hydrophilic) ends are towards liquid phase. In the case of liquid mixtures, surface area can be increased by bringing either solute or solvent species to the surface. When solute species have lower tendency to stay in the interior compared with that of solvent water, e.g. due to favourable surface structures or just weaker interactions, the solute will have increased concentrations in the surface and also solution surface tension is decreased from that of pure water. Analogously, strongly interacting solutes will be depleted from the surface and they will increase solution surface tension.

As mentioned above, droplets experience increased pressure, which depends directly on surface tension and droplet diameter (curvature). As a result, volatile species have higher partial vapour pressures compared with those over flat solution surfaces. This increased vapour pressure is described by the Kelvin term, which is the exponential term in Eq. 2.1. Figure 2.2 shows errors for equilibrium relative humidity related to differences between "real" and "expected" surface tensions used in the Kelvin terms:

$$\Delta RH = \frac{|RH^{\text{real}} - RH^{\text{expected}}|}{RH^{\text{real}}} 100\% \quad (2.4)$$

For example, the uppermost solid line shows the error for completely ignoring Kelvin term when the real and the expected surface tension are 72 and 0 mN/m, respectively. In the case of hygroscopic growth calculations, where RH is about 90 % and acceptable error is about 1 %, Kelvin term is important for droplets smaller than 200 nm and accurate surface tensions should be used for droplets smaller than 30 nm. In the modelling of cloud droplet activation, where RH is about 100.1 % and acceptable error is about 0.01 %, accurate surface tension is important for droplets smaller than 3 μm . For example, for a 3 μm droplet at 100.1 % RH, 1 mN/m error in surface tension leads to 100.11 % (= (1+0.01%/100%)100.1 %) RH, which means 10 % error from the correct 0.1 % supersaturation.

When a solute partitions to solution surface, surface tension is decreased, but also solute concentration decreases in the droplet interior. This has an effect on solvent vapour pressure (increased solvent mole fraction) as well as on solution surface tension (decreased solute concentration). It must be kept in mind that detectable droplet properties, such as solvent vapour pressure and surface tension, depend on concentrations in the interior; surface is always in thermodynamic equilibrium with the interior. The effect of partitioning depends on surface area to volume ratio of the system; it is important for small droplets, but totally

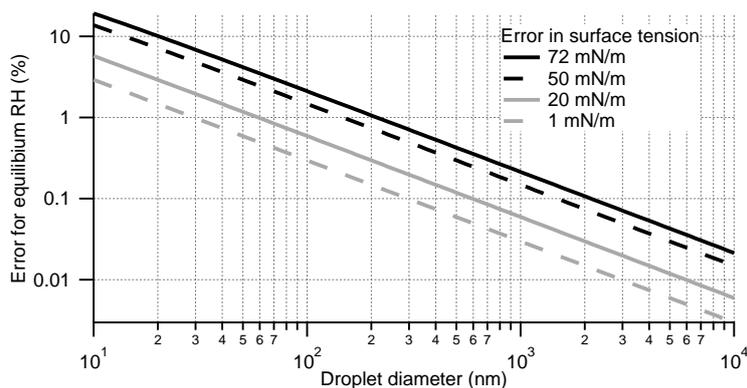


Figure 2.2: The effect of error in droplet surface tension on equilibrium RH as a function of droplet size. The 72 mN/m error represents a maximum error case, e.g. completely ignored Kelvin term, and 1 mN/m error is common due to limited accuracy of surface tension fits.

irrelevant for macroscopic solutions, e.g., used in the surface tension and activity coefficient measurements.

In order to model and describe surface concentrations, a simplified view of the gas–liquid interface is needed (Gibbs, 1928). Interfacial region is approximated by a flat surface, which just separates vapour and liquid phases. Constant concentrations equal to those far from the interface are expected throughout the liquid phase, which is from now on called bulk solution. Depending on the location of the surface, integrated bulk number concentrations may be different from the nominal total number concentrations. These lacking or extra species are therefore related to the area of the flat surface; the result is surface excess Γ (mol/m²). Absolute surface excess values depend on the location of the surface; it can be selected so that surface excess of the solvent is zero. On the other hand, surface can be selected so that the volume of the liquid is equal to the equimolar volume. Figure 2.3 shows an example of scaled molecular density (concentration) distributions near solution surface. Thick curves show the “real” density distributions and dashed lines describe approximated solution surface; horizontal lines are the constant molecular densities and the vertical line is the flat surface phase. Here surface is selected so that the solvent surface excess is zero. Solute 1 has a negative surface excess so the bulk molecular density is higher than the nominal value. On the other hand, solute 2 has a positive surface excess and decreased bulk molecular density.

When the surface is approximated as described above, Gibbs adsorption equation (Gibbs, 1928) relates surface tension gradient ($\frac{\partial\sigma}{\partial\ln a_s}$, derivative of solution surface tension with respect to surfactant activity) to the surfactant surface excess (Γ_s). The simple form of the Gibbs adsorption equation, where only one surfactant species has a non-zero surface excess, is:

$$\Gamma_s = -\frac{1}{\omega RT} \frac{\partial\sigma}{\partial\ln a_s} \quad (2.5)$$

Stoichiometric coefficient ω is needed for dissociating surfactants and for mixtures with common ions. For example, it is one for molecular and two for univalent surfactant species.

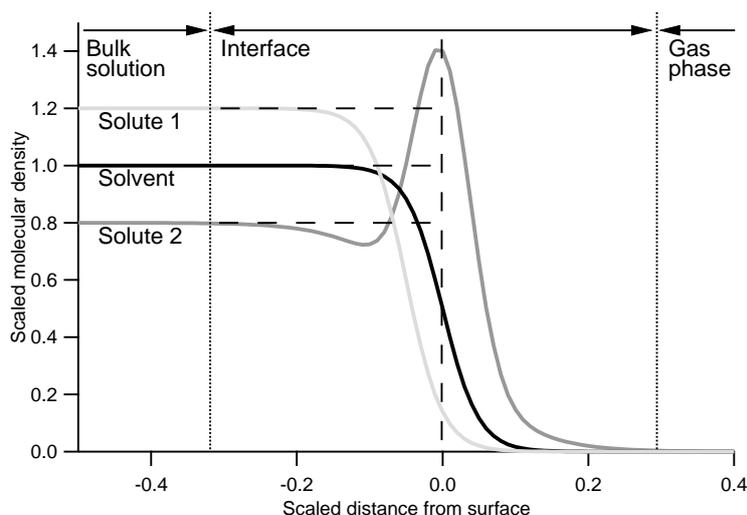


Figure 2.3: An example of real and approximated scaled molecular density distributions near solution surface.

Just as discussed above, decreasing surface tension means positive surface excess i.e. weakly interacting solute molecules are decreasing surface tension by accumulating to the solution surface. In principle, this equation can be used in estimating surface tensions from known surface activities and vice versa.

Surface activity, or tendency of a solute to accumulate on solution surface, depends on molecular or ion size, shape and interactions. Water molecules are small and polar, so they can have strong hydrogen bonds. Ions have even stronger interactions, so especially the highly hydrated "hard" metal cations have strong preference for bulk solution. Soft ions such as the largest halide and molecular ions can have increased surface concentrations. Organic molecules can have even higher surface concentrations, because they have relatively weak interactions with water molecules. This surface activity trend was seen in molecular dynamic simulations (Vrbka et al., 2004; Mucha et al., 2005; Gopalakrishnan et al., 2005; Jungwirth & Tobias, 2002, 2006; Chang & Dang, 2006), spectroscopic measurements (Ghosal et al., 2005; Baldelli et al., 1999; Brown et al., 2005; Shultz et al., 2002; Raymond & Richmond, 2004) as well as interpretations based on the Gibbs adsorption equation (**Paper II**; Donaldson, 1999; Mmereki et al., 2000; Pegram & Record, 2006, 2007; Weissenborn & Pugh, 1995, 1996).

Sometimes solution surface tension behaviour depends strongly on solution properties such as acidity. For example, ammonia and amines are decreasing surface tension just because molecular species partition to the solution surface (Donaldson, 1999). Also, simple univalent acids are decreasing solution surface tension (Weissenborn & Pugh, 1995) due to surface activity of hydronium ions (H_3O^+) (Mucha et al., 2005). When ammonia and hydrochloric acid are mixed, surface tension is greatly increased (Weissenborn & Pugh, 1995), because resulting symmetrical ammonium ions are depleted from the surface. This surface activity view presented in **Paper II** can explain surface tensions of aqueous ammonia–acid and amine–acid solutions (Hyvärinen et al., 2004, 2005), but of course accurate surface ten-

sion values can not be predicted. The view can be extended for other mixtures as well. For example, it can be expected that acidity increase surface activities of organic acids, because the acid remains less dissociated in acidic solutions.

As in the case of activity coefficient models, suitable model and experimental data is needed for surface tension parameterizations. Because purely theoretical models fail even in dilute solutions, surface tension models are often just empirical parameterizations suitable for aqueous single component solutions. Because real droplets contain several solutes, simple mixing rules based on weighted average of the binary solution limits are commonly used (Arstila et al., 1999; van Dingenen & Raes, 1993; Korhonen et al., 1999). There are several different ways to do the weighting, so this was tested in **Paper II** for the aqueous ammonia–acid and amine–acid solutions. Even if these mixtures have highly variable surface tensions, good correlation was found between simple mixing rules and experimental data, but only when an additional salt solution limit was included. As a result, two simple equations were recommended. It is clear that there are mixtures where these and other ideal mixing rules will fail. Therefore, ideal models should be used with care and, if possible, model predictions should be compared with available experimental mixture data.

Köhler theory for surface active species

Cloud droplet activation can be modelled based on the Köhler equation (Eq. 2.1). So called Köhler curves, representing equilibrium supersaturation ($SS = RH - 100\%$) as a function droplet size, can be calculated for a known dry particle size and composition. The maximum value of the curve is called critical supersaturation (SS_c). When it is exceeded, droplets start to grow spontaneously leading to formation of cloud droplets. Figure 3.1 shows an example of a Köhler curve and also the Raoult and Kelvin terms for a 40 nm NaCl particle. Again, ideal solution and constant surface tension were expected. The critical supersaturation is about 0.41 % and the critical droplet size is 345 nm.

Usually activating droplets are so dilute that surface tension is about the same as that of pure water and activity coefficients can be set to unity (Seinfeld & Pandis, 2006). However, surface active agents (surfactants), which have been found from different atmospheric samples (e.g. Seidl & Hänel, 1983; Facchini et al., 2000; Kiss et al., 2005), can accumulate to the droplet surface and decrease surface tension even in very low concentrations. Because critical supersaturation depend directly on droplet surface tension, it has been concluded that atmospheric surfactants can have a significant effect on cloud properties (e.g. Shulman et al., 1996; Facchini et al., 1999, 2000). However, these calculations did not accounted for the effect of surfactant bulk–surface partitioning, which is important for small droplets (Li et al., 1998; Sorjamaa et al., 2004).

Our purpose in **Papers III** and **IV** was to find out if and when this surfactant partitioning should be taken into account. For this purpose, three different modelling approaches were used:

- **Partitioning model:** the effect of surfactant bulk–surface partitioning on both surface tension and droplet bulk solution concentrations are fully taken into account. The model is described in Section 3.1.
- **Bulk surface tension model:** surfactant partitioning is ignored, but droplet surface tension is based on bulk concentrations. This is the same as doing calculations for a macroscopic solution, where the effect of partitioning is negligible.
- **Constant surface tension model:** partitioning is ignored and constant surface tension of pure water is used. This is a common approximation in cloud modelling, for example, due to dilute solutions or lacking surface tension data.

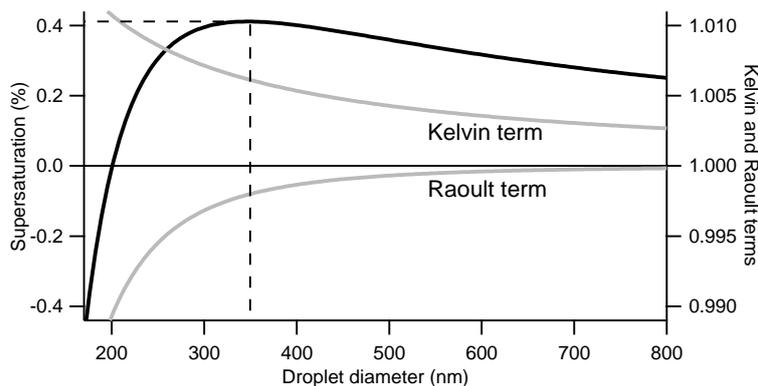


Figure 3.1: Köhler curve for a dry 40 nm NaCl particle. The grey lines are the Raoult and Kelvin terms shown in the right-hand side axis. Ideal solution was expected and the effect of the salt on droplet surface tension was ignored.

Figure 3.2 shows an example of calculations by using the three different modelling approaches. It is expected that originally the droplets are made from a macroscopic 20 mM sodium decanoate solution. When partitioning is ignored, surfactant bulk molarities, which are shown in the lower inset, are equal to the 20 mM nominal value. The effect of surfactant partitioning on bulk concentration depends on droplet size being most important for the smallest droplets and unimportant for droplets larger than 10^4 nm. As a result, droplet surface tension, which is shown in the upper inset, is between those of the pure water and the macroscopic solution. Kelvin terms of the partitioning and constant surface tension models are very similar, because surface tensions are similar for smaller droplets and the Kelvin effect becomes negligible for larger droplets. The net effect of the Raoult term on supersaturation is small, so the SS predictions of the partitioning and constant surface tension models are quite similar. Bulk surface tension model, on the other hand, predicts much lower SS values. It is not shown in Fig. 3.2, but for particles smaller than 1000 nm (positive supersaturation values), bulk and constant surface tension models predict about 20 % and 3 % lower supersaturation values than predicted by the partitioning model, respectively.

3.1 Surfactant partitioning model

The model used in **Papers III** and **IV** is similar to the model presented by Sorjamaa et al. (2004). There are some small differences, e.g. Sorjamaa et al. use an approximation of the Köhler equation, but generally model predictions are quite similar. Droplet bulk composition is solved from the adsorption equation

$$\sum_i n_i^T RT \partial \ln(a_i) = -A \partial \sigma, \quad (3.1)$$

where a_i and σ are activities of bulk solution species and surface tension, respectively. n_i^T is total (T) number concentration including both bulk (B) and surface (S) phases ($n_i^T = n_i^B + n_i^S$). Equation can be solved with the following assumptions and approximations:

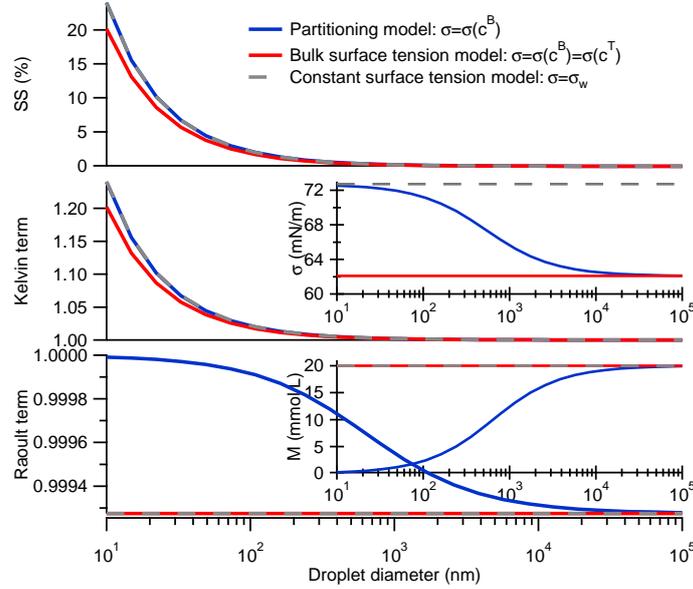


Figure 3.2: Effect of surfactant partitioning for different droplet sizes. It is expected that the droplets are made from a macroscopic 20 mM sodium decanoate solution at 293.15 K.

- Because activity coefficients were not available, these were set to unity. Sensitivity calculations (**Paper III**) showed that this is not likely to be a problem.
- It is expected that excess volume of mixing is zero and pure component molecular volumes can be used instead of partial molar volumes.
- Location of the surface is selected so that equimolar (total) and bulk volumes are equal ($V^T = V^B = \sum_i n_i^T v_i = \sum_i n_i^B v_i$). In agreement with the definition of the surface given in the previous section, this means that surface volume is zero ($V^S = \sum_i n_i^S v_i = 0$). Model predictions are not sensitive to the choice of the dividing surface, for example, surface concentrations of water and non-surface active solutes could be set to zero.
- Pseudobinary approximation is applied just to simplify calculations. Surfactant is one solution component and all the remaining species including water are considered as the other component. As a result, water and the other solutes have constant molar ratios in bulk and surface phases, and these are also equal to their total molar ratios ($n_k^T/n_j^T = n_k^B/n_j^B = n_k^S/n_j^S$).

In practice, equilibrium is solved iteratively for given total number concentrations, which can be calculated from the dry particle composition and droplet volume. Thanks to the approximations listed above, surfactant bulk concentration is the only unknown; the other bulk concentrations can be related to that of the surfactant.

3.2 Comparison with experimental data

Cloud droplet activation experiments were performed as described in **Papers III** and **IV**. Measurements in **Papers III** are for pure fatty acid sodium salts (FAS): sodium octanoate ($C_8H_{15}O_2Na$), decanoate ($C_{10}H_{19}O_2Na$), dodecanoate ($C_{12}H_{23}O_2Na$) and tetradecanoate ($C_{14}H_{27}O_2Na$). **Paper IV** is focused on mixtures of the C8, C10 and C12 fatty acid salts and sodium dodecyl sulfate (SDS) with sodium chloride (NaCl). SDS is purely an industrial surfactant, but organic acids are common in atmospheric aerosols (e.g. Anttila et al., 2005; Facchini et al., 2000). The three modelling approaches described above were used: partitioning model for fully accounting for surfactant partitioning, bulk surface tension model without partitioning, and constant surface tension model using surface tension of pure water. When the pure fatty acid salt modelling results were compared with the experimental data (**Paper III**), it was clear that the bulk surface tension model was greatly under predicting critical supersaturation. The difference was clear for all surfactants and dry particle sizes used in the experiments. On the other hand, similar predictions of the constant surface tension and partitioning models were accurate. By taking into account modelling uncertainties, such as unknown fatty acid salt densities and the ideal solution approximation, it was not possible to say which one, constant surface tension approach or the partitioning model, is better. Results were similar for the surfactant–salt mixtures (**Paper IV**), namely bulk solution surface tension model always gave far too low SSc values, and the other two models had rather similar predictions, again within experimental and modelling uncertainties. The biggest differences between partitioning and constant surface tension models are seen at high surfactant mass fractions. The difference is small for surfactant dry mass fractions less than 50 %.

The clear conclusion from the surfactant calculations is that, when surface tension is taken into account, it is highly important to consider also surfactant partitioning. Because predictions of the partitioning and constant surface tension models are quite similar, especially when the surfactant dry mass fraction is low, constant surface tension may be a good approximation. This is a useful approximation for large-scale models, because partitioning calculations are rather time-consuming. Anyway, it must be kept in mind that the good performance of the constant surface tension model is partly a coincidence and only the partitioning model is thermodynamically consistent. For example, thanks to the extensive partitioning, surfactant concentrations were always below solubility and micellisation limits.

The greatest modelling uncertainties are related to the unavailable activity coefficients and fatty acid salt densities. Some uncertainties are related to the difference between the modelling and experiments. For example, it was assumed that the dried particles are perfectly spherical and their solute mass fractions are the same as those in the solution used in generating particles. Nevertheless, the sensitivity analysis (**Paper III**) showed that our conclusions are valid.

Before the experiments and model calculations shown in **Paper III**, significant differences were expected to occur between predictions of the partitioning and constant surface tension models based on calculations done for pure surfactant particles (Sorjamaa & Laaksonen, 2006). In spite of the moderate and even high surfactant strengths, the predictions were quite similar. The effect of surfactant strength can be tested by doing model calcu-

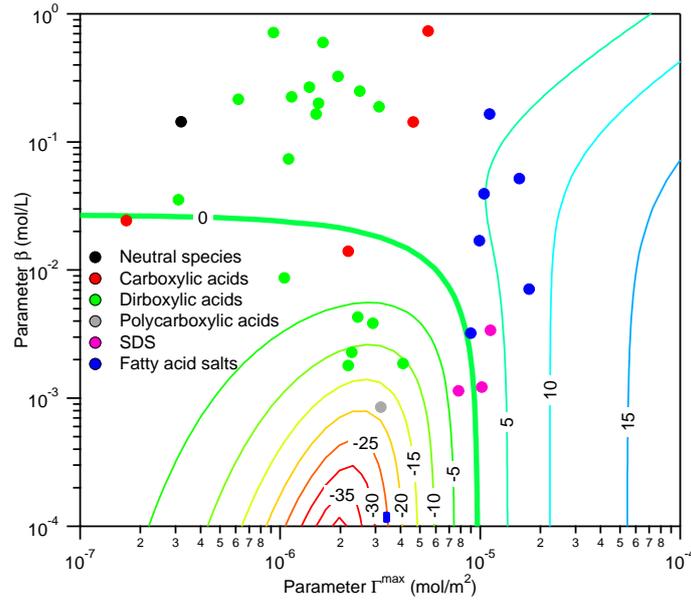


Figure 3.3: Difference between SSc from partitioning and constant surface tension models, $\frac{SSc(part.) - SSc(\sigma_w)}{SSc(part.)} 100\%$, as a function of the Szyskowski surface tension equation (Eq. 3.2) parameters. Calculations are for an ideal 100 nm sodium decanoate particle at 293.15 K.

lations for different surface tension model parameters. Figure 3.3 shows the relative difference in predicted SSc values from the partitioning and constant surface tension models, $\frac{SSc(part.) - SSc(\sigma_w)}{SSc(part.)} 100\%$, as a function of surface tension parameters Γ^{max} and β used in the Szyskowski equation (Szyskowski, 1908):

$$\sigma = \sigma_w - RT\Gamma^{max} \ln(1 + c/\beta) \quad (3.2)$$

Model calculations are for an ideal 100 nm sodium decanoate particle. Being independent of the Szyskowski parameter values, critical supersaturation from the constant surface tension model is always 0.28 %. The difference between model predictions is shown by evenly spaced contour lines ranging from -40 % to 15 %. The thickest green line represents Szyskowski parameter values leading to identical model predictions (0.28 %). Markers represent Szyskowski equation parameters of different chemical substances, e.g. dicarboxylic acids and fatty acid salts, taken directly from the literature (Tuckermann, 2007) and from fits to literature surface tension data (**Paper IV**; Campbell & Lakshminarayanan, 1965; Hyvärinen et al., 2006; Rehfeld, 1967; Alvarez et al., 1997). Note that most of these species have pure component properties different from those used in the model simulations. According to Fig. 3.3, critical supersaturation values from the partitioning and constant surface tension models can be identical even for the strongest surfactants, which have high Γ^{max} and low β parameters. Most of the markers, representing real chemical substances, are in the area where the difference between model predictions is less than 10 %. However, there are a few species (e.g. *cis*-pinonic and fulvic acids) for which the model predictions could be clearly different.

Real world organic aerosol composition is far too complicated for the thermodynamic modelling described in the previous sections. For example, it is not possible to identify all organic species from submicron particles, and even if this would be possible, it is not practical to include thousands of species into a model. So, some kind of simplification is definitely needed. Sometimes aerosol organic fraction is considered as it would be composed of a single component (e.g. Aklilu et al., 2006; Gysel et al., 2007; Sjogren et al., 2008). This is a good approximation when the chemical composition of the organic fraction is not changing much. Otherwise, organic mass could be divided into a few fractions, so that each fraction contains species with similar properties and concentration time series.

Recently new techniques based on aerosol mass spectrometry have become powerful methods for aerosol composition measurements (Canagaratna et al., 2007). For example, a quadrupole aerosol mass spectrometer (AMS) manufactured by the Aerodyne company can measure mass concentrations of non-refractory species from submicron particles. Time resolution is about 10 min and concentrations can also be measured as a function of particle size also. The instrument is described in Jayne et al. (2000); Allan et al. (2003, 2004); Jimenez et al. (2003). Briefly, air sample is lead through a critical orifice to an aerodynamic lens, where most of the air is removed by a series of turbo pumps and particles are focused to a narrow beam. Due to the pressure drop, particles gain speed depending on their size, shape and density. Sizing region contains a movable rotating chopper wheel, which can be used in recording mass spectrometer signal as a function of particle time of flight, which corresponds to particle size. After the sizing region particles hit a porous tungsten block heated to about 600 °C. Evaporated vapours are then ionized by using an electron impact ionization method and positive ions are detected by the quadrupole mass spectrometer. The quadrupole mass spectrometer can measure mass spectrum (ions/s) with a unit mass per charge (m/z) resolution up to 300 amu. Air and inorganic salts have known fragmentation patterns, so these can be separated from the measured mass spectra, and the remaining peaks are mainly from organics. Ion counts can be converted to mass concentrations ($\mu\text{g}/\text{m}^3$) by using known air sample flow rates, collection efficiency and ionization efficiencies.

Thanks to the rough ionization method, an AMS detects practically all organic species, but individual species can not be identified. However, certain numerical methods can be used in identifying factors from the extracted total organic mass spectra. The idea of these methods is to describe measured organic mass spectrum as a linear combination of a few

factors defined by concentration and mass spectrum vectors. When there is no *a priori* information about the factors, both concentration and mass spectrum vectors are considered as fitting parameters. Depending on the number of factors and if constraints are used in the fitting, methods can be called principal component analysis (Zhang et al., 2005), multiple component analysis (Zhang et al., 2007) or positive matrix factorization (Paatero & Tapper, 1994; Paatero, 1997; Lanz et al., 2007; Ulbrich et al., 2009). Positive matrix factorization (PMF), which is the latest method, was used in **Paper V**. In the PMF, concentrations and mass spectra are forced to be positive and there can be one or more factors. Type one and two Oxygenated Organic Aerosol (OOA1 and OOA2) as well as traffic-related Hydrocarbon like Organic Aerosol (HOA) are examples of typical factors (Lanz et al., 2007; Ulbrich et al., 2009). Both OOA1 and OOA2 can be counted as secondary organic aerosol (SOA); OOA1 is the highly aged and less volatile SOA fraction and OOA2 is the less processed semi-volatile SOA fraction (Lanz et al., 2007). These properties are based on their mass spectra and concentration time series. For example, OOA2 concentration shows clear anti correlation with temperature and OOA1 spectrum is similar to that of fulvic acid, a model compound representing aged and highly oxidized organic aerosol (Lanz et al., 2007).

4.1 Hygroscopicity parameters

In addition to the aerosol composition, basic physical properties such as molecular volumes (v_i) and dissociation fractions (ν_i) are needed for predicting aerosol hygroscopicity (Eqs. 2.1 and 2.2). It is not possible to measure these directly, but corresponding pure component hygroscopicity parameters can be deduced from measured aerosol hygroscopicity data. There are two commonly used pure component hygroscopicity parameters; pure component growth factors (GF_i) and so called κ_i values (e.g. Petters & Kreidenweis, 2007; Kreidenweis et al., 2008). Solute properties in Eq. 2.2 can be expressed by a constant, $\kappa_i = \nu_i v_w / v_i$, and when growth factors ($GF = D_{aq} / D_{dry}$) are used instead of dry and droplet sizes, the water mole fraction is:

$$x_w = \frac{GF^3 - 1}{GF^3 - 1 + \sum_i \xi_i \kappa_i} \quad (4.1)$$

where ξ is dry particle volume fraction. From the above equation, growth factors are

$$GF^3 = 1 + \frac{x_w}{1 - x_w} \sum_i \xi_i \kappa_i \quad (4.2)$$

Pure component growth factors, $GF_i^3 = 1 + \frac{x_w}{1 - x_w} \kappa_i$, can be inserted back to the equation above. The result is a modification from the original Zdanowkii-Stokes-Robinson (ZSR) mixing rule (Stokes & Robinson, 1966) for aerosol growth factors:

$$GF^3 = \sum_i \xi_i GF_i^3 \quad (4.3)$$

Pure component hygroscopicity parameters, GF_i in Eq. 4.3 and κ_i in Eq. 4.2, can be estimated by fitting the corresponding equation to experimental growth factor data. Volume fractions, which are also needed in the fitting, can be calculated from AMS data. Note that water mole fraction in Eq. 4.2 is just RH from the GF measurements divided by the Kelvin term.

4.2 A case study of organic aerosol properties

Organic aerosol properties including hygroscopicity, ethanol affinity and volatility were estimated by correlating measured concentrations with experimental data from three different tandem differential mobility analysers (TDMA). Also, origin of the organics were estimated based on backward trajectories (Draxler & Rolph, 2003) and a population density map. Experiments were performed during BACCI/QUEST measurement campaign in Hyytiälä, between March 31 and April 14, 2005. Hyytiälä is a rural forested measurement site in the middle of boreal forest belt (Kulmala et al., 2001). Detailed description of the calculations and results are given in **Paper V**.

Hygroscopic growth factors (HGF) were measured by hygroscopicity TDMA (HTDMA). The instrument is described in Ehn et al. (2007), but briefly, the first DMA is used in selecting a narrow size range from dried ambient particles. Then these particles are exposed to water vapour at a selected saturation and the resulting size distribution is measured by the second DMA and a condensation particle counter (CPC). Growth factor is the average size of the humidified particle sizes divided by the initial dry size. Organic TDMA (OTDMA) is similar to the HTDMA, but ethanol vapour is used instead of the water vapour (Joutsensaari et al., 2001; Vaattovaara et al., 2005). Ethanol growth factors (EGF) are indicative of particle composition as most hygroscopic species such as inorganic salts do not grow in ethanol vapour whereas many organic species tend to take up ethanol vapour.

Volatility TDMA (VTDMA) was the third TDMA instrument (Tiitta et al., 2009). It measures particle size distributions after heating dried ambient particles to 50, 150 and 280 °C. Instead of "shrink" factors, volume fractions were calculated for species evaporating at the different temperature intervals. Because nothing was evaporated at 50 °C, the lowest temperature range (<50 °C) was not included in the calculations. In practice volume can be divided to fractions evaporating before and after 150 °C. Volatilities of the species detected by the AMS can be estimated by correlating their volume fractions (ξ_i) with those from the VTDMA measurements ($\xi^{\Delta T}$):

$$\xi^{\Delta T} = \sum_i p_i^{\Delta T} \xi_i \quad (4.4)$$

Fitting parameter $p_i^{\Delta T}$ is the fraction of species i evaporating at temperature range ΔT .

Quadrupole AMS was measuring mass concentrations of sulphate, nitrate, ammonium and organics. Concentrations of the inorganic ions were strongly correlated, so these were considered as a single group ($\text{SO}_4^{2-} + \text{NO}_3^- + \text{NH}_4^+$). Measured total organic mass spectrum was analysed by the Positive Matrix Factorization (PMF) method as described in Ulbrich et al. (2009). Calculations showed that there are only two clearly independent factors; highly oxidized and aged OOA1 (oxygenated organic aerosol, type 1) and less oxidized and fresh OOA2 (OOA, type 2). Primary organics such as HOA (Lanz et al., 2007; Ulbrich et al., 2009) were not seen, and even their characteristic peaks were practically missing from the measured mass spectrum. When the number of factors was known, rotational parameter FPEAK (Ulbrich et al., 2009) was varied for determining the rotational variability of the factors. It seems that FPEAKs have the greatest effect on the mass spectra and especially on peaks at m/z 44. Because only the concentration vectors are needed in the calculations, the results are not sensitive to the FPEAK values. Reasonable solutions were found for FPEAK values from 0 to -0.3, so their mean value (-0.15) was chosen for further calcula-

tions. Taking the variability related to the FPEAKs into account, oxygen to carbon ratios (O:C) (Aiken et al., 2008) of the OOA1 and OOA2 are about 0.77 ± 0.10 and 0.23 ± 0.08 , respectively.

Mass concentrations of the OOA1, OOA2 and $\text{SO}_4^{2-} + \text{NO}_3^- + \text{NH}_4^+$ were converted to volume fractions by using densities 1400, 1200 and 1700 kg/m^3 , respectively. Their pure component growth factors were fitting parameters, when the ZSR equation (Eq. 4.3) was fitted to the experimental ethanol and water growth factors. Volatilities of the components were estimated by correlating AMS and VTDMA volume fractions according to Eq. 4.4. Finally, their origin was estimated from correlations with backward trajectories and population density maps.

It was found that OOA1 is long-range transported mainly from anthropogenic sources. On the average, OOA1 is the less volatile and hygroscopic ($\text{HGF}=1.29$ at 88 % RH for 50 nm dry diameter) organic fraction. It seems that OOA1 species have wide range of different growth factors and volatilization temperatures; the less hygroscopic OOA1 species evaporate under 150 °C and the more hygroscopic OOA1 species at higher temperatures. In fact, it appears that some of the least volatile OOA1 species can have almost as high growth factors as the inorganic species have. OOA2, on the other hand, has short atmospheric lifetime so it is mainly from local, possibly biogenic (Tunved et al., 2006), sources. Practically all OOA2 species are evaporated before 150 °C and these species are non-hygroscopic ($\text{HGF}=1.00$). It seems that OOA2 life time is so short that its concentration is independent of air mass history. On the other hand, clear diurnal concentration cycle depending on ambient temperature was found, but the explanation is still more or less open. Semi-volatility has been a common explanation at least for night time maximum (Lanz et al., 2007), but volatility studies have shown that OOA2 evaporates above 50 °C (**Paper V**; Huffman et al., 2008).

As a result of the growth factor correlations, OOA species have average pure component growth factors. When the aerosol composition is known, these can be used in predicting growth factors for real mixed organic–electrolyte particles. Predictions shown in **Paper V** are surprisingly good, at least when the simplicity of the model and experimental uncertainties are taken into account. Also, the successful correlations show that OOA1 and OOA2 are clearly independent factors, which have different chemical and physical properties and sources. Current findings are in good agreement with those of the previous studies, but the generality of the conclusions is limited by the short duration of the campaign. More data is needed from other seasons as well as from other measurements sites.

Global scale aerosol models can be used in predicting aerosol effects, e.g. for climate change, but many of the parameterized processes are based on particle-scale calculations. This thesis is focused on particle-scale modelling of aerosol hygroscopicity, including both low and high RH regions. Aerosol hygroscopicity can be predicted by using thermodynamic models accounting for solution non-idealities (**Paper I**) and surface tension effects (**Paper II**). Such models can be used in estimating the importance of different effects and processes. For example, the effect of surfactant bulk–surface partitioning on cloud droplet activation was studied in **Papers III** and **IV**. Modelling work was also extended for real atmospheric aerosols (**Paper V**). Due to the complexity of the atmospheric mixtures, surface tension and non-ideality effects had to be discarded.

Aerosol inorganic fraction can be described with a few relevant ions, which can be detected quite easily. There are also a number of accurate thermodynamic models for the inorganic species. On the other hand, the organic fraction contains thousands of different species and often a significant fraction remains unidentified. Compared with the current knowledge about the aerosol inorganic fraction, much less is known about organics or organic–electrolyte mixtures, which is the focus of this thesis. It is clear that the real atmospheric organic fraction is far too complicated to be included into any model as such. Often only small subsets of species representing larger groups are parameterized, for example, dicarboxylic acids can represent oxidized organics. Surface tension and activity coefficient models were developed for organic–electrolyte mixtures (**Papers I** and **II**). Organic species in the activity coefficient models are mainly di- and polycarboxylic acids. These had to be chosen based on availability of experimental literature data needed in the parameter fitting. Surface tension models are for mixtures of inorganic acids and ammonia or amines. Pure fatty acid salts, which represent atmospheric surfactants, and these mixed with an inorganic salt were used in testing the effect of surfactants on cloud droplet activation (**Papers III** and **IV**). It is possible to include real atmospheric mixtures to models, but due to the lack of literature data, this requires simultaneous chemical composition and e.g. hygroscopicity measurements. Such measurements were carried out during a Hyytiälä field campaign as described in **Paper V**. As a result, hygroscopicity parameters as well as volatilities were derived for two factors extracted from the total organic mass.

This thesis is focused on thermodynamic modelling of multicomponent aerosols containing both organic and inorganic species. In **Paper I** five published activity coefficients models are compared and four models are selected for fitting of new parameters for atmospherically relevant mixtures. **Paper II** is focused on testing simple surface tension models as well as explaining surface tensions based on surface activities of dissolved species. **Papers III** and **IV** examine the effect of surface active species on cloud droplet formation. **Paper V** extends the results of the previous papers for real atmospheric particles.

Paper I begins with a comparison of experimental data with predictions from five published activity coefficient models suitable for organic–electrolyte mixtures. Only one of these models was suitable for aerosol modelling. The other models included mainly organic solvents such as short chain alcohols, which are not common in the atmosphere. Based on the model comparison, four models were selected, and also modified when it was found useful, for fitting of new parameters for organic–electrolyte mixtures relevant in aerosol modelling. When predictions from the new and other published aerosol models were compared with experimental data, it was found the new models are accurate especially for aqueous organics and organic–electrolyte mixtures. Also, even the simplest new model could predict water activities with good accuracy.

Paper II starts by explaining surface tension behaviour of aqueous acid–ammonia/amine mixtures measured in two previous studies. The explanation is based on different surface activities: low for hard atomic cations, high for soft molecular ions and the highest for molecular species. Both acid and amine solutions have low surface tensions, because hydronium cations and amine molecules have high surface activities. When they are mixed, surface tension is greatly increased due to the formation of less surface active ammonium and aminium ions. The view, which is in good agreement with several published spectroscopic and molecular dynamic studies, can be used in predicting effects of different solutes on solution surface tensions. By using the available acid–ammonia/amine solution surface tension data, accuracies of several simple surface tension models, based on binary solution surface tensions, were compared. As a result, two simple models, where the salt limit is taken into account, were suggested for further use.

Paper III is focused on thermodynamic modelling of cloud droplet formation from fatty acid salt particles representing atmospheric surfactants. Surfactants have a high tendency to partition to solution surface. This decreases both solution surface tension and surfactant bulk concentration. Three different modelling approaches were compared: (1) fully accounting for partitioning, (2) ignoring partitioning, but accounting for surface tension decrease, and (3) just using surface tension of pure water. When model predictions were compared with the experimental data, it was clear that surfactant partitioning must be taken into account when accounting for the surface tension decrease. Predictions of the partitioning and constant surface tension models were accurate and thus surprisingly similar. The predictions of are similar mostly due to cancellation of errors, but it seems that the difference is often quite small.

Paper IV extends calculations from **Paper III** for mixed particles containing fatty acid salts or sodium dodecyl sulphate and sodium chloride. Again, predictions from the three modelling approaches were compared with the data from experiments. The results were very similar; surfactant partitioning can not be ignored when accounting for surface tension decrease, and the predictions from the partitioning and constant surface tension models are again very similar. The general conclusion from these two papers is that CCN (cloud condensation nuclei) activity of surfactant particles is greatly over predicted when concentration dependent surface tension is used without accounting for surfactant partitioning. Constant surface tension can be used when surfactant dry mass fraction is low, but predictions are quite good for the higher mass fractions also. Still, only the partitioning model is fully consistent from the thermodynamic point of view.

Paper V is focused on chemical and physical properties of real atmospheric particles, and especially on the organic fraction. Aerosol chemical composition and different properties were measured simultaneously in a measurement campaign conducted in a forested measurement site in southern Finland. In addition to the common inorganic species, two oxygenated organic aerosol components (OOA1 and OOA2) were identified from AMS (Aerosol Mass Spectrometer) data. Hygroscopicity parameters, volatility and origin of the components (OOA1, OOA2 and sum of the inorganic ions) were estimated by correlating concentrations with the corresponding experimental data. In good agreement with the previous studies, the more oxidized organic aerosol component (OOA1) is the hygroscopic and less volatile organic fraction. It is long-range transported mainly from anthropogenic sources. The less oxidized organic aerosol component (OOA2) is from local sources and it is practically water-insoluble and semi-volatile.

Aerosols are known to have an effect on climate change, but the magnitude of this effect is still uncertain (Solomon et al., 2007). Aerosol effects can be studied by using thermodynamic models, such as Köhler theory (Seinfeld & Pandis, 2006) with or without accounting for surfactant partitioning (Li et al., 1998; Sorjamaa et al., 2004). For the simplest calculations, at least physical properties of the solutes or corresponding hygroscopicity parameters are needed. Accuracy of the predictions can be increased by using parameterizations describing mixture properties such as activity coefficients and surface tension. The problem is that these parameterizations are rarely available for atmospheric mixtures, especially for the organics. Because atmospheric aerosols contain thousands of different organic species, it is neither practical nor possible to include all of these to the models. Instead, either detectable organic components (e.g. HOA) or known model species representing real world organic aerosol subsets (e.g. dicarboxylic acids) can be used.

Most of the published activity coefficient models are designed for industrial processes, where organic solvents such as short chain alcohols are common. These are not common in the atmosphere, but the models can be extended for atmospheric mixtures by fitting new parameters. Of course, all models are not equally good as was seen when different models were compared with each other and with experimental data (**Paper I**). When suitable models were found, the next problem was the lack of experimental data, especially for organic–electrolyte mixtures, needed in parameter fitting. For this reason, fitted models are valid for a limited group of species. In comparison with published models and experimental data, the new models were found to be accurate for aqueous organics and organic–electrolyte mixtures. Even if these models are predictive, there are a lot of possible mixtures, which can not be modelled accurately. Better model formulation could increase model accuracy, but the lack of experimental data is still the biggest problem. Activity coefficient models are not valid for real atmospheric particles simply due to the huge amount of different species. However, it should be possible to develop a simplified model for aerosol containing inorganic species and organic aerosol components such as OOA1, OOA2 and HOA. Again, the problem is that there is not enough experimental data for the parameter fitting.

Just like activity coefficients, also solution surface tensions are needed in thermodynamic modelling. Organic electrolytes such as amines can have a significant effect on solution surface tension depending on solution acidity (**Paper II**). When the neutral solution limit is taken into account, surface tensions of solutions containing ammonia or amines

and inorganic acids can be predicted by using simple mixing rules. Furthermore, observed surface tension behaviour of the ammonia/amine–acid solutions can be explained based on surface activities of different ions and molecular species; hard ions are depleted from surfaces, unsymmetrical and polar ions can partition to the surface, and molecular species prefer partitioning to the surface. This view can be used in estimating effects of solutes on surface tension. For example, it is likely that organic acids have high surface activities in acidic solutions, where the molecular form dominates.

Unsymmetrical ions with a long non-polar hydrocarbon "tail" and a polar ionic "head" can have exceptionally high tendencies to partition to solution surface. These surfactant species thus decrease surface tension and also have an effect on solution concentrations. Surface tension effects are often completely ignored or only the surface tension decrease is taken into account; both surface tension and concentration effects are rarely considered. These three considerations were tested by comparing model predictions with cloud condensation nucleus activation data on pure fatty acid salts (**Paper III**) and their mixtures with sodium chloride (**Paper IV**). It was seen that surfactant cloud droplet activation capabilities are greatly overestimated when surfactant partitioning is ignored and surface tension decrease is taken into account. On the other hand, predictions were accurate and surprisingly similar for the full partitioning model and the model using just surface tension of pure water. This seems to be just a coincidence, but large differences between predictions are not expected at least for reasonable surfactant strengths and concentrations. Even if constant surface tension seems to be a good approximation, the full partitioning model is the only one that can explain the experiments on a thermodynamically consistent basis. Even if partitioning and constant surface tension models predict similar critical supersaturation values, critical droplet sizes and solution concentrations are different. Critical droplet size is relevant in cloud droplet activation where the availability of water vapour is limited. Solution concentrations, on the other hand, are important at least for chemical equilibria and vapour–liquid partitioning of volatile vapours.

In the case of real atmospheric particles, the first step before fitting activity coefficient and surface tension models is to find reasonable pure component properties. Simultaneous property (hygroscopicity, ethanol affinity and volatility) and composition measurements were done in Hyytiälä during an intensive field campaign (**Paper V**). Properties and origin were estimated for detected inorganic species and for two oxygenated organic aerosol (OOA) fractions extracted from total organic mass. It seems that one component (OOA2) contain species that are fresh, semi-volatile and non-hygroscopic. The other species (OOA1) are aged, highly oxidized, long-range transported and hygroscopic. To our knowledge this was the first time, when all of these OOA1 and OOA2 properties were determined quantitatively and at the same time. In good agreement with the expectations, organic aerosol hygroscopicity, oxygen to carbon ratio (O:C) and volatility seem to be correlated. The fresh and especially primary organic species are mostly volatile, water-insoluble and they have low O:C values. When oxidation processes start to increase the O:C ratio, volatility decreases and hygroscopicity increases. In a few days, these processes lead to the highly oxidized, less volatile and hygroscopic OOA1, the end product of the organic oxidation chains.

Even if atmospheric organics have been extensively studied especially during the re-

cent years, much is still unknown. With the development of the aerosol mass spectroscopic methods capable of detecting aerosol chemical composition including organics, it has become possible to model real world aerosol hygroscopicity. To test the general validity of the aerosol component hygroscopicity approach, hygroscopicity parameters should be determined for the known organic aerosol components by using data from different locations. This kind of fairly simple description of the complex real world aerosol could be very useful for large scale models.

In spite of differences between model species and the real atmosphere, simple activity coefficient and surface tension models are still needed, at least for testing different theories. For example, due to experimental and modelling uncertainties, it was not possible to show that there is a clear difference between predictions from surfactant partitioning and constant surface tension models. Differences could be seen, if accurate thermodynamic parameters were available.

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