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Mixing of the Organic Aerosol Fractions: Liquids as the Thermodynamically Stable Phases

Claudia Marcolli,* Beiping Luo, and Thomas Peter

Institute for Atmospheric and Climate Science, ETH Zurich, Switzerland

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An increasing number of single-particle measurements show that organic and inorganic constituents of the atmospheric aerosol are internally mixed within the particles. Therefore, the phases of the aerosol will be influenced by both mixing of the organic substances with each other and mixing between organic and inorganic constituents. In this work, the mixing properties of the organic aerosol fractions have been investigated theoretically and experimentally with respect to melting and deliquescence. We show that a liquid (or an amorphous solid) is the thermodynamically stable phase—even in the absence of water as a solvent—provided that a sufficiently high number of miscible components are present. Furthermore, we show experimentally that the deliquescence relative humidity of aqueous solutions of dicarboxylic acids decreases with an increasing number of components present in the solution. A five-component mixture consisting of malic, malonic, maleic, glutaric, and methylsuccinic acids deliquesces at a relative humidity (RH) as low as 45.4% RH, while the pure dicarboxylic acids exhibit deliquescence points between 72 and 96% RH. A further reduction of the deliquescence relative humidity is observed when an inorganic salt is added to the dicarboxylic acid five-component mixture. For NaCl, deliquescence of the eutonic composition occurred at 41.3%, for ammonium sulfate at 36.4%, and for ammonium nitrate even at 27.1% RH. Interactions between the solutes lead to either higher or lower solubilities in the multicomponent mixture as compared to the respective single-component aqueous solutions. In the mixed dicarboxylic acids/inorganic salt solutions, the solubilities of ammonium nitrate and sulfate are increased by ∼40%, the one of sodium chloride is decreased by a similar amount. In summary, these mixing properties suggest that small fractions of organic species prevent tropospheric aerosols from becoming fully solid, and the organic fraction may even stay fully liquid irrespective of tropospheric humidity.

Introduction

The impact of organic matter in the tropospheric aerosol on its hygroscopicity, phase transitions, and light scattering is of prime interest in determining the aerosol's cloud forming and climatic properties. However, its chemical composition and physical properties are not well understood. Whereas the inorganic fraction contains a limited number of relatively well-characterized major components, the organic fraction consists of a complex mixture of substances. By now, only a minor part of this organic mass can be resolved into specific molecular compounds.[1] Therefore, alternative approaches have been proposed which classify the organics according to functional groups or spectroscopic properties.[2] Thus, the water-soluble organic fraction can be divided into mono- and diacids, polyols, dialkyl ketones, polyphenols, and polycarboxylic acids.[3] The water-insoluble fraction contains alkanes, long chain alkanols, and alkanoic acids as well as polycyclic aromatic hydrocarbons (PAH).[1] However, to understand the chemical and physical properties of an aerosol, knowledge is required not only on its composition but also on its physical state.

To a certain extent, the thermodynamically stable phases can be derived on the basis of the degree of internal mixing within one particle and the physicochemical properties of the aerosol constituents. An increasing number of single-particle measurements show that organic and inorganic constituents of the aerosol are indeed internally mixed.[4−8] Therefore, the phases of the aerosol will be influenced by both mixing of the organic substances with each other and mixing between organic and inorganic constituents. A high degree of internal mixing is expected if one considers the vapor pressures of the so far identified constituents of the organic fraction. Thermodynamic equilibration between particles by gas-phase diffusion promotes a selective mixing of the organic fraction in itself and with the other aerosol constituents.[9]

A number of laboratory studies have investigated the influence of the organic fraction on CCN activity[10−14] and hygroscopic growth[15−17] using a single organic substance—often a dicarboxylic acid—as a representative model compound. Brooks et al.[17] showed by saturation solubility and water activity measurements of dicarboxylic acid/ammonium sulfate mixtures that the presence of a water-soluble dicarboxylic acid causes deliquescence to occur at a lower relative humidity (RH) than observed for pure ammonium sulfate. For other systems, the presence of an organic substance had no significant effect on the deliquescence relative humidity of the salts.[15,16] However, up to now, little attention has been paid to the fact that the organic fraction of the tropospheric aerosol constitutes a complex mixture.

In the recent literature, aerosols from smog chamber experiments—which are rather hydrophobic—are often treated as an absorptive well-mixed liquid (or an amorphous solid).[18−22] In stark contrast, on the basis of the solid state properties of the individual constituents in their pure forms, the water-soluble organic fraction is considered as fully or partly solid even up to very high relative humidity.[14,22,23]

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* Author to whom correspondence should be addressed. Tel: +41-1-633-27-69. Fax: +41-1-633-10-58. E-mail: claudia.marcolli@env.ethz.ch.

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In this study, we show that this asymmetry in the treatment of organic aerosols is lifted if one considers the actual mixing state of the aerosol. First, by assuming ideal solution behavior, we analyze the mixing characteristics of the organic fraction. Second, we investigate the deliquescence relative humidity of mixtures. To do this, a series of dicarboxylic acids was chosen to represent the water-soluble organic fraction. Dicarboxylic acids have been observed abundantly in aerosols from the urban,[24−27] marine,[28] polar,[29] and tropical atmosphere.[30,31] We prepared saturated aqueous solutions consisting of up to five dicarboxylic acids and compared the deliquescence relative humidities of these mixed aqueous solutions with those of aqueous solutions of the pure constituents.

Ammonium nitrate and sulfate as well as sodium chloride were chosen to represent the inorganic salt components of the tropospheric aerosol. The composition and the water activity of saturated aqueous solutions of mixtures of these inorganic constituents with dicarboxylic acid mixtures have been analyzed and compared with solution properties of the pure solutes.

Experimental Methods

Saturated aqueous solutions were prepared in an iterative procedure by adding small portions of material until the solution was saturated with respect to each component. Between additions, the mixtures were allowed to equilibrate in a thermostated water bath at 25.0 ± 0.1 °C. The water activities, a_w, were measured using an AquaLab water activity meter (Model 3TE, Decagon Devices, U.S.A.). For the measurements of the mixtures containing NaCl and NH_4NO_3, the volatile sample block available as an accessory to the instrument was used. Experimental errors for the measurements with the standard sample block are ± 0.003 a_w, for the volatile sample block ± 0.015 a_w. The organic substances and NaCl were obtained from Fluka; $(NH_4)_2SO_4$ and NH_4NO_3 were obtained from Aldrich. We used analytical grade reagents with purities >99% with the exception of glutaric and methylsuccinic acids with purities of ~98 and ≥97%, respectively. The substances were used without further purification.

Theory

In this section, we will show theoretically that the number of components influences the stable physical state of mixtures and the deliquescence relative humidity of mixed aqueous solutions.

It is well-known for two-component systems that their melting temperature is below the ones of the pure compounds if their melts are miscible.[32] The melting process is accompanied by a mixing process of the melts leading to a stabilization of the liquid phase with respect to the pure crystalline solids. Similarly, it can be proven theoretically that the deliquescence relative humidity of a mixture of two soluble solids is lower than the ones of the respective single-component systems.[33] This behavior can be explained the same way as the melting point depression, if one views the dissolution as a combination of a melting and a mixing process.

Since the water-soluble and the water-insoluble organic fraction consist of a high number of substances with similar physical properties, the stabilization of the mixed liquid phases with respect to the pure crystalline solids has to be taken into account. In the following paragraphs, we will show that this effect may be strong enough to shift the stable physical state from a conglomerate of crystalline solids to a liquid or an amorphous solid at room temperature—even in the absence of water as a solvent.

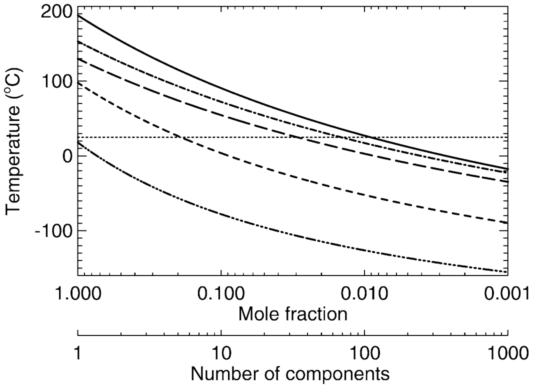

Figure 1. Melting points of organic acids as a function of their mole fractions in an ideal solvent. These values can be translated into the melting points of hypothetical mixtures consisting of an increasing number of equally abundant components with the same melting temperatures and enthalpy of fusions as the model compounds. Values are shown for the compounds succinic (—; solid line), adipic (– • –; dash–dot line), malic acid (– – –; long dashed line),[34] glutaric (- - - ; short dashed line),[35] and lactic (– ••• – , dash-3-dots line) acid.[36] Dotted line: room temperature.

Melting Point Depression of Ideal Solutions. The concentration of an individual organic component in the aerosols is usually small. If the corresponding organic solid is in equilibrium with a liquid mixture phase, the equilibrium temperature, i.e., the melting point, is lower than if the equilibrium is established between the crystalline solid and the pure melt. The magnitude of the melting point depression depends on the abundance of this component in the liquid mixture phase.

At the melting temperature $T_{m,i}$ the chemical potentials of the component i in the solid and the liquid phase are the same and the free energy of fusion $\Delta_{fus}G_i$ is zero:

$$\Delta_{fus}G_i = G_{liquid,i} - G_{solid,i} = \Delta_{fus}H_i - T_{m,i}\Delta S_i = 0 \quad (1)$$

where $\Delta_{fus}H_i$ is the enthalpy of fusion and ΔS_i the entropy change of fusion and subsequent mixing. The melting temperature of the solid i in the mixture is then given by

$$T_{m,i} = \Delta_{fus}H_i/\Delta S_i \quad (2)$$

We may demonstrate the effectiveness of the melting point depression for multicomponent mixtures by assuming the liquid phase to be an ideal solution. For an ideal solution, the enthalpy, $\Delta_{fus}H_i$, and the entropy of fusion, $\Delta_{fus}S_i$, may be approximated by the values of the solid dissolving into the pure melt and ΔS_i is given by

$$\Delta S_i = \Delta_{fus}S + \Delta_{mix}S_i = \Delta_{fus}S_i - R\ln(x_i) \quad (3)$$

In this expression, x_i is the mole fraction of component i in the mixed solution, R is the universal gas constant, and $\Delta_{mix}S_i$ is the mixing entropy of the component i in the mixed ideal solution, i.e., the entropy change occurring when the pure melt mixes ideally with the other components in the liquid. From eqs 2 and 3, the melting temperature of component i in the mixed solution, $T_{mix,i}$ becomes

$$T_{mix,i} = \frac{T_{m,i}}{1 - RT_{m,i}\ln x_i/\Delta_{fus}H_i} \quad (4)$$

Figure 1 shows the melting temperatures for selected substances with known $T_{m,i}$ and $\Delta_{fus}H_i$ as a function of mole fraction of component i in the ideal solvent based on eq 4. It can be seen

TABLE 1: Physical Properties of the Investigated Substances (dec = decomposition)

substances	molecular weight[a]	melting point (°C)[a]	aqueous saturation concentration (wt %) at 25 °C[b]	deliquescence RH (%) at 25 °C[c]	octanol−water partition coefficient log P[d]	dissociation constant pK_a at 25 °C[a]
oxalic acid	90.04	189.5 dec	10.1 (9.81)	97.8	−2.22	1.23; 4.19
malonic acid	104.06	135 dec	61.3 (62.2)	72.4	−0.81	2.83; 5.69
succinic acid	118.09	188	7.2 (7.459)	99.1	−0.59	4.16; 5.61
glutaric acid	132.12	97.8	58.8 ($56.52^{23.9°C}$)	88.2	−0.29	4.31; 5.41
malic acid	134.09[d]	131[d]	57.4 (58.0)	80.5	−1.26	3.40; 5.11
maleic acid	116.07	130.5	44.0 (44.3)	89.1	−0.48	1.83; 6.07
methylsuccinic acid	132.12	115	35.6	95.5	−0.34	4.13; 5.64
adipic acid	146.14	153.2	2.2	99.9	0.08	4.43; 5.41
ammonium nitrate	80.043	dec 210	67.5 (67.63)	62.1	−	−
ammonium sulfate	132.141	dec 280	43.2 (43.3)	80.2	−	HSO_4^-: 1.99
sodium chloride	58.443	800.7	26.4 (26.43)	75.3	−	−

[a] Ref 35. [b] This study, values in parantheses are from ref 38. [c] This study. [d] Ref 39.

that the melting point decreases as the mole fraction decreases. It reaches room temperature even for the substance with the highest melting point, i.e., succinic acid, when the mole fraction is as small as 0.01. This means that at room temperature, a mole fraction of 0.01 of succinic acid dissolves into an ideal solvent. For glutaric acid, room temperature is reached when the mole fraction becomes less than 0.2. With a vapor pressure of 0.0813 mmHg, lactic acid will also partition into the aerosol phase.[37] At room temperature this substance is present in liquid form even when pure (mole fraction equal 1.0).

The second x-scale in Figure 1 refers to the eutectic melting temperatures of idealized mixtures consisting of an increasing number of components that all exhibit the same melting point and enthalpy of fusion. For this hypothetical situation, the eutectic composition is realized when all components are equally abundant in the mixture. The melting point of a mixture consisting of 100 substances with the same physical properties as those of succinic acid will be around room temperature. For substances with the same physical properties as glutaric acid, only five to six components are needed to form a liquid at room temperature. Thus, even in the absence of a specific solvent (e.g., water), a liquid or an amorphous solid will form at ambient temperature provided that a sufficiently high number of components are present. This conclusion is valid for the water-soluble as well as for the water-insoluble organic fraction.

Deliquescence Relative Humidity of Mixed Aqueous Solutions. From the Gibbs−Duhem relation and assuming ideality for all solutes, the relative humidity, RH, of air in equilibrium with an aqueous solution is given by

$$\mathrm{RH} = \exp(-M_{\mathrm{w}}\sum_{s} m_s) \tag{5}$$

where m_s is the molality of solute s (moles of s per kilogram of solvent) and M_w (= 0.018 kg/mol) the mole mass of water (the solvent). Upon choosing m_s as the molality of the eutonic composition, eq 5 allows us to determine the deliquescence relative humidity (DRH). Assuming ideal solution behavior, the saturation concentration of each solute at a specific temperature can be calculated on the basis of eq 4. For a more accurate estimate, the saturation solubilities of single solute systems can be used: if one neglects interactions between the dissolved species in mixed aqueous solutions, the saturation concentration of each solute will be equal to its value in a saturated solution of the pure compound. In many cases, the aqueous saturation solubilities of the pure solutes will be available and can be used to estimate the deliquescence relative humidity of multicomponent solutions.

Solubility and Water Activity Measurements

To investigate experimentally how strongly the number of components influences the deliquescence relative humidity of the water-soluble organic fraction, we will stepwise increase the number of components present in a model aqueous solution. In the theoretical section, we have calculated the solubility of different dicarboxylic acids by eq 4. However, in reality, deviations from ideality will occur depending on the polarity, size, and acidity of the solutes and the solvent. We performed solubility and water activity measurements for model systems containing a series of dicarboxylic acids and the inorganic salts sodium chloride, ammonium nitrate (AN), and ammonium sulfate (AS). Table 1 lists the physical properties of the investigated dicarboxylic acids and inorganic salts. The dicarboxylic acids can be divided into the highly soluble malonic, glutaric, malic, maleic, and methylsuccinic acids and the less soluble oxalic, succinic, and adipic acids. The octanol−water partition coefficients log P—defined as the ratio of the equilibrium concentration of the substance in the octanol-rich phase to that in the water-rich phase in the limit of zero concentration—show that all these acids partition preferentially into the aqueous phase with the exception of adipic acid. They form crystalline solids with melting points in the range of 100−200 °C. Although oxalic and succinic acid have negative log P values, they exhibit low saturation solubilities in water since they form very stable crystalline solids.

Experiments on Eutonic Mixtures. In a first step, mixtures containing an increasing number of the highly soluble dicarboxylic acids were prepared at 25 °C by adding component after component in the order of decreasing hydrophilicity. As a measure of hydrophilicity, the octanol−water partition coefficient log P was used. In this way the following eutonic mixtures (i.e., mixtures saturated with respect to all components) were prepared: M2 = malic + malonic, M3 = M2 + maleic, M4 = M3 + glutaric, M5 = M4 + methylsuccinic acids. In a second step, an inorganic salt was added to the five-component mixture M5. To reach the eutonic composition, the mixtures were iteratively saturated with respect to each solute. After saturation was reached, we measured the water activity, which is equivalent to RH. Figure 2 shows the water activity as a function of the water content for the saturated solutions of the pure substances and the mixtures. It can be seen that the aqueous solubility of the dicarboxylic acids and the inorganic salts cover similar concentration ranges, with malonic acid and ammonium nitrate being most soluble. For a given solubility, the deliquescence relative humidities of the dicarboxylic acids are typically higher than the ones of the inorganic salts. This is expected, since the investigated inorganic salts exhibit lower molecular

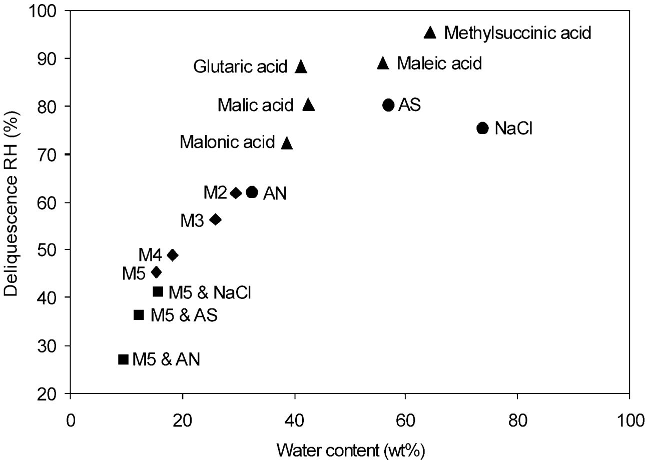

Figure 2. Deliquescence relative humidity and water content at the deliquescence relative humidity for the pure organic (solid triangles) and the pure inorganic (solid circles) substances, as well as for the organic mixtures M2−M5 (solid diamonds) and the organic/inorganic mixtures (solid squares). M2: malic + malonic acids; M3: malic + malonic + maleic acids; M4: malic + malonic + maleic + glutaric acids; M5: malic + malonic + maleic + glutaric + methylsuccinic acids. All mixtures are eutonic, i.e., are saturated with respect to all components.

weights and a higher degree of dissociation in solution than the dicarboxylic acids. The different deliquescence relative humidities for the almost equally soluble malic and glutaric acid can be explained by differences in their hydrophilicity. The more hydrophilic malic acid associates more strongly with water than glutaric acid, thus causing a more pronounced reduction of the water activity.

The eutonic mixtures M2−M5, consisting of two to five dicarboxylic acids, all show lower deliquescence relative humidities than the pure components they consist of. It can be seen from Figure 2 that the water content as well as the deliquescence relative humidity decrease with an increasing number of components. Thus, the eutonic five-component mixture M5 deliquesces at the lowest relative humidity, namely already at 45.4 % RH. A further reduction of the deliquescence relative humidity is observed when an inorganic salt is added to the organic five-component mixture. For M5 + NaCl, deliquescence of the eutonic composition occurs at 41.3 %, for M5 + ammonium sulfate at 36.4 %, and for M5 + ammonium nitrate even at 27.1 % RH. These results confirm that a liquid as the thermodynamically stable state of the water-soluble organic fraction becomes increasingly favored the more components a mixture consists of.

Table 2 lists the measured saturation concentrations in molality units—as moles of solutes per kilogram of water—for the pure substances and the eutonic mixtures. If no interactions between solutes occurred, the aqueous saturation solubility of each component would be equal to its value in a saturated solution of the pure compound. The comparison of the measured aqueous solubilities of the dicarboxylic acids in pure water and in the presence of other dicarboxylic acids shows deviations from this behavior: The solubilities of the more hydrophilic dicarboxylic acids—malic, malonic, maleic acid—are decreased by up to ∼30%, whereas the solubilities of the less hydrophilic ones—glutaric and methylsuccinic acid—are increased by a similar amount. The relatively low solubility of maleic acid in the mixture with the other dicarboxylic acids could be due to its quite strong acidity. Dissociation will enhance the solubility of an acid in aqueous solution. This effect will be more pronounced, the lower its pK_a value and the more dilute the solution is. In the highly concentrated mixtures, the equilibrium is shifted to the undissociated acids and thus the solubility is reduced.

The eutonic composition of the five dicarboxylic acids plus sodium chloride contains 3.3 wt % of NaCl and 15.7 wt % of water. This corresponds to a reduction of the aqueous solubility of sodium chloride by 41%. Hence, the presence of the dicarboxylic acids has a negative effect on the aqueous solubility of sodium chloride. The eutonic composition with ammonium sulfate contains 13.5 wt % of AS and 12.3 wt % of water, the one with ammonium nitrate 27.7 wt % of AN and only 9.6 wt % of water. These eutonic compositions show an enhancement of the aqueous solubility of ammonium nitrate and sulfate by ∼40%, as compared with the solubility in pure water. In addition, Table 2 shows that the solubility enhancement of the dicarboxylic acids on one hand and ammonium sulfate and nitrate on the other hand is mutual: the solubilities of malic, malonic, and maleic acid are considerably increased in the presence of ammonium nitrate or sulfate. The most probable explanation for this behavior is that hydrogen bonding between the acidic protons of the dicarboxylic acids and the oxygen atoms of the sulfate and nitrate ions enhance the solubilities of both, the organic acids and the inorganic salts. Acid/base reactions seem to be of minor importance. Principally, they could take place between the dicarboxylic acids and the sulfate ion. However, only maleic acid exhibits a pK_a value that is comparable to the one of the bisulfate ion. Malic, malonic, glutaric, and methylsuccinic acids are all not sufficiently acidic for acid/base reactions with sulfate to be effective. Moreover, the solubility enhancement is also observed for ammonium nitrate, which is not basic under the given conditions.

TABLE 2: Measured Concentrations of the Solutes in Moles Per Kilogram of Water for the Saturated Solutions of the Pure Substances and the Eutonic Compositions of the Mixtures (The deliquescence relative humidity (DRH) is given in %. All data refer to 25 °C.)

	pure substances	M2	M3	M4	M5	M5 + AN	M5 + AS	M5 + NaCl
malic acid	10.05	7.3	7.3	7.0	6.8	9.1	7.8	7.1
malonic acid	15.21	13.5	13.1	14.6	14.8	23.8	21.1	15.2
maleic acid	6.76		4.4	5.2	5.3	6.6	8.7	5.3
glutaric acid	10.82			10.3	12.4	11.0	9.5	10.7
methylsuccinic acid	4.18				5.5	4.4	4.0	4.3
ammonium nitrate	26.00					36.0		
ammonium sulfate	5.76						8.3	
sodium chloride	6.14							3.6
DRH (measured)	−	61.8	56.4	48.8	45.4	27.1	36.4	41.3
DRH (calculated)[a]		63.5	56.2	46.2	42.9	16.8	31.4	34.4

[a] Based on eq 5 and assuming the same solubilities in the mixed as in the single-component aqueous solutions.

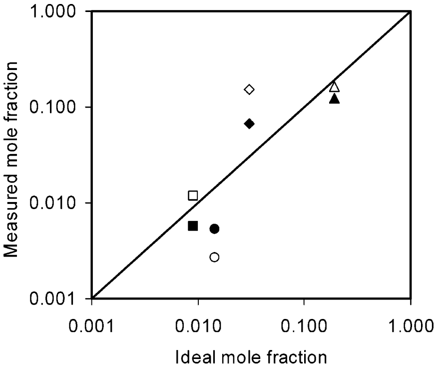

Figure 3. Comparison between the ideal and the measured saturation concentration at 25 °C for malic (diamonds), glutaric (triangles), succinic (squares), and adipic acids (circles). Open symbols: solubility in water; solid symbols: solubility in the M5 eutonic composition. The diagonal corresponds to ideal mixing in the solution. The ideal solubilities have been calculated from eq 4 in the form of $x_i = \exp[\Delta_{\mathrm{fus}}H_i(1/RT_{m,i} - 1/RT_{\mathrm{mix},i})]$.

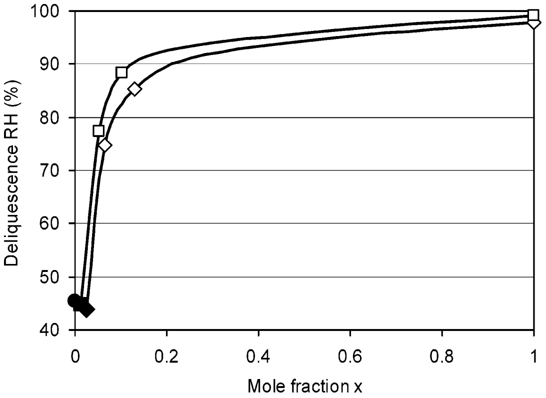

Figure 4. Relative humidity of full deliquescence of oxalic (diamonds) and succinic (squares) acids in the mixture M5 of the five dicarboxylic acids (malic, malonic, maleic, glutaric, and methylsuccinic acids) as a function of oxalic and succinic acids mole fraction of dry substance. Eutonic compositions are indicated by solid symbols: M5 (solid circle), M5 + oxalic acid (solid diamond), M5 + succinic acid (solid square).

Table 2 shows that the theoretically derived deliquescence relative humidities based on eq 5 and assuming the same solubilities in the mixed as in the single-component aqueous solutions are in quite good agreement with the experimentally determined ones for the mixtures M2 to M5. However, considerable deviations are observed for the organic/inorganic mixtures. Interestingly, if one calculates the deliquescence relative humidity with the experimentally determined solubilities instead of the ones of the pure solutes, the agreement between measured and calculated deliquescence relative humidity decreases for the organic mixtures. The reasons for this behavior are not known at present. Figure 3 relates the measured saturation concentrations of malic, glutaric, succinic, and adipic acid in water and in the aqueous solution M5 to the theoretically derived melting point depressions given by eq 4. The mixture M5 contains malic and glutaric acid at their respective saturation concentrations. To determine the saturation solubility of succinic and adipic acid in M5, these acids were added to M5 as a sixth solute, respectively. For points on the diagonal in Figure 3, the measured solubilities at 25 °C are the same as the ideal ones for this temperature calculated on the basis of eq 4. For points above this line, the measured saturation concentration is higher, for points below it, lower than the ideal one. It can be seen from Figure 3 that the investigated mixtures show deviations from the solubilities derived for ideal solutions in both directions. The direction and degree of the deviations depend on the hydrophilicities of the solutes. Water is an excellent solvent for the very hydrophilic malic acid, leading to a saturation concentration at room temperature that is distinctly higher than the ideal one. The saturation concentrations of the less hydrophilic succinic and glutaric acids are higher in water than in the mixed solution M5, and quite close to the theoretically derived value for ideal solutions. For the rather hydrophobic adipic acid ($\log P = 0.08$), the saturation concentration in M5 is higher than the one in pure water, but distinctly lower than the ideal value. Thus, the assumption of ideality leads only to a very rough estimate of the measured solubilities. For an accurate description of solubilities, the excess enthalpy and entropy must be considered.

Noneutonic Solutions. So far, we have investigated the solubility and water activity of mixtures of dicarboxylic acids and selected inorganic salts in their eutonic compositions. For these compositions the concentration of each constituent is fixed. If the abundance of a component in the mixture exceeds its eutonic concentration, it is dissolved only partly at the deliquescence relative humidity in thermodynamic equilibrium; full deliquescence is established at a higher relative humidity. It can be assumed that in the tropospheric aerosol, the concentrations of most organics in the particulate matter are low enough for complete dissolution even at very low relative humidities. Some organics, however, such as oxalic or succinic acid can be quite abundant. Succinic acid was found to comprise up to 3.5% of total aerosol carbon in Antarctic aerosols.[29] Oxalic acid was the most abundant dicarboxylic acid in urban aerosol samples from Tokyo, where it made up 2−7% of the water-soluble organic fraction.[27]

We therefore determined the eutonic compositions of the five dicarboxylic acids (M5) plus either oxalic or succinic acid as a sixth dicarboxylic acid. They were found to contain only 1.3 wt % (mole fraction: 0.013) of dry mass succinic acid, and 1.8 wt % (mole fraction: 0.024) oxalic acid, respectively. If more of these substances are present, additional water must be added to reach full dissolution. This was done for compositions with 5 and 10 wt % of dry mass oxalic or succinic acid, respectively. After a clear solution was obtained, the water activity was determined. The results of these measurements are shown in Figure 4. The solid symbols indicate the eutonic compositions. At the deliquescence relative humidity, the noneutonic compositions are saturated with respect to oxalic acid and succinic acid, respectively, but subsaturated with respect to the other five dicarboxylic acids. The measurement points for $x = 1$ correspond to the deliquescence relative humidity of pure oxalic and succinic acid, respectively. It can be seen that the relative humidity of full deliquescence shows a steep increase for mixtures with excess succinic or oxalic acid. Thus, given their tropospheric aerosol concentrations, and assuming equilibrium conditions between the phases in the aerosol, these two substances could in some instances be present as solids at typical tropospheric relative humidities.

Similarly, the eutonic compositions of the five dicarboxylic acids and an inorganic salt contain 3.9 wt % (mole fraction: 0.077) of dry mass sodium chloride, 15.6 wt % (mole fraction: 0.142) ammonium sulfate, and 30.7 wt % (mole fraction: 0.396) ammonium nitrate, respectively. If these concentrations are exceeded, the inorganic salts will be partly present as solids above the deliquescence relative humidity of the respective eutonic compositions. This will be a typical situation for sodium chloride and ammonium sulfate in marine and continental aerosol compositions, respectively.[6,40,41]

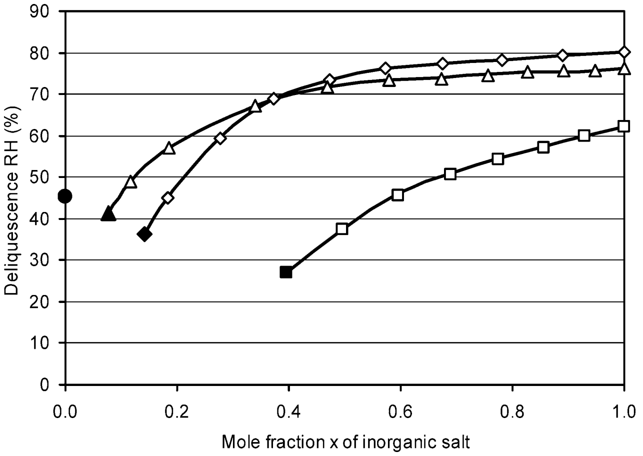

Figure 5. Relative humidity of full deliquescence of ammonium sulfate (diamonds) and nitrate (squares), and sodium chloride (triangles) in the mixture M5 of the five dicarboxylic acids (malic, malonic, maleic, glutaric, and methylsuccinic acids) as a function of the inorganic salts mole fraction *x*. Eutonic compositions of the organic/inorganic mixture are indicated by solid symbols, M5 (solid circle), M5 + AS (solid diamond), M5 + AN (solid square), M5 + NaCl (solid triangle), noneutonic mixtures by open symbols.

Figure 5 shows the relative humidity of full deliquescence of the inorganic salts as a function of their mole fraction with respect to the dry mixture. The solid symbols indicate the eutonic compositions. For these compositions, the deliquescence relative humidities are lowest. For compositions with higher concentrations of the inorganic salts, full deliquescence occurs at a higher relative humidity. In Figure 5, the relative humidities of full deliquescence for noneutonic compositions are labeled by open symbols. At the deliquescence relative humidity, only the eutonic compositions are saturated with respect to all solutes, the indicated noneutonic compositions are saturated with respect to the inorganic constituent but subsaturated with respect to the dicarboxylic acids. It can be seen that the relative humidities of full deliquescence rise continuously with increasing quantities of inorganic salts present in the mixture. For $x = 1$, we have the purely inorganic salt solutions with the deliquescence relative humidities as listed in Table 1. The deliquescence relative humidities of mixtures with $x(\mathrm{NaCl}) = 0.6$ is almost equal to the value of the pure salt. In Figure 6 the saturation concentration in moles of inorganic salt per kilogram of water are given as a function of the dry composition of the mixtures. Compositions with $x = 1$ correspond to the purely inorganic salt solutions with aqueous solubilities as listed in Table 1. For sodium chloride, the saturation concentration is lowest in the eutonic composition and rises continuously the less dicarboxylic acids are present in the solution. For ammonium sulfate and nitrate, the saturation concentrations are highest in the eutonic compositions. They drop off steeply and go through a minimum value. This minimum is more distinct for ammonium sulfate than for ammonium nitrate. Thus, the aqueous solubilities of ammonium sulfate and nitrate are enhanced with respect to the one in pure water only in the presence of high quantities of dicarboxylic acids, namely, for solutions that contain more dicarboxylic acids than water in terms of weight percent. The exact composition of the discussed mixtures is given in Table 3.

Discussion

Water Uptake of Aerosol Particles. In field measurements, hygroscopicity of the aerosol is commonly determined using a hygroscopicity tandem differential mobility analyzer (H-TDMA). If the hygroscopic growth is monitored as a function of relative humidity, smooth growth curves with water uptake already at low relative humidity are often observed.[4,37,42−44] This suggests that the aerosol particles remain partly or totally liquid even for extremely dry conditions. Organics are suspected to be associated with the more and the less hygroscopic particles and to influence their hygroscopic behavior.[4,40] The analysis of H-TDMA data indicates that the organic-associated water content is considerably less than that of sulfate compounds for high RH, but comparable or greater for low RH.[43]

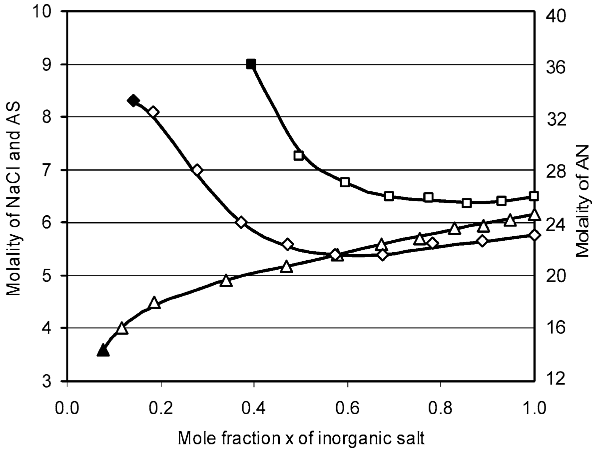

Figure 6. Moles of solute per kilogram of water for NaCl (triangles) and AS (diamonds) (scale on the left axis) and for AN (squares) (scale on the right axis) as a function of the mole fraction *x* of the inorganic salts. Eutonic compositions are indicated by solid symbols: M5 + AS (solid diamond), M5 + AN (solid square), M5 + NaCl (solid triangle), noneutonic mixtures by open symbols.

Figure 7 shows the water uptake for mixtures of the five dicarboxylic acids and ammonium sulfate with organics to ammonium sulfate ratios of 1:4, 1:1, and 4:1. The data points below full deliquescence were constructed from the measured water activities shown in Figure 5 and represent the deliquescence branch of the water uptake. For the data points above full deliquescence, we prepared subsaturated solutions and determined their water activity. As a comparison, the water uptake of pure ammonium sulfate and the purely organic mixture M5 are also shown. For all three organics to ammonium sulfate ratios, hygroscopic growth starts at 36.4% RH, the deliquescence relative humidity of the eutonic composition. At this relative humidity, the dicarboxylic acids dissolve completely and ammonium sulfate partly, since it is present in excess with respect to the eutonic composition. This point is indicated in the graph by the first solid symbol. The second solid symbol at higher relative humidity represents the relative humidity of full deliquescence of the ammonium sulfate. It can be seen that the dicarboxylic acids take up water moderately at medium relative humidity whereas ammonium sulfate is responsible for a stronger water uptake at higher relative humidity. Thus, for the mixtures with 20 wt % and 50 wt % ammonium sulfate, smooth or almost smooth growth curves are observed. Only for the mixture with 80 wt % ammonium sulfate can the relative humidity of full deliquescence be unambiguously identified on the basis of the growth curve. However, even then, the sharp onset visible in the purely inorganic system is lost. These results confirm that the water-soluble organic fraction is responsible for water uptake at low relative humidity.[43] Moreover, they show that the hygroscopic growth at low relative humidity does not imply a supersaturated state but represents thermodynamic equilibrium.

Comparison with ZSR Predictions. The water uptake of malic, malonic, maleic, and glutaric acids have been determined

TABLE 3: Deliquescence Relative Humidities of Multi-component Aqueous Solutions of the Dicarboxylic Acids and Inorganic Salts[a]

composition of aqueous solutions in moles per kilogram of water										deliquescence RH (%)
hC4	C3	M	C5	iC5	C2	C4	AN	AS	NaCl	
6.8[b]	14.8[b]	5.3[b]	12.3[b]	5.4[b]	1.05[b]					43.8
2.14	4.66	1.66	3.87	1.70	1.00[b]					74.8
1.16	2.53	0.90	2.10	0.92	1.14[b]					85.3
6.8[b]	14.9[b]	5.3[b]	12.4[b]	5.5[b]		0.58[b]				44.8
2.07	4.53	1.61	3.77	1.67		0.74[b]				77.3
1.06	2.31	0.82	1.92	0.85		0.79[b]				88.3
4.87	12.73	3.57	5.88	2.35			29.0[b]			37.4
3.02	7.89	2.21	3.65	1.46			27.0[b]			45.6
1.94	5.08	1.42	2.34	0.94			26.0[b]			50.7
1.24	3.25	0.91	1.5	0.60			25.9[b]			54.2
0.71	1.87	0.52	0.86	0.34			25.4[b]			57.0
0.32	0.84	0.23	0.38	0.15			25.6[b]			59.9
5.48	14.86	6.24	6.80	2.86				8.1[b]		45.1
2.76	7.48	3.15	3.43	1.44				7.0[b]		59.4
1.54	4.15	1.71	1.87	0.79				6.0[b]		68.8
0.95	2.57	1.08	1.17	0.49				5.6[b]		73.3
0.61	1.65	0.69	0.76	0.32				5.41[b]		76.1
0.39	1.06	0.45	0.49	0.20				5.40[b]		77.3
0.24	0.64	0.27	0.30	0.12				5.62[b]		78.3
0.11	0.29	0.12	0.13	0.06				5.66[b]		79.3
5.13	10.84	3.78	7.62	3.07					4.0[b]	49.0
3.24	7.05	2.42	4.89	1.99					4.5[b]	57.0
1.58	3.43	1.18	2.38	0.96					4.9[b]	67.2
0.97	2.11	0.72	1.46	0.60					5.2[b]	71.7
0.66	1.4	0.49	0.98	0.40					5.4[b]	73.3
0.46	0.97	0.34	0.68	0.27					5.6[b]	73.8
0.31	0.66	0.23	0.46	0.19					5.7[b]	74.4
0.20	0.44	0.15	0.31	0.12					5.9[b]	75.3
0.12	0.26	0.09	0.18	0.07					5.95[b]	75.7
0.05	0.12	0.04	0.08	0.03					6.04[b]	75.6
4.97	10.90	3.88	9.08	4.01						55.0
3.51	7.71	2.74	6.43	2.84						65.0
2.64	5.80	2.06	4.83	2.14						72.7
1.95	4.27	1.52	3.56	1.57						80.0
1.46	3.22	1.14	2.68	1.18						85.1
1.11	2.43	0.86	2.02	0.89						89.3
0.80	1.75	0.62	1.46	0.64						92.7
0.51	1.12	0.40	0.93	0.41						95.6
0.22	0.48	0.17	0.40	0.18						98.4
4.15	11.20	4.62	5.06	2.13				6.07		52.7
2.59	6.99	2.88	3.16	1.33				3.79		66.1
1.88	5.08	2.09	2.29	0.96				2.75		74
1.48	3.99	1.65	1.80	0.76				2.16		79.1
1.22	3.29	1.36	1.48	0.62				1.78		82.7
1.03	2.79	1.15	1.26	0.53				1.51		85.2
0.77	2.07	0.85	0.93	0.39				1.12		88.9
0.81	2.18	0.90	0.98	0.41				4.72		77.2
0.69	1.85	0.76	0.84	0.35				4.02		80.4
0.54	1.45	0.60	0.66	0.28				3.15		84.5
0.43	1.16	0.48	0.52	0.22				2.52		87.7
0.29	0.79	0.32	0.35	0.15				1.70		91.7
0.15	0.41	0.17	0.18	0.08				0.89		96.0
0.06	0.15	0.06	0.07	0.03				0.33		99.2
0.21	0.58	0.24	0.26	0.11				5.05		80.4
0.18	0.50	0.21	0.23	0.10				4.32		83.3
0.16	0.43	0.18	0.20	0.08				3.78		85.7

[a] Abbreviations: C2: Oxalic acid, C3: Malonic acid, C4: Succinic acid, iC5: Methylsuccinic acid, C5: Glutaric acid, M: Maleic acid, hC4: Malic acid, AN: Ammonium nitrate, AS: Ammonium sulfate. [b] Saturation concentrations.

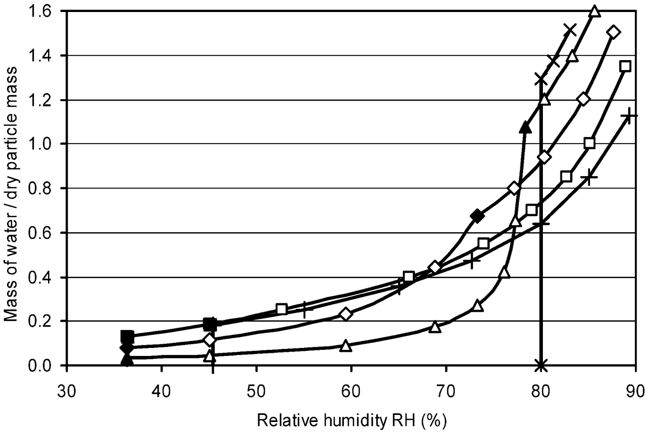

Figure 7. Water uptake of dicarboxylic acids/ammonium sulfate mixtures with wt % ratios 4:1 (squares), 1:1 (diamonds), 1:4 (triangles). The first solid symbol at 36.4% RH indicates the deliquescence of the dicarboxylic acids, the second solid symbol represents the full deliquescence of the inorganic salts. As a comparison, the water uptake of pure ammonium sulfate (×; ref 45) and the mixture M5 (+, this study) are also shown.

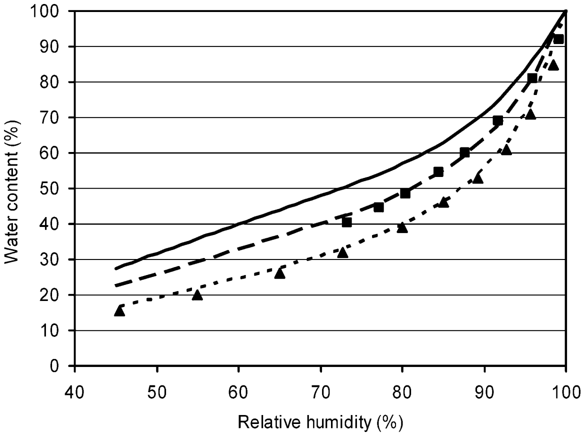

Figure 8. Comparison of measured water contents with the ZSR predictions. The triangles and the squares indicate the experimental data of the dicarboxylic acids mixture M5 (solid triangles) and the dicarboxylic acids/ammonium sulfate mixture with a wt % ratio of 1:1 (solid squares). The dotted and the dashed lines represent the ZSR predictions for the dicarboxylic acids mixture M5 and the dicarboxylic acids/ammonium sulfate mixture with a wt % ratio of 1:1, respectively. The solid line shows the parametrization by Chan et al.[49] for ammonium sulfate.

well into the supersaturated region using single droplets levitated in an electrodynamic balance.[46,47] Using the Zdanovskii-Stokes-Robinson (ZSR) approach,[48] it is therefore possible to predict the water uptake of the multicomponent dicarboxylic acid solutions based on the single solute data. Figure 8 shows the comparison between the experimentally determined water uptake of the mixture M5 in the subsaturated region and the ZSR predictions. For methylsuccinic acid, the same parametrization was used as for glutaric acid, since no water activity data is available for supersaturated solutions of this substance. The comparison shows, that the water uptake of the mixture M5 can be predicted quite well based on the single solute data. The same is true for a mixture consisting of the five dicarboxylic acids and ammonium sulfate (Figure 8). The exact composition of the discussed mixtures is given in Table 3.

Organics to Act as CCN. Atmospheric cloud condensation nuclei (CCN) measurements have shown indications of organic matter in the cloud nucleating portion of the aerosol mass.[50−53] Moreover, on the basis of field studies, a key role in CCN formation was suggested for the organic aerosol.[54,55] Laboratory studies have confirmed the potential of organic species to act as CCN.[10,11] For slightly soluble substances, Shulman et al.[23] introduced a modified Köhler equation which accounts for the gradual dissolution of solid substances into the growing droplet. Thus, CCN ability of organic substances should correlate with their aqueous solubility. Such a dependency was indeed found by Corrigan and Novakov[11] in laboratory experiments. However, subsequent studies[14,56] also showed deviations from this relationship. Hori et al.[14] therefore concluded that the critical supersaturation could depend significantly on the particle phase (solid or liquid) exhibited in the initial condensation stages. In the real atmosphere, the initial particle phase should be considered as a key factor to evaluate the actual CCN ability.

The present study shows that the water-soluble organic fraction can be viewed as a liquid. The activation of this liquid will depend on its hydrophilicity and miscibility with water. These properties are reflected by the octanol–water partition coefficient, log *P*.

Summary and Conclusions

To understand the solid-state properties of an aerosol particle consisting of a high number of miscible components, the entropy of mixing was taken into account. For ideal conditions, we showed theoretically that a liquid or an amorphous solid becomes the thermodynamically stable phase provided that a sufficiently high number of miscible components are present. Furthermore, we investigated experimentally the deliquescence relative humidity for aqueous solutions of dicarboxylic acids: the deliquescence relative humidity of the eutonic compositions decreases with an increasing number of components present in the solution. Thus, the five-component mixture consisting of malic, malonic, maleic, glutaric, and methylsuccinic acids deliquesces already at 45.4% RH. A further reduction of the deliquescence relative humidity was observed by the addition of an inorganic salt to the organic five-component mixture. Interactions between different solutes present in the solution leads to higher and lower solubilities than in pure water. The aqueous saturation solubilities of ammonium nitrate and sulfate are increased by ∼40%, the one of sodium chloride is decreased by a similar amount when compared with the saturation concentrations of the pure compounds in water. The strong increase of the aqueous solubilities of ammonium nitrate and sulfate is restricted to very concentrated solutions that contain more weight percent dicarboxylic acid than water.

In laboratory studies, the influence of the organic fraction on aerosol properties are often investigated using one organic substance—often a dicarboxylic acid—as a representative model compound. Thus, the aqueous solubility of the pure organic solid strongly influences the experimental results as could be seen for CCN activation experiments. However, the aqueous solubility of the organic solid loses much of its importance as soon as the water-soluble organic fraction is viewed as a mixture of organic components. For atmospheric conditions, it can be assumed that gas/liquid partitioning of the organic fraction may be more important than liquid/solid partitioning. This work has shown that even at very low relative humidity, the tropospheric aerosol will contain a liquid phase which is highly concentrated with respect to water-soluble organics as well as inorganic salts. This phase will be a reaction medium with quite different properties than the dilute aqueous solutions of fog or rain droplets. The reactions that take place in this medium remain to be elucidated.

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