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A curved multi-component aerosol hygroscopicity model framework: Part 2 – Including organic compounds

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Abstract. This paper describes the inclusion of organic particulate material within the Aerosol Diameter Dependent Equilibrium Model (ADDEM) framework described in the companion paper applied to inorganic aerosol components. The performance of ADDEM is analysed in terms of its capability to reproduce the behaviour of various organic and mixed inorganic/organic systems using recently published bulk data. Within the modelling architecture already described two separate thermodynamic models are coupled in an additive approach and combined with a method for solving the Kohler equation in order to develop a tool for predicting the water content associated with an aerosol of known inorganic/organic composition and dry size. For development of the organic module, the widely used group contribution method UNIFAC is employed to explicitly deal with the non-ideality in solution. The UNIFAC predictions for components of atmospheric importance were improved considerably by using revised interaction parameters derived from electro-dynamic balance studies. Using such parameters, the model was found to adequately describe mixed systems including 5–6 dicarboxylic acids, down to low relative humidity conditions. By comparison with electrodynamic balance data, it was also found that the model was capable of capturing the behaviour of aqueous aerosols containing Suwannee River Fulvic acid, a structure previously used to represent the functionality of complex oxidised macromolecules often found in atmospheric aerosols. The additive approach for modelling mixed inorganic/organic systems worked well for a variety of mixtures. As expected, deviations between model predictions and measurements increase with increasing concentration. Available surface tension models, used in evaluating the Kelvin term, were found to reproduce measured data with varying success. Deviations from experimental data increased with increased organic compound com-

plexity. For components only slightly soluble in water, significant deviations from measured surface tension depression behaviour were predicted with both model formalisms tested. A Sensitivity analysis showed that such variation is likely to lead to predicted growth factors within the measurement uncertainty for growth factor taken in the sub-saturated regime. Greater sensitivity was found for the value of dry density used in the assumed form of the dried out aerosol. Comparison with a coupled thermodynamic approach showed that assumed values for interactions parameters may lead to erroneous results where a simple additive approach may provide more accurate results. However, where available, the use of coupled thermodynamics can better reproduce measured behaviour. Further work (and laboratory data) is required to assess whether this difference lies within the experimental uncertainty of observed hygroscopic behaviour for a variety of systems.

1 Introduction

A companion paper (Topping et al., 2004) describes the development of a diameter dependent inorganic hygroscopic aerosol model. The subject of this paper is to extend this to include organic components but also to analyse our ability to model such components using recently published data for various mixed systems. Using a variety of sampling techniques for analysing ambient aerosols it is becoming increasingly apparent that organic components may constitute a substantial fraction of the aerosol composition, ranging from 20–60% of the fine particulate matter depending on the location (Alfarra et al., 2004; Chow et al., 1994; Decesari et al., 2000; Rogge et al., 1993), and that these components are likely to play an important role in radiative forcing (Kanakidou et al., 2005; Kumar et al., 2003; Lohmann and Feichter, 2005). Including organics into any modelling framework is complicated since, unlike the inorganic fraction, the organic fraction

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is composed of hundreds of individual components covering a wide range of molecular forms, solubilities, reactivities and physical properties (Jacobson et al., 2000). This makes a complete characterisation of the organic aerosol extremely difficult, forcing more general techniques to be developed in which model components are suggested as representative candidates for water soluble organic carbon (WSOC) (e.g. Decesari et al., 2000). This also makes it necessary to analyse our ability to model a wide variety of compounds using laboratory data for various mixed and single solute systems whenever possible. Field studies indicate that 20–70% of the condensed phase organic carbon is water soluble (Facchini et al., 2000; Saxena and Hildemann, 1996) and that this soluble material includes low molecular weight carboxylic acids, dicarboxylic acids, alcohols, aldehydes, ketones, nitrates and multifunctional compounds (Peng et al., 2001). By analysing the water solubility, condensability and atmospheric abundance, Saxena and Hildemann (1996) proposed that this fraction could also include C2-C7 polyols, amino acids and other oxygenated multifunctional compounds. Recent studies have also shown that as much as 50% of the WSOC can exist as poly-carboxylic acids with chemical functionalities analogous to humic material (HULIS) (Decesari et al., 2001; Krivacsy et al., 2001; Zappoli et al., 1999). Natural fulvic acids, a bi product of larger humic acids (HA) have been suggested as representative substances for atmospheric HULIS (Brooks et al., 2004). Extending the limited analysis of macromolecular compounds, Mikhailov et al. (2004) also studied the behaviour of the protein bovine serum albumin (BSA), chosen as a representative compound for proteins and other macromolecular organics, and the inorganic salts sodium chloride and ammonium nitrate by laboratory experiments and model calculations.

Observations of aerosol hygroscopicity, coupled with this chemical information, highlight the wide range of effects organic components may have, in both the sub and supersaturated regime. The hypothesis that organics influence aerosol hygroscopicity is driven largely by an inability to explain the observed behaviour through the consideration of inorganic components alone. Field studies using hygroscopic tandem differential mobility analysers (HTDMA) have indicated that organics can hinder or enhance water uptake by the inorganic portion (e.g. Pitchford and Mcmurry, 1994; Saxena et al., 1995). Similar laboratory studies have mostly focused on pure and low molecular weight organic acids such as carboxylic acids, di-carboxylic acids and multifunctional organic acids (Choi and Chan, 2002a; Na et al., 1995; Peng and Chan, 2001; Prenni et al., 2001) and their combinations with inorganic salts (Choi and Chan, 2002a, b; Cruz and Pandis, 2000; Lightstone et al., 2000). Results are often contradictory in the literature which points to different overall effects depending on the organic components and particle morphology and chemistry (Cruz and Pandis, 2000). Nonetheless, the potential of organics to influence aerosol hygroscopicity is clear, requiring the development of theoretical models which

can not only be used for comparisons with experimental data, but also as predictive tools where measured hygroscopic data may not be available.

Including the physical and chemical characteristics of such a wide range of components in a modelling environment is difficult, especially when experimental data is bound to be lacking. To explicitly treat the non-ideality of the organic fraction requires a technique for predicting the activity coefficients of a large number of components from a much smaller subset of parameters. Treating each compound as a molecule would not only be cumbersome but also require binary aqueous data for each and every compound (Saxena and Hildemann, 1997). Fortunately the problem of characterising activity coefficients in multiple organic solutions has been faced previously in many engineering processes and group contributions methods have been developed, the most widely used being UNIFAC (Fredenslund et al., 1975). Though it has been noted to have various shortcomings (e.g. Choi and Chan, 2002a; Cruz and Pandis, 2000; Koo, 2003), numerous attempts to improve its predictive capability have been made in relation to components of atmospheric importance. This study uses recently published data for mixed organic solutions and the model described in the following sections to analyse our ability to treat such systems in Sect. 2. This includes a brief analysis of a representative acid for larger macromolecular compounds (Suwannee River Fulvic Acid).

Treating the interactions between the inorganic and organic fractions forms the main crux of the problem when attempting to model mixed inorganic/organic systems. Attempts have been made to formulate a coupled thermodynamic approach, namely the models of Ming and Russell (2002) and Clegg et al. (2001). In the model of Ming and Russell (2002) ions were treated as new groups within UNIFAC, whereas Clegg et al. (2001) formulated a molality based model for coupling the two separate fractions. Both utilised the same activity coefficient models for the separate fractions (organics – UNIFAC; inorganics – mole fraction based activity model of Clegg and Pitzer, 1992; Clegg et al., 1992). Unfortunately, these coupled models are currently hampered by a severe lack of experimental data from which important interaction parameters can be derived. As such, it has become necessary to neglect this coupling with the future intent to improve the description as and when the data becomes available, or indeed as new coupled models are developed. Thus, aerosol hygroscopicity models can be developed in a variety of fashions. The model presented here uses an additive approach for treating mixed inorganic/organic systems analogous to the ZSR mixing rule (Stokes and Robinson, 1966) where the inorganic and organic fractions are assumed to act independently of each other. However, the interactions between the water associated with each fraction and the respective solutes are treated explicitly by combining two separate thermodynamics models, the only interactions neglected being those between the inorganic and organic components. Concentrations in solution are calculated by using

the independent water contributions associated with each separate fraction, unlike the models of Clegg et al. (2001) and Ming and Russell (2002). This enables the principles of the ZSR relationship to be retained within the model without having to use a model for the osmotic coefficient of the total water content which does not reduce to the ZSR relationship when interactions between the inorganic and organic fractions are not treated explicitly. Comparisons between this additive approach, using theoretical predictions for water uptake, and recent experimental data in the literature for binary and higher order mixed systems are carried out before conclusions regarding the ability of such an approach to deal with a variety of mixed systems made. This is done in Sect. 2.

Using the diameter dependent framework discussed in the companion paper, it is also necessary to model the surface tension of the mixed solution. Incorporating the influence of organic components on the aerosol surface tension is complex yet crucial to understanding their influence on the hygroscopic growth. It is well known that some organic compounds are surface active and their presence in solution can significantly affect the surface tension of cloud droplets (Facchini et al., 2000; Shulman et al., 1996; Tuckermann and Cammenga, 2004). However, incorporating any such effects into a model is again hampered largely by a lack of experimental data. Shulman et al. (1996) measured the surface tension of various acids of atmospheric importance in the laboratory while Facchini et al. (2000, 2001) measured the surface tension of wet aerosol and cloud/fog samples. Whilst such studies provide useful parameterisations (e.g. Abdul-Razzak and Ghan, 2004; Ming and Russell, 2004), it would be beneficial to use a model that could calculate the change in surface tension with varying organic composition, which may be very different from those defined in such experiments. To this end, different available surface tension models are tested for atmospherically important components before investigating the sensitivity of the hygroscopic growth to the choice of model. This is carried out in Sect. 3. Firstly the development of the separate organic module is described along with the parallel investigations on a variety of systems described earlier.

2 Thermodynamics

The equilibrium composition of the aerosol is determined by using the thermodynamic framework described in the companion paper to this report, so this will only be briefly described here. The model employs the constrained minimisation algorithm FFSQP (Zhou et al., 1997), to minimise the Gibbs free energy of the system. The description of the Gibbs energy is critically dependent on the treatment of nonideality in solution; this is described in the following section. First multiple organic solutions are analysed before methods for treating mixed inorganic/organic systems are discussed. The Gibbs free energy (G) is a function of temperature, pressure and the number of moles of each component being considered:

$$G = \sum_i n_i \mu_i \tag{1}$$

where μ_i is the chemical potential of component 'i', and n_i the corresponding number of moles. The definition of chemical potentials for aqueous components is given by:

$$\mu_i = \mu_i^o(T) + RT \ln(\gamma_i m_i) \tag{2}$$

where $\mu_i^o(T)$ is the standard state chemical potential (kJ mol^{-1}), R is the universal gas constant (0.0083145 kJ mol^{-1}), T is the temperature (K), γ_i the activity coefficient, m_i the molality (mol kg^{-1} water). Where data is unavailable for $\mu_i^o(T)$ it may be estimated using the third order group contribution method of Marrero and Gani (2001). Whilst possible to include solid precipitation for the organic/water systems by using what little data is available to constrain the model, this is not covered in extensive detail here. However it is useful to give an example of how the model can deal with solid precipitation, as was demonstrated in the companion inorganic paper. Marcolli et al. (2004) presented physical properties of individual compounds (e.g. molecular weight and deliquescence RH (DRH) at 25°C) including 8 dicarboxylic acids. Using the technique of Marrero and Gani (2001) and the recorded DRH for the individual compounds reported by Marcolli et al. (2004) it is possible to derive energies of formation for the pure species before deliquescence. It is then possible to calculate mutual DRH points assuming no other solids form other than the individual species treated above, thus neglecting any complex or double salts for example. Using the activity coefficient model described in the following report and the above procedure, the energies of formation for pure malic, malonic, maleic and glutaric acid were calculated as -847.720102 kj mol^{-1}, -701.149623 kj mol^{-1}, -605.642671 kj mol^{-1} and -685.441896 kj mol^{-1}, respectively. Using these parameters, the mutual DRH points of three mixtures treated by Marcolli et al. (2004) can be calculated. These mixtures included: malic/malonic, malic/malonic/maleic and malic/malonic/maleic/glutaric reported at the eutonic composition. The measured DRH points were found to be 61.8, 56.4 and 48.8%, respectively. ADDEM calculated the DRH points to be at 66.1, 60.2 and 51.5%, respectively. Deviations of only 4.3, 3.8 and 2.7% show good agreement between model results and observed DRH points for these systems even when only simple compounds are allowed to precipitate out of solution. Whether this occurs in reality is in question and requires further research. The gradual deliquescence behaviour, as calculated ADDEM, of the four component mixture mentioned above is illustrated in Fig. 2. Including solid precipitation within the mixed inorganic/organic modelling framework cannot be justified as the full range of interactions taking place is not considered (Fig. 5). Whilst the behaviour of simple mixed inorganic/organic aerosols is often
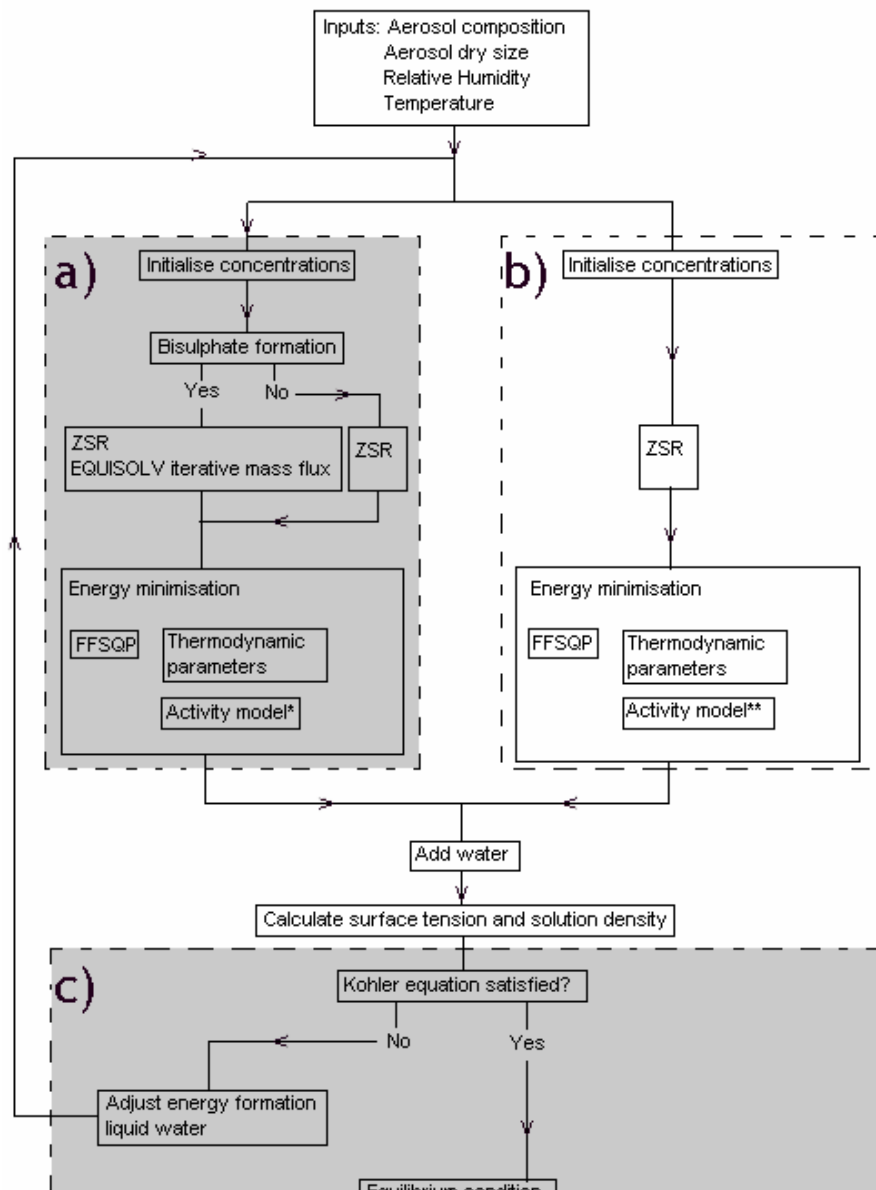
Fig. 1. ADDEM model schematic. **(a)** Inorganic module described in the companion paper (Topping et al., 2004). **(b)** Organic module described in this paper. **(c)** Iterative scheme for solving the Kohler equation, described in the companion paper (Topping et al., 2004).

described using the properties of the individual components (e.g. Bilde and Svenningsson, 2004; Shulman et al., 1996), the role of organics on the crystallisation RH and the deliquescence RH of inorganic aerosols is not well understood (Choi and Chan, 2002b). Also it is likely that aerosols harbour a wider range of organics than the simple systems often studied in the laboratory (e.g. Decesari et al., 2000; Rogge et al., 1993). Results from field measurements suggest that aerosols may remain aqueous at low RH (Dick et al., 2000; Massling et al., 2003; Saxena and Hildemann, 1996; Weingartner et al., 2002). Similarly, the laboratory study of Marcolli et al. (2004) showed that the liquid phase may be the

most stable phase for mixtures involving inorganic and organic components at low RH.

Hence, this paper focuses on purely aqueous aerosol, the restriction of such an approach becoming necessary when treating mixed inorganic/organic systems using uncoupled thermodynamics. Similarly, since there is no solid precipitation or complex formation treated here, the sensitivity to energies of formation for the solute components need not be carried out. A thorough examination of such sensitivity was given in the development of the inorganic model. Only a sensitivity to the energy of formation of water in the liquid phase is found when determining the equilibrium composition for

an organic aerosol in this instance. This sensitivity was discussed in the accompanying paper to this report and the same value used in this model. A model schematic for the inclusion of organics is shown in Fig. 1. The areas marked out with a grey background represent aspects of the model already covered in the companion paper. The reader is referred to this for a more thorough discussion of the numerics and theory of the diameter dependent model. In the following section the separate organic module is described (Fig. 1b) before the coupling of the inorganic and organic modules discussed.

2.1 Solute activity coefficients in organic systems

As with the inorganic model one must calculate the activity coefficients of the solutes. Unlike electrolytes, organic components have diverse chemical structures and possess quite different properties, both from each other and from electrolytes (Ming and Russell, 2002). UNIFAC is perhaps the most widely used technique for calculating activity coefficients in mixed organic systems and has been used in previous atmospheric applications involving organics in mixed aqueous solutions (Clegg et al., 2001; Ming and Russell, 2002). The model equations, consisting of a combinatorial and residual contribution (Eq. 3), can be found in the literature (Fredenslund et al., 1975; Poling, 2000) and will not be presented here.

$$\ln \gamma_i = \ln \gamma_i^{combinatorial} + \ln \gamma_i^{residual} \qquad (3)$$

The combinatorial part is determined by the composition, size and shape of the molecule hence relying on pure component data. The residual part depends on the intermolecular forces taking place (Prausnitz, 1986) and uses binary interaction parameters derived from numerous systems. There are inherent limitations to the UNIFAC model that are important to consider, though methods which exist for circumventing these problems are discussed below. Originally designed for chemical separation processes where the chemical components of interest are short chain mono functional compounds, its estimates for properties of multifunctional compounds that are common in the atmosphere can be uncertain (Koo, 2003). In addition, UNIFAC is a first order technique whereby the position of functional groups within a molecule are not considered, precluding its use for distinction between isomers. Indeed, recently Marcolli and Peter (2005) developed a modified UNIFAC parameterisation to discriminate between three types of alkyl groups, for polyol/water systems, depending on their position in the molecule. They found a distinctly improved agreement of model predictions with experimental results compared to the original UNIFAC model. Sources in the literature do not recommend UNIFAC for compounds in which 2 strongly polar groups are separated by less than 3 to 4 carbon atoms because the interaction between these groups are not accounted for Saxena and Hildemann (1997). This includes some atmospherically
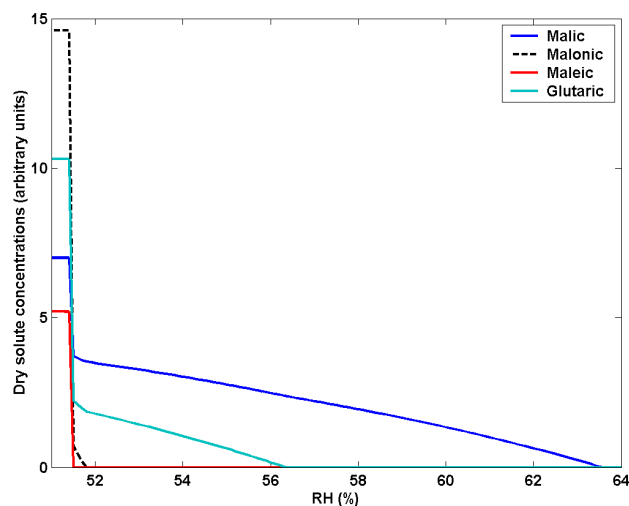
Fig. 2. ADDEM model predictions for solid precipitation in a multiple organic dicarboxylic acid mixture as described by Marcolli et al. (2004). The energies of formation used in this scheme were constrained using reported DRH values given by Marcolli et al. (2004) as discussed in the text.

important components such as low molecular weight dicarboxylic acids (Choi and Chan, 2002b). There are however ways of improving UNIFAC. There have been numerous attempts to modify the original equations. These include modified UNIFAC (Dortmund) (Gmehling et al., 1993, 1998; Weidlich and Gmehling, 1987), and modified UNIFAC (Lyngby) (Larsen et al., 1987) models. There are other derivatives of the original model and the user is referred to the literature for more information (e.g. see Zhang et al., 1998) and references therein). One of the main differences between the original UNIFAC and the Modified UNIFAC (Dortmund) is the introduction of temperature-dependent interaction parameters (Gmehling et al., 1998). In addition, in both modifications, the combinatorial part was modified in order to improve the results for asymmetric systems (Lohmann et al., 2001) where the area and volume parameters are adjustable values derived from experimental data. However, the interaction parameter matrices of the modified versions are smaller than the original version (e.g. no interaction considered between the COO and aromatic COH group in the Dortmund model) and the temperature at which the new parameters have been derived may make them unsuitable for typical atmospheric conditions. Bypassing the need for model equation adjustments, one can also readjust the interaction parameters and improve predictions considerably. Ninni et al. (2000) improved predictions for polyol components by readjusting some parameters. More recently, Peng et al. (2001) used an electrodynamic balance to modify the functional group interaction parameters of the COOH-H_2O, OH-H_2O, and OH-COOH pairs. These groups were chosen as they are most affected by hydrogen bonding (Peng et al., 2001). These new interaction
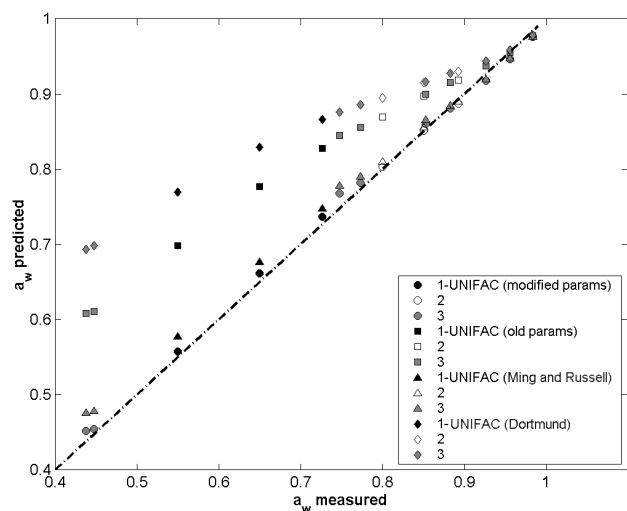
Fig. 3. Measured versus predicted water activity for 3 different composition types using different approaches to calculating activity coefficients in solution. UNIFAC (modified params) – original UNIFAC model with interaction parameters of Peng et al. (2001); UNIFAC (old params) – original UNIFAC model; UNIFAC (Dortmund) – Modified UNIFAC equations; UNIFAC (Ming and Russell, 2002) – original UNIFAC model using the interaction parameters of Ming and Russell (2002). Composition 1 – Malic acid, Malonic acid, Maleic acid, Glutaric acid, Methylsuccinic acid. Composition 2 = composition 1 + Oxalic acid, Composition 3 = composition 1 + Succinic acid. Experimental data taken from Marcolli et al. (2004).

parameters and the original equations are used in the model described here. It is thus important to evaluate the ability of these new interaction parameters to describe the behaviour of mixtures. Recently Choi and Chan (2002a) found good agreement with measured water activity data for mixed maleic/malic acid and malonic/glutaric acid systems using these improved interaction parameters, even at low relative humidity (ca. 20%). Data is sparse, however it is also possible to compare with the data of Marcolli et al. (2004) who measured the water uptake for 5 and 6 component organic mixtures. The components studied included Oxalic, Malonic, Succinic, Methylsuccinic, Glutaric, Maleic and Malic acid. The results are shown in Fig. 3 which compares predicted and measured water activities for the given systems using variations of the UNIFAC model. The original UNIFAC model equations combined with the 'old' interaction parameters refer to the use of the parameter matrix updated by Hansen et al. (1991) which has been published by Poling (2000). The use of 'new' interaction parameters refers to the inclusion of the revised parameters of the selected groups described earlier within the matrix of Poling (2000). Clearly, the modified parameters improve predictions significantly for all systems studied, even at low RH. Also shown are the results using the 'meta-groups', defined by Ming and Russell (2002), within the original UNIFAC model. Ming and

Russell (2002) tried to improve the accuracy of UNIFAC by defining more specific types of functional groups (for example COOH in hydroxy-acids, COOH in diacids). Interestingly, whilst proving to correlate with experimental data very well for all systems, these meta-groups do not have any advantage over the modified parameters of Peng et al. (2001) which use the more basic functional groups defined in the original UNIFAC description. Indeed, it would seem that the predictions using the original functional groups and the modified interaction parameters of Peng et al. (2001) are closer to experimental data, though the increase in accuracy is small. This result is encouraging with regard to treating mixed organic systems using UNIFAC. Of course, more studies on complex systems need to be carried out. For example, it would be useful to analyse the ability of UNIFAC to treat systems where functional group positioning may become important.

Recent field studies have shown that large fractions of previously uncategorized organic compounds are poly-carboxylic acids resembling humic materials (Brooks et al., 2004, and references therein). Indeed, using the H^+-NMR technique, Decesari et al. (2001) identified as much as 40% of the water soluble organic carbon, in the Po Valley Italy, as poly-carboxylic acids having molecular structures analogous to humic materials. Thus, the presence of such large macromolecular materials in aerosols requires that their behaviour is adequately modelled. This is difficult as the structural characteristics of such materials may vary significantly and no single structural model can be used to describe humic acids from different sources (Diallo et al., 2003). Brooks et al. (2004) found that the water uptake behaviour varies with the type, source, and isolation method of the humic material. Laboratory studies have used model compounds, such as the naturally occurring Suwannee River Fulvic Acid and Nordic Aquatic Fulvic Acid, to investigate the hygroscopic properties of humic material (Brooks et al., 2004; Chan and Chan, 2003; Gysel et al., 2004). The ability of the UNIFAC technique described above to model such compounds is shown in Fig. 4 where the electro-dynamic balance data of Chan and Chan (2003) (Fig. 4b) is used in conjunction with a proposed model structure used to explain results taken from extended chemical analysis of the Suwannee River fulvic acid (Fig. 4a) (c.o. Stefano Decesari. Structure taken from Averett (1989). Whilst Suwannee River fulvic acid does not reproduce fully the chemical features of atmospheric polyacids, since the latter are much less enriched in H-C-O groups, it remains the best guess because there are no better alternatives among the commercial standards of humic substances (Stefano Decesari personal communication). The mass ratio M/Mo represents the solute plus water mass over the original dry solute mass. Also shown in Fig. 4b is the mass ratio parameterisation provided by Chan and Chan (2003), which is based on the author's scattered experimental data. Despite this scatter, the model matches up very well with the parameterised fit. In addition, the improvement made by using the interaction
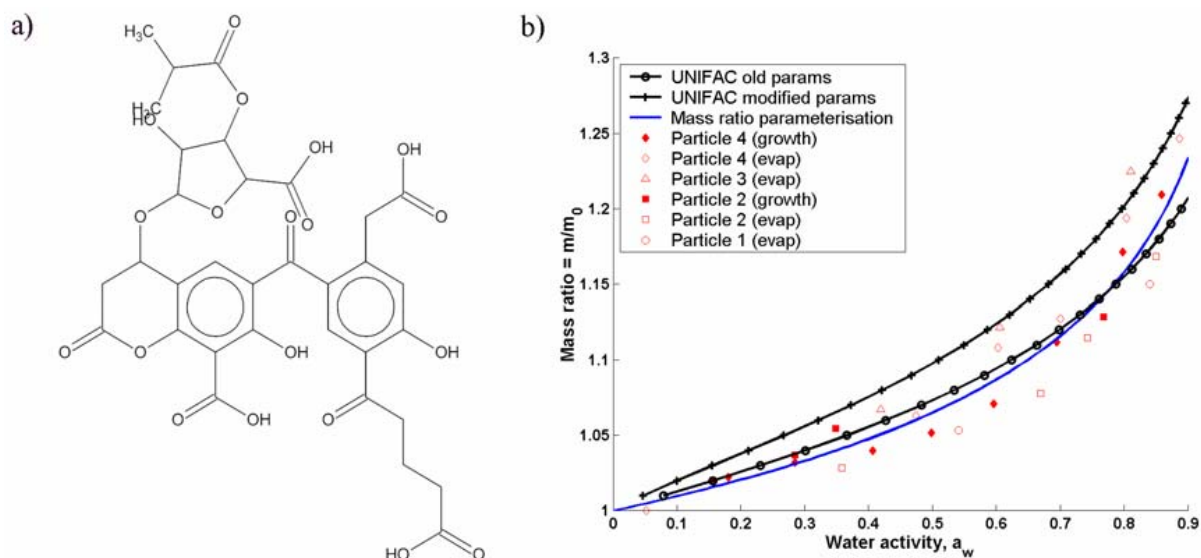
Fig. 4. (a) – Proposed model structure of Suwannee River Fulvic Acid. Structure taken from Averett (1989). **(b)** Mass ratio of Suwannee River Fulvic Acid, experimental data versus theoretical results. Experimental data taken from Chan and Chan (2003). This includes single particle growth and evaporation data (evap/growth) and a mass ratio parameterization, derived from this data, provided by the authors. The UNIFAC lines indicate use of the original UNIFAC equations (Fredenslund et al., 1975) with old binary interaction parameters (old params – Hansen et al., 1991) and recently modified binary parameters between the OH, COOH and H_2O groups (modified params – Peng et al., 2001).

parameters of Peng et al. (2001) is clear. Both model predictions use the original UNIFAC equations. The use of 'old' parameters refers to the inclusion of the updated parameter matrix of Hansen et al. (1991). The use of 'modified' parameters refers to the inclusion of the updated parameter matrix of Peng et al. (2001). Using the old interaction parameters, the model over predicts the water content, thus leading to a smaller mass fraction of solute. It is of course necessary to analyse the ability of UNIFAC to model mixed organic systems involving such complex components. Nonetheless, these results are encouraging.

2.2 Mixed organic/inorganic systems

As discussed in the introduction, when developing general equilibrium models applicable to a wide range of compositions without suitable interaction parameters, it becomes necessary to treat the inorganic and organic fractions as though acting independently of each other. This additive concept is essentially analogous to the ZSR mixing rule approach. However combining two separate thermodynamic models is different to a 'complete' ZSR approach in that the interactions between the inorganic/organic solutes and water are treated explicitly. Unlike the coupled approaches of Ming and Russell (2002) and Clegg et al. (2001), the model here treats the solute concentrations using the independent water concentrations associated with each separate fraction. Using the model of the osmotic coefficient for the total water content provided by Clegg et al. (2001) means that when the
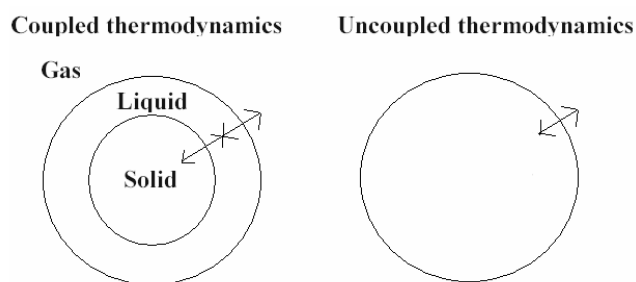
Fig. 5. Systems one can treat using the diameter dependent growth factor scheme described in the text and coupled/uncoupled thermodynamics.

inorganic-organic interactions are neglected, the water content differs slightly from a simple additive ZSR approach (the water activity of the two separate fractions should equal the ambient RH). It was decided that the principles of the ZSR rule were to be retained in this model, thus requiring the technique described above. It is likely that the difference between the two models is negligible, though a comparison should be made in the future for a wide variety of compounds and mixture types. Ming and Russell (2002) made a brief comparison between two such approaches and found that the largest difference between an internal and external mixing assumption occurred for highly soluble components (in their case malonic acid), and the deviation was around 10%. For
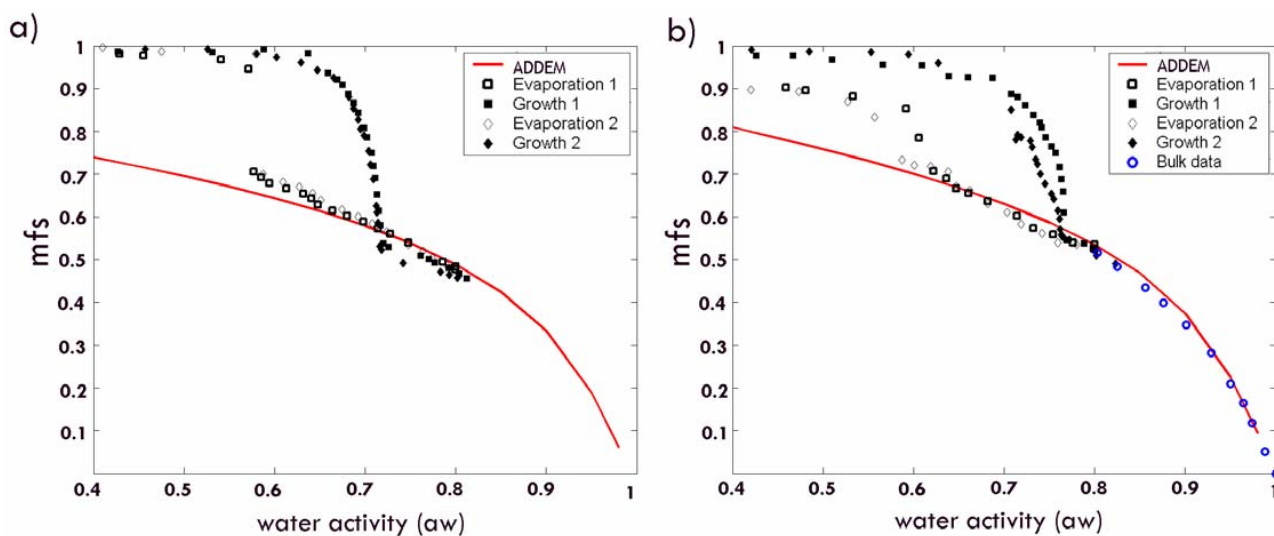
Fig. 6. (a) Mass fraction of solute (mfs) versus water activity (aw) for an NaCl-Glutaric acid mixture (mass ratio=1:1). **(b)** Mass fraction of solute (mfs) versus water activity (aw) for an $(NH_4)_2SO_4$-Glutaric acid mixture (mole ratio=1:1). ADDEM model predictions use theoretical results for the inorganic and organic component and add the water contents using a ZSR approach. The experimental single particle evaporation and growth data is taken from Choi and Chan (2002).

less soluble components (succinic and glutaric acid), the two types of growth generally agree within 3% (Ming and Russell, 2002).

It is now necessary to analyse how well this additive approach works for mixed inorganic/organic systems, which is carried out here. Using the data of Choi and Chan (2002b) it is possible to see how well the approach works for binary organic/inorganic systems. Here the authors analyse the effects of glycerol, succinic acid, malonic acid, citric acid and glutaric acid on the water cycles of NaCl and $(NH_4)_2SO_4$. Examples are shown in Fig. 6 for mixtures of glutaric acid with NaCl and $(NH_4)_2SO_4$ (mass ratio of 1:1 and molar ratio of 1:1, respectively) using the combination of the two separate thermodynamic models described in this paper and (Topping et al., 2004). For both systems the technique works very well, even at low to moderate RH. Indeed, for the whole range of systems studied Choi and Chan (2002b) found that the ZSR approach, using measured water activity data, worked very well. Other studies have used the ZSR approximation to analyse the hygroscopicity of mixtures of carboxylic, dicarboxylic or multifunctional acids with single inorganic salts at sub-saturated RH with relative success (Chan and Chan, 2003, 2002b; Cruz and Pandis, 2000; Hameri et al., 2002; Hansson, 1998). However, as pointed about by Gysel et al. (2004) a more detailed analysis often shows positive or negative interactions between organic and inorganic compounds. For example, Cruz and Pandis (2000) found that the ZSR relationship could explain the hygroscopic growth of an internally mixed inorganic-organic particle within 20% by using measured growth factors for the pure components. However, they also note that results suggest a more complex

interaction between the organic and inorganic ions that can be positive or negative depending on the organic volume fraction and type of salt (Cruz and Pandis, 2000). Despite the ability of the ZSR relationship to reproduce the of Prenni et al. (2001) observed behaviour of the systems shown in Fig. 6, it is crucial to analyse its ability to reproduce bulk data for multi-component systems. For this, the data of Marcolli et al. (2004) can be used. They studied the water activity for multi-component organic mixtures (5 components) with a single inorganic salt. This provides a test on both the ZSR approximation but also on the ability of the thermodynamic model to deal with such mixed systems. Unfortunately, a direct comparison with a 'complete' ZSR approach cannot be made due to the lack of water activity data for methylsuccinic acid. Results are shown in Fig. 7 for the mixtures of 5 dicarboxylic acids and three inorganic salts at their saturation concentrations (Fig. 7a, b and c). Figure 7d also shows the predictions of the same acids and $(NH_4)_2SO_4$ that is not at its saturation concentration. Though the dry mole fractions vary, there are some conclusions that can be drawn from these graphs. The results show that at higher relative humidity, when the solutions are more dilute, then the additive approximation works very well. One might expect this as the interaction between the organic and inorganic fractions are not a strong as in more concentrated solutions. For the first three cases (Fig. 7a ,b and d) the maximum deviation is found for the mixture with NH_4NO_3, where a difference of 23.9% between predicted and measured molalities is found at a low 37.4% RH. At higher RH (77.3%) the difference drops significantly to only 3.18%. Better results are found for the other two salts. A maximum difference of 20.73% and
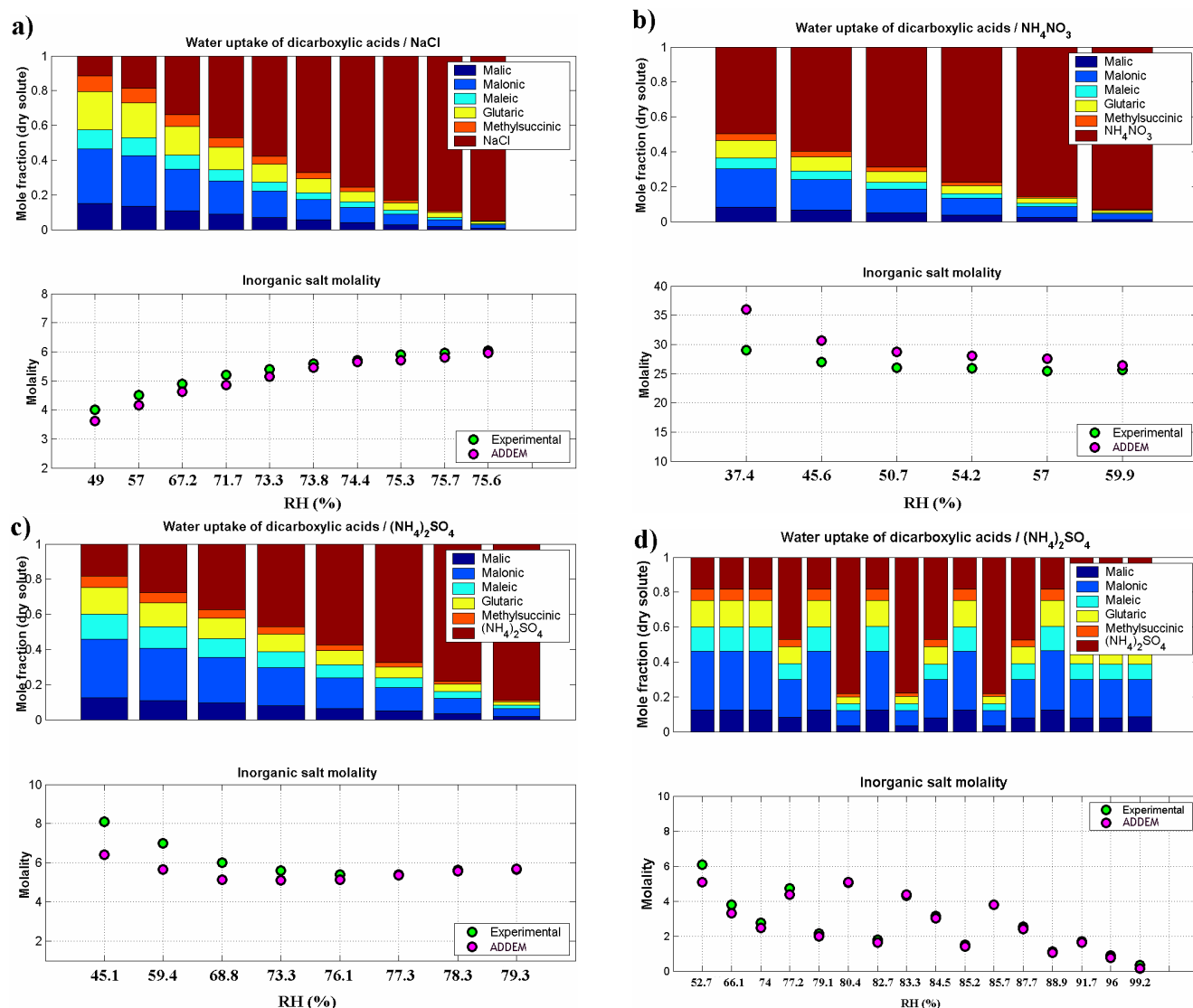
Fig. 7. **(a)** Water uptake for a mixture of dicarboxylic acids and NaCl at its saturation point. Experimental versus theoretical results. Experimental data taken from marcolli et al. (2004). ADDEM organic water content calculated using the original UNIFAC equations and the modified interaction parameters of Peng et al. (2001). **(b)** Water uptake for a mixture of dicarboxylic acids and NH$_4$NO$_3$ at its saturation point, experimental versus theoretical results. Experimental data taken from Marcolli et al. (2004). ADDEM organic water content calculated using the original UNIFAC equations and the modified interaction parameters of Peng et al. (2001). **(c)** Water uptake for a mixture of dicarboxylic acids and (NH$_4$)$_2$SO$_4$ at its saturation point, experimental versus theoretical results. Experimental data taken from Marcolli et al. (2004). ADDEM organic water content calculated using the original UNIFAC equations and the modified interaction parameters of Peng et al. (2001). **(d)** Water uptake for a mixture of dicarboxylic acids and (NH$_4$)$_2$SO$_4$, experimental versus theoretical results. Experimental data taken from Marcolli et al. (2004). ADDEM organic water content calculated using the original UNIFAC equations and the modified interaction parameters of Peng et al. (2001).

9.49% for (NH$_4$)$_2$SO$_4$ and NaCl, respectively, at 45.1% and 49% RH. Minimum deviations as small as 0.35% and 1.03% are found for the same two salts at 77.3% and 74.4% RH, respectively. In three of the four cases (Fig. 7a, c and d) as deviations increase with decreasing relative humidity, the model tends to over predict the observed water content. In this case it seems as though the organic-inorganic interactions lead to

negative contributions to the total water content for NaCl and (NH$_4$)$_2$SO$_4$. Such a conclusion is validated by the ability of UNIFAC to reproduce measured water activity for the mixtures discussed in Sect. 2.1 at low relative humidity. For the mixture with NH$_4$NO$_3$ however, the model seems to under predict the observed water content, thus leading to the notion that the organic-inorganic interactions lead to positive

contributions to the total water content in this case. Thus, the uncoupled thermodynamic approach matches experimental data for both binary and multi-component systems quite well. Deviations begin to increase in all cases at lower relative humidity, which one might expect due to the increased interactions at higher solute concentrations. More measurements need to be made on other components of atmospheric importance but the results discussed above are encouraging. It would also be useful to compare predictions for more complex components and not just lower molecular weight dicarboxylic acids. Chan and Chan (2003) studied the interaction between two model humic like substances, including Suwannee River FA, and two inorganic salts. They found that the FA-$(NH_4)_2SO_4$ mixtures had a larger uptake than the sum of the individual contributions at 90% RH that also increased as the RH decreased. Similarly, for mixtures with NaCl they found a reduced water content compared with the sum of the individual uptakes. Interestingly, this proved to be a function of RH as found earlier. They found the ZSR approach to over predict the mass ratios of NaCl-FA mixtures by around 10% and under predict the mass ratios of $(NH_4)_2SO_4$-FA by around 20%. However, when translated into hygroscopic growth measurements, Brooks et al. (2004) found that a ZSR approach could predict the observed growth behaviour of $(NH_4)_2SO_4$-FA reasonably well. The chemical interactions between the FA and inorganic components are likely to be very different from those between the simpler organic components and inorganic components thus requiring further research to elucidate the impacts of such large macromolecular materials on atmospheric aerosols (Chan and Chan, 2003). Thus, it would appear that an additive approach for treating mixed inorganic/organic systems works well over a range of compositions and concentrations. However, it is also crucial to extend the analysis to a wider variety of compounds in the future, than those treated here. This should include attempted coupled thermodynamic approaches where possible. As stated by Clegg et al. (2001), it is important to assess the effects of the inorganic/organic interaction on the thermodynamic properties of mixtures and to determine the degree of accuracy to which the ion-organic interaction parameters need to be known to represent atmospherically important properties such as deliquescence behaviour.

The range of ambient conditions for which the equilibrium model will give reliable results is largely dictated by the accuracy of the activity coefficient model. For the H^+-NH_4^+-SO_4^{2-}-NO_3^--H_2O inorganic model excluding Na^+ and Cl^-, Clegg et al. (1998) derived interaction parameters designed to make predictions over the temperature range <200 K–330 K. In ADDEM no ice or acid hydrate formation is treated, thus precluding its use for a range of upper tropospheric conditions where such species may be important. Having said that, studies have shown that mixed ambient aerosols remain aqueous at low RH and low temperatures (−10°C) (e.g. Weingartner et al., 2002). For the organic model, the ability of UNIFAC to model systems of atmospheric importance has only been done at room temperature (ca. 298.15 K) since data is severely lacking in the literature. The Dortmund UNIFAC model, though including a temperature dependence, was found to be particularly bad at modelling simple atmospheric systems (see Fig. 3). Thus the model can be considered reliable at a range of lower tropospheric conditions yet further proof is inhibited by a lack of data in the literature.

3 Curvature treatment

The technique for including the Kelvin effect was discussed in some detail in paper 1 (Topping et al., 2004 and the reader is referred to this for a more mathematically rigorous discussion. Using the same framework combined with the approach for calculating the water content described earlier, it is now possible to calculate the water content associated with a mixed aqueous organic/inorganic aerosol for a given composition and dry size. At each ambient RH the 'bulk' water content is calculated. The associated physical characteristics are then calculated using appropriate surface tension and density models that define the Kelvin factor associated with the aerosol. Using the Kohler equation, a difference relationship is defined (Eq. 4), the root of which lies at the solution pertaining to the new definition of equilibrium.

$$\frac{RH}{Kelvin\ factor} - a_w = 0 \tag{4}$$

The energy of formation of liquid water is adjusted and the new water content calculated. Combined with a bisection approach the process becomes iterative until a solution to Eq. (3) is found. A model schematic is shown in Fig. 1. In this way, the solute effect is calculated using an energy minimisation and the resulting concentrations used as inputs to various surface tension models. Thus, the partitioning between the bulk and surface phase is treated only within the different surface tension models. A recent study by Sorjamaa (2004) showed that the shape of the Kohler curve is altered upon consideration of the solute partitioning within the solute effect. The authors found that, using the model compound Sodium Dodecyl Sulphate, the critical super-saturation may be underestimated if surfactant partitioning is neglected. Such effects are not analysed here and beyond the scope of the current model. It would however be interesting to analyse how such effects influence behaviour in the sub-saturated regime.

4 Mixture parameters

In solving the Kohler equation one must calculate the density and surface tension of the mixed inorganic/organic solution. For the density of the mixed solution the mass fraction mixing rule of Tang (1997) is used, which relies solely on binary data. This was discussed in paper 1 (Topping et

al., 2004). When binary organic data is not available it can be calculated using the same rule. Whilst some studies in the literature use the solid organic density for this purpose, it is possible to calculate the liquid density of the organic component using the Yens-Wood method (Yens and Woods, http://www.pirika.com).

4.1 Surface tension

Calculating the surface tension of the mixed solution is difficult as there are no apparent techniques for combining the effects of the separate inorganic/organic fractions. For this model, the effects are assumed additive, the two separate contributions calculated using the total water content of the solution. This assumption needs to be tested in future studies as data is currently severely lacking. The only study found in the literature is that of Shulman et al. (1996) who found that the increase in concentration of $(NH_4)_2SO_4$ had little or no effect on the surface tension of organic solutions of adipic, oxalic, succinic, glutaric, malonic and pthalic acid. For cis-pinonic acid however, the least soluble model compound, the addition of $(NH_4)_2SO_4$ appeared to drive the acid molecules to the surface thus decreasing the droplet surface tension. It is thus necessary to consider how the organic contribution to the droplet surface tension is calculated. The current modelling approach has the flexibility to use any number of surface tension models, some of which are analysed here.

4.2 Organic surface tension

4.2.1 Pure component surface tensions

Whereas for non-aqueous solutions the mixture surface tension in some cases can be approximated by a linear dependence on mole fraction, aqueous solutions show pronounced non-linear characteristics. The hydrocarbon portion of the organic molecule behaves like a hydrophobic material and tends to be rejected from the water phase by preferentially concentrating at the surface (Poling, 2000). Predictive methods are available which often rely on the use of pure component surface tension data. Again, there is a lack of such data, many organic components of atmospheric importance being solid at room temperature. For such components the pure surface tensions with respect to the super-cooled liquid state must be calculated (Gaman et al., 2004). The Macleod-Sugden correlation is employed here (Poling, 2000) and is shown below:

$$\sigma_O^{1/4} = [P](\rho_L - \rho_V) \tag{5}$$

Where σ_O is the pure component surface tension, $[P]$ the parachor, ρ_L the pure component liquid density and ρ_V the vapour density. Usually the vapour density is neglected and one has to calculate the parachor value and liquid density if required. Quayle (1953) suggested an additive scheme to correlate $[P]$ with structure using experimental

data for surface tension and density for many compounds. In this study, the parachor is calculated using the "Advanced Chemistry Development Inc. (ACD/Labs)" software Chemsketch v5.0 (ChemSketch, 2003) by inputting the appropriate structure. Such structures are found in the NIST chemistry web book (http://www.nist.gov). In addition, one may need to calculate the liquid density. Following Gaman et al. (2004) the pure sub-cooled acid densities can be calculated as a function of temperature using the Yens-Woods method (Yens and Woods, http://www.pirika.com). The calculated pure surface tension is very sensitive to the value of the liquid density used. For example, the ACDlabs Chemsketch 5.0 and the Yens-Wood technique give density values of 1.408 and 1.266 gcm^{-3} for Succinic acid, respectively. Similarly for Glutaric acid the values are 1.316 and 1.2013 gcm^{-3}. Whilst they differ by around 10% this translates to a difference in the pure surface tension of 21.44 and 17.22 dynecm^{-1} for succinic and glutaric acid, respectively (Yens-Wood $\sigma_{O,glutaric}$=38.88, $\sigma_{O,succinic}$=40.15; ACD-Labs $\sigma_{O,glutaric}$=56.1, $\sigma_{O,succinic}$=61.6). A larger difference was found for oxalic acid where the ACDlabs prediction calculated a surface tension greater than that of pure water. The Yens-Wood method however leads to a value of around 56.1 dynecm^{-1}.
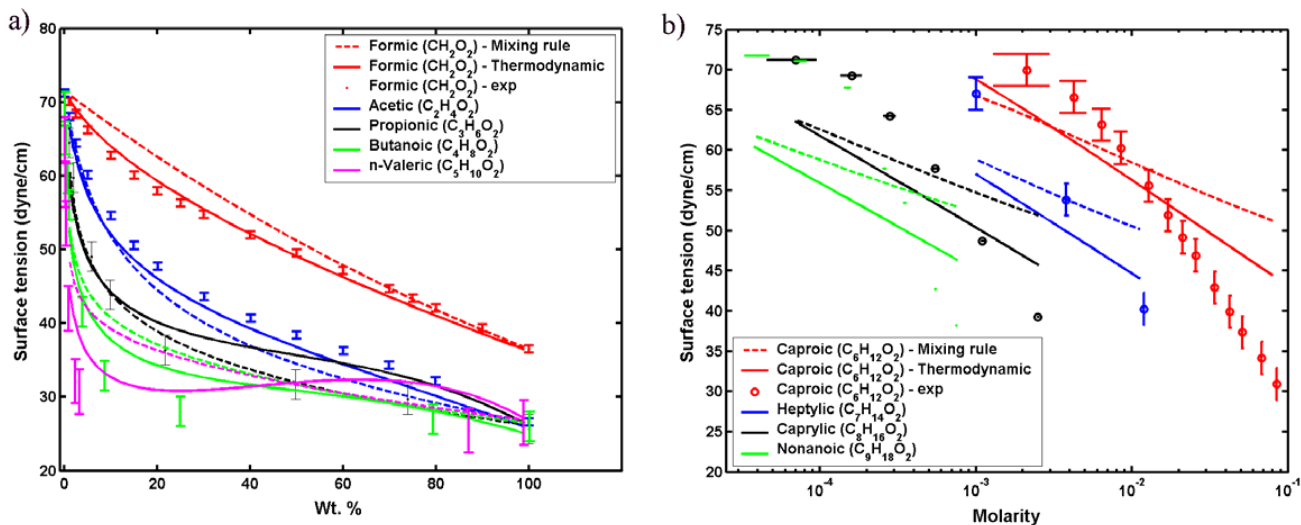
4.2.2 Binary surface tension

As with other mixture rules one often relies upon the use of binary information to describe the behaviour of a mixture. Fainerman (2001, 2002) developed a thermodynamic model to describe the adsorption behaviour of mixed surfactant systems. Only requiring the use of information regarding the single-surfactant systems, without extra interaction parameters, the authors have successfully applied the model to a number of mixed systems including non-ionic surfactant mixtures and an anionic-nonionic mixture (Fainerman, 2001). This report however only focuses on the different methods for predicting the binary surface tensions and the sensitivities that can occur from such approaches since data for mixed systems is lacking.

A brief introduction and review is given by Poling (2000). Two models presented by the authors, and discussed in more detail here before a comparison is made, include the techniques of Tamura et al. (1955) and Sprow and Prausnitz (1966a, b). The method of Tamura et al. (1955), which uses the Macleod-Sugden correlation as a starting point (Poling, 2000), considers densities and concentrations in the surface layer to define the relationship given by Eq. (6).

$$\sigma_m^{1/4} = \psi_w \sigma_w^{1/4} + \psi_o \sigma_o^{1/4} \tag{6}$$

$$\psi_o = 1 - \psi_w \tag{7}$$

where σ_m is the surface tension of the mixture, σ_w that of pure water and σ_o the surface tension of the pure organic

Fig. 8. (a) Surface tension (dyne/cm) for binary aqueous mixtures of C1-C5 monocarboxylic acids as a function of solute weight percentage (Wt. %), experimental versus theoretical results. **(b)** Surface tension (dyne/cm) for binary aqueous mixtures of C6-C9 monocarboxylic acids as a function of solution molarity, experimental versus theoretical results. Experimental data (exp) taken from "The International critical tables of numerical data, physics, chemistry and technology" (Washburn, 2003). Theoretical calculations made using two separate models: Mixing rule-the method of Tamura et al. (1955), Thermodynamic – The method of Suarez et al. (1989).

component. ψ_w is given by Eq. (8).

$$\log_{10} \frac{(\psi_w)^q}{(1-\psi_w)} = \log_{10} \left[\frac{(x_w V_w)^q}{x_o V_o} (x_w V_w + x_o V_o)^{1-q} \right]$$
$$+44.1 \frac{q}{T} \left[\frac{\sigma_o V_o^{2/3}}{q} - \sigma_w V_w^{2/3} \right] \tag{8}$$

where x_w is the bulk mole fraction of water, x_o the bulk mole fraction of the organic component, V_w the molar volume of pure water (m^3 kmol^{-1}), V_o the molar volume of the pure organic component (m^3 kmol^{-1}), T the temperature (K) and q is a constant that depends on the size and type of organic compound (for fatty acids and alcohols q = the number of carbon atoms; for ketones q = one less than the number of carbon atoms; for halogen derivatives of fatty acids q = number of carbon atoms times the ratio of the molar volume of the halogen derivative to the parent fatty acid). Tamura et al. (1955) applied the above model to 14 aqueous systems and found percentage errors of less than 10% when $q < 5$ and within 20% for $q > 5$. The same model is applied to atmospheric relevant components in Fig. 8a and b. A thermodynamic based relationship was provided originally by Sprow and Prausnitz (1966a, b). Using assumptions of equilibrium between the surface and bulk phase (which were treated as completely separate phases) and the partial molar area of component 'i' being the same as the molar area leads to the relationship given by Eq. (9).

$$\sigma_m = \sigma_i + \frac{R'T}{A_i} \ln \frac{x_i^\sigma \gamma_i^\sigma}{x_i \gamma_i} \qquad (i = 1, 2....N) \tag{9}$$

where σ_i is the pure component surface tension (dyne cm^{-1}), R'=8.314×10^7 dyne cm^{-1}/mol K, T the temperature (K), A_i the surface area of component 'I' in cm^2 mol^{-1}, x_i the bulk mole fraction of component 'i', x_i^σ the surface mole fraction of component 'i', γ_i the activity coefficient of component 'i' in the bulk phase and γ_i^σ the activity coefficient of component 'i' in the surface phase.

This has already been employed in the thermodynamic model of Ming and Russell (2002). Whilst a solution to Eq. (9) can be found using a bisection approach, Ming and Russell (2002) use a constant of proportionality between the bulk and surface phase. Suarez et al. (1989) improved on previous attempts to utilise the above relationship (Sprow and Prausnitz, 1966b) by using a more accurate way of calculating the different activity coefficients (UNIFAC; Fredenslund et al., 1975). However, the surface tension calculated in this way is more sensitive to the choice of 'A'. Goldsack and White (1983) derived an equation for A based on the assumption that molecules were spherical and that the effective surface area is best represented by the cross sectional area as given by Eq. (10).

$$A_i = 1.021 \times 10^8 V_c^{6/15} V_b^{4/15} \tag{10}$$

where V_c and V_b are the critical and bulk molar volumes, respectively (cm^2 mol^{-1}).

When the critical volume or bulk molar volume (for the pure liquid) data are not available, the values must be calculated. For the critical volume the third order group contribution method of Marrero and Gani (2001) can be used. For bulk molar volumes, the super-cooled liquid density may have to be calculated, again using Yen-Woods method
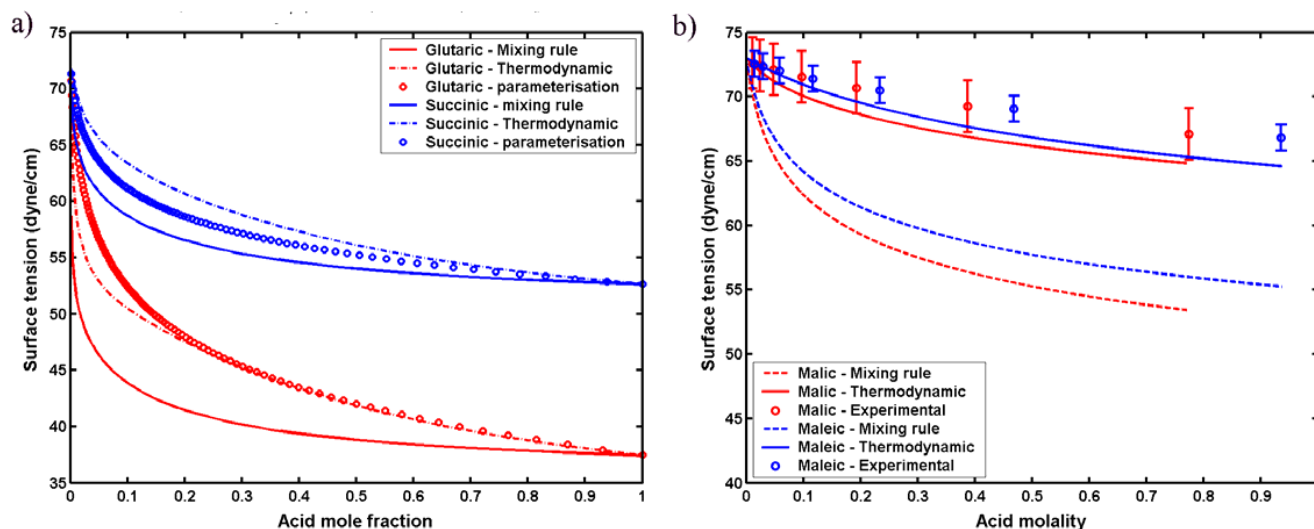
Fig. 9. (a) Surface tension (dyne/cm) for binary aqueous mixtures of Glutaric and Succinic acid as a function of mole fraction of organic in solution (Acid mole fraction), experimental versus theoretical results. Experimental data (exp) taken from Gaman et al. (2004). The legend caption "parameterisation" is explained in the main text. Theoretical calculations made using two separate models: Mixing rule-the method of Tamura et al. (1955), Thermodynamic – The method of Suarez et al. (1989). **(b)** Surface tension (dyne/cm) for binary aqueous mixtures of Malic and Maleic acid as a function of molality, experimental versus theoretical results. Experimental data (exp) taken from Washburn (2003). Theoretical calculations made using two separate models: Mixing rule-the method of Tamura et al. (1955), Thermodynamic – The method of Suarez et al. (1989).

(Yen and Woods, http://www.pirika.com). Whilst Suarez et al. (1989) reported an average error of 3.5% using the above relationship for A_i for non-aqueous mixtures, the authors also state that deviations may be 15% or more for aqueous systems which may be due to orientation effects giving rise to molar areas which differ significantly from those calculated using Eq. (10). Indeed, Suarez et al. (1989) improved results considerably when deriving special area parameters from available experimental data. Unfortunately, such improvements may not be available for systems of atmospheric importance and only a small number of improved parameters have been reported (see Poling, 2000). The ability of the model to reproduce the surface tensions for different components is shown in Figs. 8 and 9.

As shown in Fig. 8a, both models reproduce the surface tension depression for the smaller (<C5) acids quite well, the thermodynamic model agreeing with experimental results better over a wider range of concentrations than the simple mixing rule. As shown in Fig. 8b, for the C6-C9 monoacids, neither model can reproduce the experimental behaviour well, even at relatively lower concentrations. Thus for components that are only slightly soluble in water, neither model can reproduce the surface tension depression behaviour with much accuracy. This is an interesting result as components such as caprylic acid, and other hydrophobic oxygenated compounds that share similar properties with components such as stearic acid (Zhang et al., 2003), have been found in aerosols. This questions our ability to model these systems accurately when using models such as those

presented here. Maximum percentage errors are around 15% for these systems, translating to an absolute value of around $10\,\mathrm{dyne\,cm^{-1}}$. Figures 9a and b show a comparison between model predictions and measured values for 4 typical dicarboxylic acids. For malic and maleic acid (Fig. 9b) the thermodynamic model agrees well with observed results. Tamura's method however seems to under predict the surface tension by around $10\,\mathrm{dyne\,cm^{-1}}$ even at very low concentrations (data is limited to a molality of 1). Using the parameterisations of Gaman et al. (2004), who fit experimental data to the Szyskowski-Langmuir equation (Eq. 11), it is also possible to compare model predictions with experimental data for the two common dicarboxylic acids succinic and glutaric acid.

$$\sigma_m = \sigma_w - aT \log_{10}(1 + bx_o) \tag{11}$$

where a and b are experimentally determined parameters (Succinic: $a = 0.0127$, $b = 175.28$, Glutaric: $a = 0.0222$, $b = 189.61$ (Gaman et al., 2004). The pure component surface tensions were calculated using the scheme described earlier. For succinic acid both models reproduce the depression well, Tamura's scheme under predicting and the thermodynamic model over predicting slightly. The maximum errors are around $2–3\,\mathrm{dyne/cm^{-1}}$ at lower concentrations. The experimental data for this system was taken within the mole fraction range 0–0.2 where neither model agrees with the observed behaviour exactly. For glutaric acid the thermodynamic model agrees better with the measured data overall,
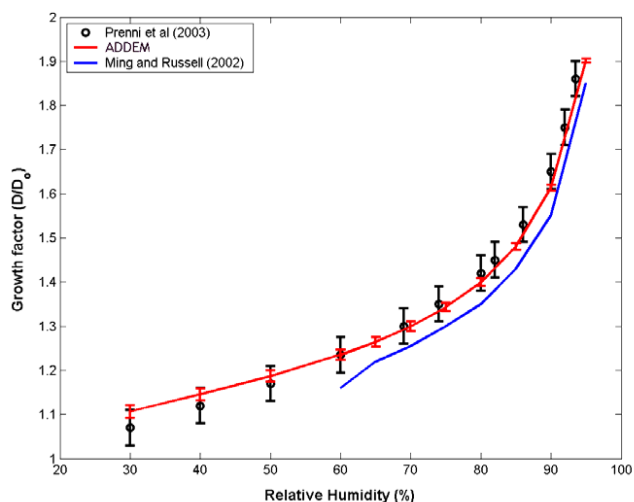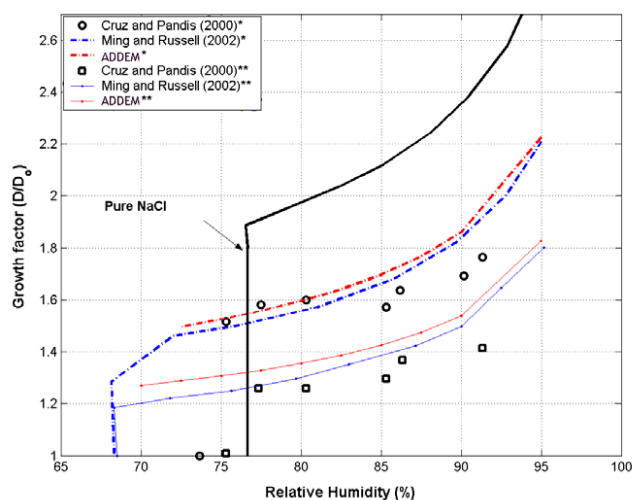
Fig. 10. Growth factor for a 100 nm $(NH_4)_2SO_4$/Malonic acid aerosol (1:1 mass ratio), experimental versus theoretical results. Experimental data (open circles) taken from Prenni et al. (2003). Theoretical predictions made using ADDEM (this paper) (ZSR approach neglecting inorganic/organic interactions) and the model of Ming and Russell (2002) (inorganic/organic interactions treated explicitly).

Fig. 11. Growth factor for a 100 nm NaCl/Glutaric acid aerosol (* 1:1 mass ratio, ** 1:4 mass ratio), experimental versus theoretical results. Experimental data (open circles 1:1 mass ratio, open squares 1:4 mass ratio) taken from Cruz and Pandis (2000). Theoretical predictions made using ADDEM (this paper) (ZSR approach neglecting inorganic/organic interactions) and the model of Ming and Russell (2002) (inorganic/organic interactions treated explicitly).

though again neither model can reproduce the observed behaviour exactly.

The results given above suggest that the differences in surface tension predictions for atmospherically relevant components may introduce inconsistencies within a purely theoretical hygroscopic model. It is first, however, appropriate to analyse the sensitivity of the hygroscopic predictions to such deviations. This is done in Sect. 5. It is now possible to compare growth factor predictions with experimental data found in the literature for mixed inorganic/organic aerosols.

5 ADDEM model predictions

Various studies in the literature, all focused on simple binary mixed inorganic-organic aerosols, have used the ZSR assumption to analyse measured data with varying success. Experimental results derived from HTDMAs often indicate reasonable agreement with ZSR predictions (e.g. Cruz and Pandis, 2000; Hameri et al., 2002; Prenni et al., 2003), even for complex components such as humic like substances (Brooks et al., 2004). However, further work is required on more complex mixtures to analyse the benefit of using two separate thermodynamics over a general ZSR approach. Thus, rather than reproduce such results, two cases are chosen which allow a comparison with the model of Ming and Russell (2002) which attempts to treat the ion-organic interactions explicitly. It should be noted that there may be equilibration time or evaporative problems when sampling organic systems using the HTDMA. This has been shown in vari-
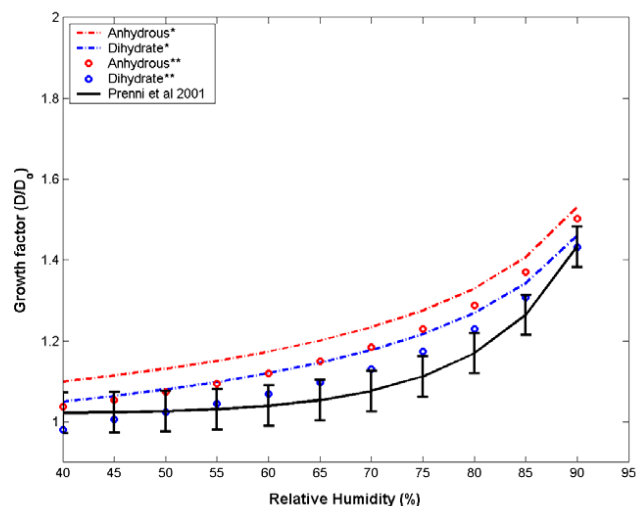
ous studies where the residence time of the aerosol within an instrument influences the measured hygroscopic growth (e.g. Choi and Chan, 2002a; Peng et al., 2001; Prenni et al., 2001). Thus, care must be taken when comparing theoretical and measured results for certain systems. Such effects were not reported for the tabulated experimental data used here. Any results taken from the HTDMA are usually reported as the growth factor (D/Do) where D is the wet particle diameter and Do the dry particle diameter. The first system is an equal mass mixture of $(NH_4)_2SO_4$ and malonic acid. Results are shown in Fig. 10 for a 100 nm dry diameter aerosol. The model results include surface tension predictions using the model of Chen (1994) for $(NH_4)_2SO_4$ and the thermodynamic model described in Sect. 4 for malonic acid. Densities of $1.769\,gcm^{-3}$ and $1.63\,gcm^{-3}$ were used for the inorganic and organic component, respectively (Perry's Chemical Handbook). The error bars for the model prediction represent the range of values obtained when using two separate dry density values for malonic acid, and two separate density values for calculation of the binary aqueous organic density ($1.63\,gcm^{-3}$ (Perry's Chemical handbook) and $1.34\,gcm^{-3}$ Yens-Wood liquid density calculation (Yens Woods, http://www.pirika.com)). Experimental data was taken from the study of Prenni et al. (2003) who analysed the hygroscopic behaviour using a HTDMA. Both models reproduce the observed behaviour well, the ZSR approach within this modelling framework predicting growth factors within the experimental uncertainty of the measured data. The coupled model of Ming and Russell (2002) however
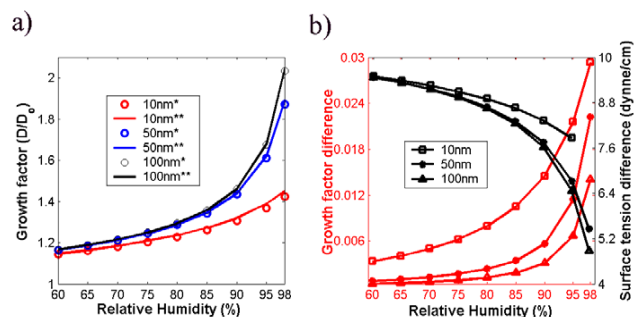
Fig. 12. (a) Predicted growth factor of Malic acid, using ADDEM, for three different dry diameters (10, 50 and 100 nm) and two different surface tension models. * Surface tension calculated using the method of Tamura et al. (1955), ** Surface tension calculated using the method of Suarez et al. (1989). **(b)** Growth factor difference and surface tension difference arising from the two separate surface tension models versus relative humidity. Analysis carried out for the three different dry sizes.

Fig. 13. Calculated growth factor of 100 nm oxalic acid aerosol versus relative humidity using two different values for calculation of the dry and aqueous density, experimental versus theoretical results. Experimental results (thick black line with error bars) taken from Prenni et al. (2001) Dry density calculated using the anhydrous and dihydrate values as shown in the legend. * Binary aqueous density calculated using the mass fraction mixing rule of Tang (1997) and Yens-Wood calculated liquid density value for oxalic acid. ** Binary aqueous density calculated using the mass fraction mixing rule of Tang (1997) and the dihydrate density value for oxalic acid.

under predicts the growth factor. In their model, Prenni et al. (2003) replace the interaction parameters of NH_4^+, SO_4^{2-} and organic groups with those of Na^+ and Cl^-, simply because the data does not exist to constrain the model. However, in this instance, this assumed interaction leads to erroneous results, where the experimental data would suggest a possible positive, rather than negative, interaction. In this instance a positive interaction refers to a larger uptake of water compared with the summed contributions from the individual systems. Thus, a more consistent ZSR approach appears to be beneficial in this instance. The second example is shown in Fig. 11 for a mixed NaCl-Glutaric acid aerosol. Two different mass fractions are analysed using the hygroscopicity data of Cruz and Pandis (2000) (NaCl:Glutaric mass ratios of 1:1 and 1:4). Again, both models reproduce the data quite well, though the explicit treatment of the ion-organic interactions appears to improve predictions somewhat. Indeed, despite the scatter in the experimental data, the coupled model correctly predicts a negative interaction leading to a lower predicted growth factor. This negative interaction was also found by Cruz and Pandis (2000) who used the ZSR approach and measured growth factors for the pure components. As the organic fraction increases then the negative interactions seem to increase. Again, as the RH decreases, then deviations also increase. The maximum difference between both models was found to be 0.05 at 75% RH for a mass ratio of 1:4 NaCl:Glutaric acid. This is likely to be within the experimental uncertainty of the HTDMA, though error bars were not provided here. Thus, where possible, explicit treatment of the ion-organic interactions offers an advantage as one might expect, though a wider range of systems need to be analysed to assess whether this advantage remains within the boundaries of experimental uncertainty. Also, assumed types of interaction, between components for which

there is no direct experimental data, may lead to erroneous results where a simpler additive scheme can offer better predictions.

6 Sensitivity studies

The mixed model described above is subject to various sensitivities. Since there is no solid precipitation or complex formation treated here, the sensitivities to energies of formation for the solute components need not be carried out. A thorough examination of this was given in the development of the inorganic model. Only a sensitivity to the energy of formation of water in the liquid phase is found when determining the equilibrium composition for an organic aerosol in this instance. This sensitivity was discussed in the accompanying paper to this report (Topping et al., 2005) where the same value is used in this model.

The following section looks briefly at the sensitivity introduced by using a variety of available techniques to describe the chemical and physical characteristics of the organic fraction.

6.1 Surface tension

The ability of different surface tension models to reproduce experimental results for various components of atmospheric

Table 1. Concentrations of dicarboxylic acids versus relative humidity for three different systems. Data reproduced from Marcolli et al. (2004) (Table 3 p. 2222). To be used in conjunction with Fig. 3.

System	RH	Dicarboxylic acid molality						
		Malic	Malonic	Maleic	Glutaric	Methylsuccinic	Oxalic	Succinic
1	0.55	4.97	10.9	3.88	9.08	4.01		
	0.65	3.51	7.71	2.74	6.43	2.84		
	0.727	2.64	5.8	2.06	4.83	2.14		
	0.8	1.95	4.27	1.52	3.56	1.57		
	0.851	1.46	3.22	1.14	2.68	1.18		
	0.893	1.11	2.43	0.86	2.02	0.89		
	0.927	0.8	1.75	0.62	1.46	0.64		
	0.956	0.51	1.12	0.4	0.93	0.41		
	0.984	0.22	0.48	0.17	0.4	0.18		
2	0.438	*6.8*	*14.8*	*5.3*	*12.3*	*5.4*	*1.05*	
	0.748	2.14	4.66	1.66	3.87	1.7	*1*	
	0.853	1.16	2.53	0.9	2.1	0.92	*1.14*	
3	0.448	*6.8*	*14.9*	*5.3*	*12.4*	*5.5*		*0.58*
	0.773	2.07	4.53	1.61	3.77	1.67		*0.74*
	0.883	1.06	2.31	0.82	1.92	0.85		*0.79*

Values in bold represent saturation concentrations

importance was analysed in Sect. 4. Here the sensitivity of growth factor predictions to these different models is analysed using one example. Malic acid was chosen due to the relatively larger difference in the prediction of σ_m. The results for three different dry sizes are shown in Fig. 12. As found with the inorganic model, the difference between the two models increases with decreasing dry size and increasing RH. For a 10 nm aerosol, the growth factors differ by 0.015 at 90% RH. At this RH both surface tension models differ by 8.33 dyne cm^{-1}, the thermodynamic model at 65.70 dyne cm^{-1} and Tamura's method at 57.37 dyne cm^{-1}. At a lower RH of 60% the difference in σ_m increases to 9.5 dyne cm^{-1}. However, this translates to a difference in growth factor of only 0.003. As the dry size increases to 50 and 100 nm, this difference falls to 8.3×10^{-4} and 4.3×10^{-4}, respectively. For 90% RH again the difference decreases to 5.7×10^{-4} and 3.1×10^{-3}. Thus, the choice of surface tension model becomes more important for growth factor calculations as the RH increases and also as the dry diameter decreases. It is likely, however, that deviations between different models will produce results that are within experimental uncertainty of measured hygroscopic behaviour. It is also likely that choice of surface tension model may be important for extension into the super saturated humid regime. This will be the subject of further work.

6.2 Density

Assumptions must be made regarding the dry state of the aerosol when comparing with growth factor predictions using instruments such as the HTDMA. Normally one assumes that the 'dry' aerosol sampled by such an instrument is best represented by its anhydrous form and that a bulk density value may be used. However, there are complicating issues. Firstly, structural complexities in smaller particles may introduce errors when using bulk density values (e.g. Hameri et al., 2000). Secondly, the most stable form of the organic solid may be a hydrous state. Oxalic acid is used as an example here. Prenni et al. (2001), who studied the hygroscopic behaviour of oxalic acid, using the model of Ming and Russell (2002), found that theoretical predictions were larger than measured growth factors. Whilst the authors suggest slow liquid phase diffusion in the particle, they also use other results in the literature that indicate that below 5% RH oxalic acid will be anhydrous but at or above 11% RH the acid di-hydrate will form. Indeed, when using the di-hydrate density value, growth factor predictions are lowered considerably. Results are shown in Fig. 13 that shows growth curves for two different dry density (di-hydrate: 1.653 gcm^{-3} (Prenni et al., 2003), anhydrous form: 1.9 gcm^{-3} (Perry's Chemical Handbook)) values and two different aqueous binary density calculations. Curves with the superscript (*) use the Yens-Wood liquid density value for oxalic acid (1.478 gcm^{-3}) in calculating the binary liquid density. Curves with the superscript (**) have used the solid di-hydrate density in the binary aqueous calculation. The deviations are larger than those found for the surface tension sensitivity studies. Use of the di-hydrate density reduces the growth factor by 0.07 at 90% RH, a reduction of around 5%. However, when using the Yens-Wood liquid density, the predictions are still outside the experimental uncertainty of the measurements. When using a higher density value in the binary liquid phase calculation, the results drop further. Indeed, the assumption of the di-hydrate as the stable solid form and use of this density

Table 2. Basic physical properties of selected organic species.

Name	Formula	Molecular weight (g mol^{-1})	Aqueous solubility (g 100g^{-1} of solution) at 20°C unless noted	Pure surface tension at 298.15K (dyne cm^{-1})
Formic	CH_2O_2	46.03 [a]	infinite [a]	38.62 [d]
Acetic	$C_2H_4O_2$	60.05 [a]	infinite [a]	26.99 [d]
Propanoic	$C_3H_6O_2$	74.08 [b]	infinite [b]	26.7 [b]
Butanoic	$C_4H_8O_2$	88.1 [a]	infinite [a]	26.8 [b]
n-Valeric	$C_5H_{10}O_2$	102.13 [a]	3.3 (16) [a]	26.81 [d]
Caproic	$C_6H_{12}O_2$	116.16 [a]	1.1 [a]	34.705 [e]
Heptylic	$C_7H_{14}O_2$	130.19 [c]	slightly soluble [c]	28.31 [b]
Caprylic	$C_8H_{16}O_2$	144.22 [c]	slightly soluble [c]	28.82 [b]
Nonanoic	$C_9H_{18}O_2$	158.24 [c]	insoluble [c]	29.82 [d]
Maleic	$C_4H_4O_4$	116.07 [a]	79(25) [a]	40.15 [e]
Succinic	$C_4H_6O_4$	118.09 [a]	6.8 [a]	38.88 [e]
Glutaric	$C_5H_8O_4$	132.11 [a]	63.9 [a]	37.514 [e]
Malic	$C_4H_6O_5$	134.09 [a]	144(26) [a]	40.096 [e]

[a] - Perrys Chemical Enginneers handbook (7th edition) (www.knovel.com)
[b] - International critical tables of numerical data, physics, chemistry
    and technology (1st electronic edition) (www.knovel.com)
[c] - CRC Handbook of chemistry and physics 59th edition.
[d] - Chemical properties handbook 1999 (www.knovel.com)
[e] - Calculated value using Macleod-Sugden correlation (see text)

value in the liquid density calculation produces results that agree with experimental data well using the given uncertainties.

7 Conclusions

Following the development of a diameter dependent inorganic hygroscopic model, the influence of organic components is included by using uncoupled thermodynamics. Two separate thermodynamic models are combined in an additive approach, retaining the principles of the ZSR mixing rule, and combined with a method for solving the Kohler equation in order to develop a tool for predicting the water content associated with an aerosol of known inorganic/organic composition and dry size. As discussed in the accompanying paper (Topping et al., 2004), the model architecture uses a bisection approach to find a solution to the Kohler equation in which a variety of surface tension models can be employed with ease. It was first necessary to build a separate organic module before techniques for treating mixed organic/inorganic systems discussed. Given the wide range of organics found in aerosols, a technique for treating the non-ideality in solution is required for systems where experimental data is bound to be lacking. The most widely used group contribution method UNIFAC (Fredenslund et al., 1975) is employed here. Despite noted shortcomings in its ability to model components

of atmospheric importance, predictions are improved considerably when using revised interaction parameters derived from electro-dynamic balance studies (Peng et al., 2001). Such parameters were also used to model mixed systems that included 5–6 dicarboxylic acids very well, even at low relative humidity. The advantage of using more specific functional group definitions was not found using the systems studied here, though again such an approach matched experimental data very well. Also, using a proposed structure for Suwannee River fulvic acid in conjunction with electro-dynamic balance data also showed that these parameters may be used to model complex humic like material often found in aerosols, though comparisons involving mixtures with these components need to be made. The additive approach for modelling mixed inorganic/organic systems worked well for a variety of mixtures, as has been found in previous studies for simple binary inorganic/organic systems. However it was also found to work very well for mixtures involving 5 dicarboxylic acids and one inorganic salt. As concentrations increase then deviations between predicted and measured data increase as one might expect.

Two types of surface tension models available were found to reproduce measured data with varying success. As the organic component increased in complexity then deviations from experimental data increased. For components that are only slightly soluble in water, neither model could reproduce

the surface tension depression behaviour with much accuracy. A Sensitivity analysis showed however that such variation is likely to be within the experimental uncertainty for hygroscopicity measurements taken in the sub-saturated humid regime. Greater sensitivity was found for the value of dry density used in the assumed form of the dried out aerosol. Indeed, following on from the previous report, it is thus likely that the history of the aerosol studied in a HT-DMA, specifically the nature of the drying process that will influence the final crystalline form, will create systematic uncertainties upon comparisons with theoretical predictions. Comparison with a coupled thermodynamic approach and experimental hygroscopic measurements for an equi-mass $(NH_4)_2SO_4$:malonic acid aerosol showed that assumed values for interactions parameters may lead to erroneous results where a simple additive approach may provide more accurate results. However, where available, the use of coupled thermodynamics can reproduce measured behaviour better as one might expect. Further work is required to asses whether this difference lies within the experimental uncertainty of observed hygroscopic behaviour for a variety of systems.

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