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Phase Changes during Hygroscopic Cycles of Mixed Organic/Inorganic Model Systems of Tropospheric Aerosols

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A correct description of the aerosol's phases is required to determine its gas/particle partitioning, its reactivity and its water uptake and release. In this study, we investigate organic/electrolyte interactions of ammonium sulfate, nitrate and sodium chloride with substances containing carboxylic acids (COOH) and hydroxyl (OH) functional groups. As organic model compounds, we chose polyols with different OH/CH_n ($n = 0-3$) ratios—namely, glycerol, 1,4-butanediol, and 1,2-hexanediol—as well as PEG 400 and a mixture of dicarboxylic acids consisting of malic, malonic, maleic, glutaric, and methylsuccinic acid. Bulk solubility and water activity measurements of these model systems together with a survey of literature data showed that NaCl is a salting-out agent for alcohols and organic acids whereas ammonium nitrate and sulfate exhibited salting-in and salting-out tendencies depending on the nature and number of functional groups as well as on the concentration of the solution. All investigated salts induce a liquid−liquid phase separation in the 1,2-hexanediol/water system. Considering the composition of the tropospheric aerosol, such phase separations might indeed occur frequently when particles in the atmosphere are exposed to varying relative humidity. To complement the bulk experiments, we investigated single particles consisting of ammonium sulfate and dicarboxylic acids as well as of ammonium sulfate and PEG 400 in an electrodynamic balance. Whereas the relative humidities of total deliquescence as well as the water uptake and release of the fully deliquesced particles are in good agreement with the bulk results and represent thermodynamic equilibrium, the water uptake before full deliquescence shows significant deviations. These deviations may be caused by morphological effects.

1. Introduction

Organic species constitute an important fraction of the tropospheric aerosol.[1] Moreover, an increasing number of single-particle measurements[2−5] as well as theoretical considerations[6] show that organic and inorganic constituents are internally mixed within aerosol particles. Therefore, the mutual influence of the organic and inorganic aerosol fractions on each other alter the volatility, solubility and water uptake of the components in the mixture, thus changing the total amount of particulate matter as well as its phases and water content. A correct description of multicomponent aerosols is therefore needed to determine the amount of light they scatter, their cloud nucleating ability and their reactivity.

To date, organic/electrolyte interactions of the aerosol constituents are lacking in thermodynamic models,[7−9] mainly because the experimental data for a reliable parametrization are missing. Most laboratory studies so far concentrated on the water uptake and release of dicarboxylic acid/inorganic salt mixtures.[10−16] Few have investigated the hygroscopicity of mixed particles containing other substance classes such as alkanes and surfactants,[17,18] polyols[12,19] or fulvic and humic acids.[20,21] These studies showed that the water uptake of the mixed systems can usually be well estimated assuming that each component contributes independently to the total water content[10,12,15,22,23] and that for organic mole fractions up to 0.6 the deliquescence relative humidity of ammonium sulfate (AS) remains within 10% of the RH of pure AS for the investigated systems.[14,16,19]

In a part of these studies, the organic model compound exhibited a low aqueous solubility and was present as a solid up to high relative humidity. In ambient aerosols, however, the organic matter is expected to be predominantly present in the form of liquid or amorphous phases.[24] Therefore, realistic model systems for tropospheric aerosols should contain a liquid or amorphous organic phase down to low relative humidities. This condition is for example fulfilled for humic and fulvic acids that show a continuous water uptake and release in electrodynamic balance[20] and HTDMA experiments.[21] The organic matter therefore constitutes an absorptive medium in which gaseous species and inorganic ions may dissolve. In the case of repulsive interactions between components, semivolatile species partition more strongly to the gas phase. Moreover, phase separations into a predominantly organic and an aqueous phase may occur. In this case, a too low aerosol yield would be expected if the phases were not described correctly. Such effects have been found by Erdakos and Pankow[25] for purely organic systems. The addition of a salt influences the activity of the organic phase components and water, altering their miscibility and their equilibrium composition in the vapor phase. These changes of phase equilibria due to the addition of salts are known as salt effects: components with increased equilibrium vapor composition are said to be "salted out" whereas the other components are said to be "salted in". Such effects have been investigated in detail to optimize distillation for systems of industrial interest.[26,27]

In this study, we investigate the salt effects of ammonium sulfate, nitrate and sodium chloride on dicarboxylic acids and polyols. The carboxylic acid and hydroxyl groups represent two

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of the most important functional groups in the organic aerosol. Mono- and dicarboxylic acids as well as polyols together with polyethers have been identified by HNMR as main classes of the water-soluble organic fraction.[28,29] Dicarboxylic acids are common aerosol constituents throughout the atmosphere;[30−32] different individual polyols and carbohydrates have been identified in biomass burning samples.[33−35]

We present water activities and solubilities of model bulk mixtures at thermodynamic equilibrium. We chose polyols with different OH/CH$_n$ ($n = 0-3$) ratios (namely, glycerol, 1,4-butanediol, and 1,2-hexanediol) as well as PEG 400 to represent the organic fraction in bulk measurements and compare the results with literature data of simple alcohols and mono- and dicarboxylic acids. On the basis of these findings, general trends for organic/electrolyte interactions in aerosols are formulated assuming thermodynamic equilibrium. To estimate how well the condition of thermodynamic equilibrium is fulfilled for aerosol particles, we investigate levitated particles during humidity cycles in an electrodynamic balance. These single particle experiments are limited to organic model substances with low or no vapor pressures, namely a mixture of five dicarboxylic acids and PEG 400.

2. Experimental Methods

The water activities, a_w, were measured using an AquaLab water activity meter (Model 3TE, Decagon Devices, U.S.A.). This instrument allows us to perform measurements in the temperature range from 16 to 40 °C. For most measurements, the volatile sample block available as an accessory to the instrument was used. With this sample block, the water activity in the presence of other semivolatile components can be determined. Experimental errors for the volatile sample block are $\pm 0.015\ a_w$. To correct for instrument drifts and offset, the performance of the sample block was frequently controlled and readjusted with reference samples. Dilute ammonium sulfate/PEG 400/water and PEG 400/water mixtures were measured with the standard sample block, for which an accuracy of $\pm 0.003\ a_w$ is specified by the manufacturer. All measurements were performed at 298 ± 1 K unless stated otherwise. The operating principle of this instrument is described in more detail in ref 36.

Saturated aqueous solutions were prepared by adding small portions of material until the solutions were saturated. Between additions, the mixtures were allowed to equilibrate in a thermostated water bath at 25.0 ± 0.1 °C. This procedure led to an estimated error in the saturation solubility of $\pm 0.1-0.3$ wt %. The substances were purchased from Sigma-Aldrich. We used analytical grade reagents with purities of 99% or higher with the exception of methylsuccinic acid and 1,2-hexanediol with purities of $\geq 97\%$. The substances were used without further purification. The solutions were prepared by mass percent with MilliQ water using an analytical balance. The compositions of the electrolyte/polyol/water mixtures were corrected to include the water which was present in the compounds as purchased as described in ref 36.

The electrodynamic balance[37] used in our experiments is described in detail elsewhere.[38,39] An electrically charged particle (typically $2-20\ \mu$m in diameter) is balanced in an electrodynamic trap. The balance is hosted within a three wall glass chamber with a cooling agent flowing between the inner walls and an insulation vacuum between the outer walls. A constant flow (typically 30 sccm (standard cubic centimeters per minute)) of a N_2/H_2O mixture with a controlled H_2O partial pressure is pumped continuously through the chamber at a constant total pressure adjustable between 200 and 1000 mbar. During an experiment, the temperature is kept constant and the relative humidity within the chamber is increased or decreased continuously by changing the N_2/H_2O ratio, using automatic mass flow controllers. The relative humidity is registered by a capacitive thin film relative humidity sensor (MiniCap 2, Panametrics, U.S.A.) that is mounted in close vicinity of the levitated particle (<10 mm). The sensor was calibrated directly in the trap using the deliquescence relative humidity of different salts. Its accuracy is ±1.5% RH between 10 and 90% RH. A single-particle generator (Hewlett-Packard 51633A ink jet cartridge) is used to inject a liquid particle.

The mass of the particle is calculated from the dc voltage compensating the gravitational force, which is adjusted by an automatic feedback loop using a near field video image of the particle on a CCD sensor. A change in dc voltage is therefore a direct measurement for the particle's mass change. Also, the two-dimensional angular scattering pattern is recorded with a second CCD sensor by measuring the elastically scattered light over observation angles ranging from 78° to 101°. If the particle is liquid and therefore of spherical shape, the mean distance between fringes can be used to calculate the radius of the particle. If a liquid-to-solid transition occurs, the fringe pattern loses its regular periodic structure and becomes totally irregular. Additionally, information about particle shape and morphology is deduced from measurements of the intensity fluctuations of the laser light scattered in 90°: Because of its symmetry, a homogeneous spherical particle will show a constant scattering intensity and hence a very small fluctuation amplitude. A nonspherical particle will scatter light with different intensity in the detection angle depending on its orientation relative to the incoming laser beam.[40] All experiments in the electrodynamic balance were performed at 290 ± 0.5 K.

3. Results and Discussion

3.1. Solubilities and Deliquescence Relative Humidities of Ammonium Sulfate, Ammonium Nitrate and Sodium Chloride in Polyol/Water Mixtures. The investigated polyols and PEG 400 are all in liquid state at room temperature and miscible at any molar ratio with water. In the series glycerol, 1,4-butanediol, and 1,2-hexanediol the ratio of OH/CH$_n$ ($n = 0-3$) and the polarity decreases. The water uptake of these substances as a function of relative humidity has been described by Marcolli and Peter.[36] With an average molecular weight of 400, PEG 400 represents oligomeric or polymeric nonvolatile material, whereas the investigated polyols are semivolatile molecules.

In electrolyte/organic/water mixtures, the organic component can be viewed as a solvent or as a solute. If it is a crystalline solid at the measurement temperature, it is more appropriately viewed as a solute; if it is a liquid, it is rather considered as a solvent or an antisolvent, depending on whether it increases or decreases the solubility of the electrolyte in the medium. Because, in tropospheric aerosols, the organic particulate matter is expected to be predominantly present in liquid form, we discuss the organic substances in terms of solvents/antisolvents even if they are present as crystalline solids in our experiments.

Figure 1 shows the saturation concentration in terms of moles per kilogram of water and the water activity at saturation of sodium chloride for the investigated NaCl/polyol/water systems. At 25 °C, pure NaCl deliquesces at a relative humidity of 75.3%, corresponding to a water activity $a_w = 0.753$. Above this value, crystalline NaCl is not stable. In the ternary system, NaCl may dissolve to a certain degree in the polyol/water mixture at relative humidities well below the deliquescence relative humid-

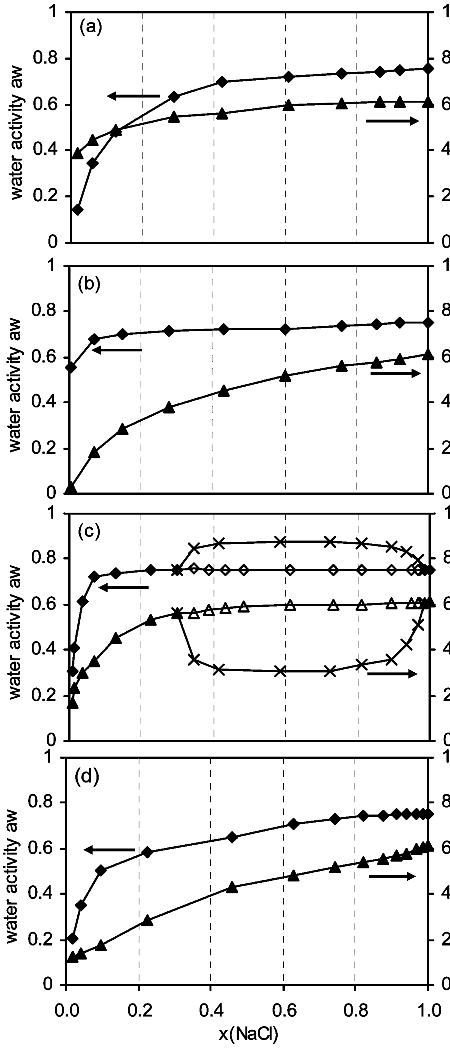

Figure 1. Solubility in terms of moles per kilogram of water (triangles; right scale), and water activity at saturation (diamonds; left scale) of NaCl for (a) NaCl/glycerol/water, (b) NaCl/1,4-butanediol/water, (c) NaCl/1,2-hexanediol/water, and (d) NaCl/PEG 400/water systems as a function of x(NaCl), the NaCl mole fraction of the dry mixture. Key: filled symbols, one liquid phase; open symbols, two liquid phases; crosses, two-liquid-phase/one-liquid-phase boundary. The lines are guides to the eye only.

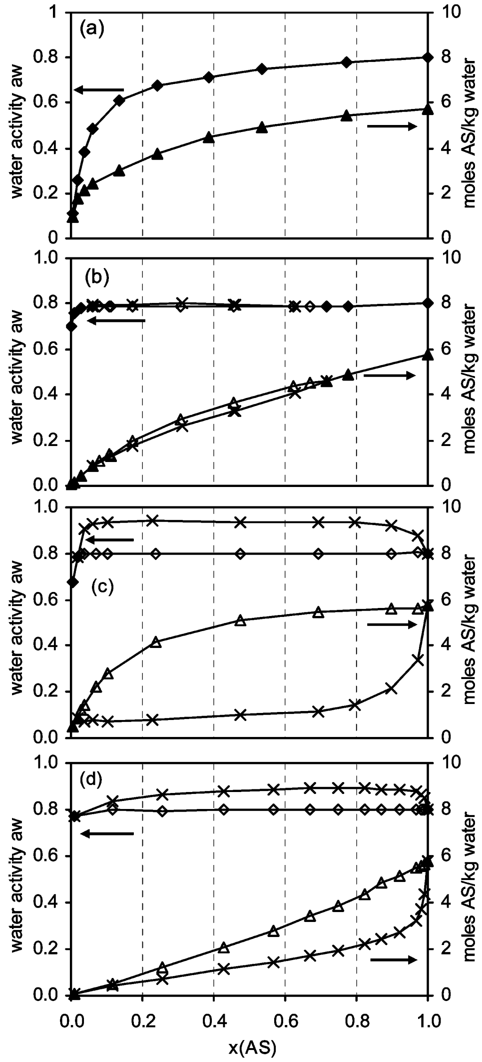

Figure 2. Solubility in terms of moles per kilogram of water (triangles; right scale), and water activity at saturation (diamonds; left scale) of AS for (a) AS/glycerol/water, (b) AS/1,4-butanediol/water, (c) AS/1,2-hexanediol/water, and (d) AS/PEG 400/water systems as a function of x(AS), the AS mole fraction of the dry mixture. Key: filled symbols, one liquid phase; open symbols, two liquid phases; crosses, two-liquid-phase/one-liquid-phase boundary.

ity (DRH) of pure sodium chloride and also reach the endpoint of dissolution at a lower relative humidity. In the following we refer to this point as the total deliquescence relative humidity (DRH*) as done previously by Parsons et al.[19] and Clegg et al.[7] For a NaCl mole fraction of 0.3, the DRH* is reduced to 63%, 72%, and 60%, in the presence of glycerol, 1,4-butanediol, and PEG 400, respectively. It is not reduced in the presence of 1,2-hexanediol. This indicates that the depression of the DRH* increases with increasing OH/CH$_n$ ratio of the polyol. Moreover, Figure 1 shows that all investigated polyols act as antisolvents for NaCl and decrease the salt's solubility per kilogram of water. At low NaCl mole fractions, this effect is weakest for glycerol and strongest for 1,4-butanediol. For NaCl/1,2-hexanediol mixtures with $x(\text{NaCl}) = 0.3-0.97$, two liquid phases form at the DRH*. At this relative humidity, both phases are saturated with respect to the salt. When more water is added to the system, the water activity, which is the same in both phases, increases. Depending on the exact composition, the two-phase region covers a water activity range from $a_w = 0.749-0.875$, the lower limit almost matching the deliquescence relative humidity of pure NaCl. At the upper limit, indicated by the crosses in Figure 1c, the two liquid phases merge into one.

At 25 °C, the concentration of a saturated aqueous solution of ammonium sulfate (AS) is 5.8 mol/kg of water, its water activity $a_w = 0.802$.[24] Figure 2 shows that the presence of the polyols strongly decreases the solubility of AS with respect to water, indicating that the polyols act as antisolvents for AS. For AS/glycerol mixtures with an AS mole fraction of 0.4, the DRH* is reduced to 72%, closely matching the result obtained by Parsons et al.[19] for the same system. In the presence of all other investigated polyols, the DRH* is reduced by less than 2%. In the presence of 1,4-butanediol, 1,2-hexanediol, and PEG 400 two liquid phases form at the DRH* over a wide range of AS/polyol ratios. The phase separation spans a water activity range from $a_w = 0.786-0.801$ for 1,4-butanediol, $a_w = 0.798-0.940$ for 1,2-hexanediol, and $a_w = 0.795-0.892$ for PEG 400. Thus AS acts as a very effective salting-out agent for the investigated polyol/water mixtures.

Being the most water-soluble one of the investigated salts, ammonium nitrate (AN) deliquesces at 62.1% RH at 25 °C.[24] Figure 3 shows how the presence of the polyols influences the

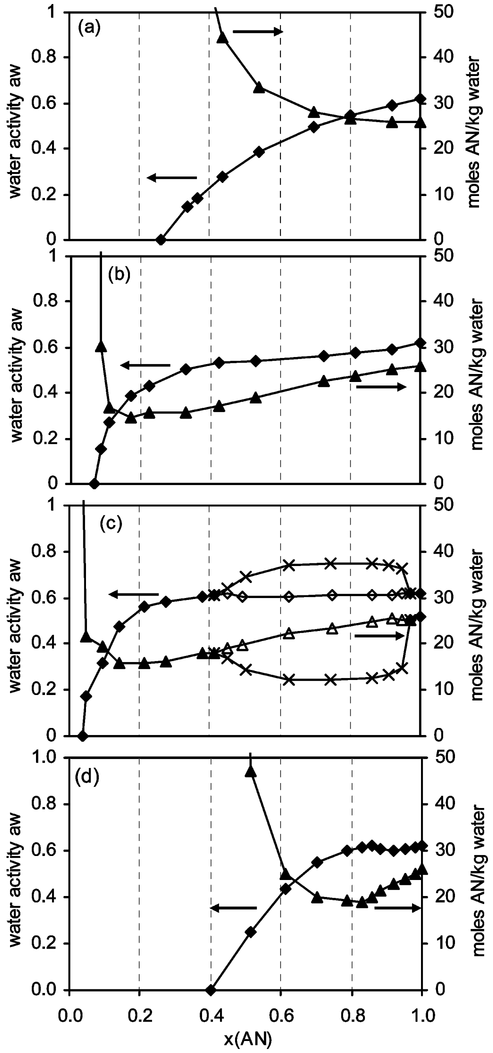

Figure 3. Solubility in terms of moles per kilogram of water (triangles; right scale), and water activity at saturation (diamonds; left scale) of AN for (a) AN/glycerol/water, (b) AN/1,4-butanediol/water, (c) AN/1,2-hexanediol/water, and (d) AN/PEG 400/water systems as a function of x(AN), the AN mole fraction of the dry mixture. Key: filled symbols, one liquid phase; open symbols, two liquid phases; crosses, two-liquid-phase/one-liquid-phase boundary.

solubility and DRH* of AN: the aqueous solubility reaches infinity at high polyol concentrations, indicating that it is soluble in the pure polyols. On the other hand, the aqueous solubility is reduced for medium AN/polyol mixing ratios. Moreover, two liquid phases form at the DRH* for certain AN/1,2-hexanediol/water mixtures, in accordance with a salting-out effect of AN for 1,2-hexanediol.

Table 1 summarizes the organic/electrolyte interactions for the systems investigated in this and a previous study.[24] Organic substances are denoted as antisolvents if the aqueous solubility of the electrolyte is reduced in their presence and as solvents if it is increased. The tendency of an organic substance to reduce the aqueous solubility of an electrolyte comes along with a salting-out effect of the electrolyte for the corresponding organic substance. As a result of this mutual repulsion, vapor pressures are increased, solubilities are decreased, and phase separations may occur. On the basis of Table 1 and the results from Figures 1-3, one can see that the presence of the polyols decreases the aqueous solubility of AS and NaCl. This effect is most pronounced for polyols of medium hydrophilicity that are still well miscible with water but hardly dissolve the salts. Literature data show that the solubility of NaCl in monofunctional alcohols decreases with decreasing OH/CH$_n$ (n = 0−3) ratios: the solubility of NaCl in water is 26.5 wt %, but only 1.38 wt % in anhydrous methanol and 0.065 wt % in absolute ethanol, and further decreases for longer chain alcohols.[41] Liquid−liquid equilibria measurements showed that the ternary mixtures NaCl/n-propanol/water and NaCl/2-propanol/water—both with OH/CH$_n$ ratios of the alcohols of 1:3—exhibit a miscibility gap whereas the binary systems without the salt are completely miscible.[42,43] This behavior corresponds with the one of the NaCl/1,2-hexanediol/water system where the polyol also exhibits a OH/CH$_n$ ratio of 1:3. A reduced aqueous solubility of AS in the presence of the alcohol and a miscibility gap has also been observed for the system AS/2-propanol/water.[44] One can therefore conclude that AS and NaCl in general act as salting-out agents for alcohols and that the ability of alcohols to dissolve AS and NaCl depends on the OH/CH$_n$ ratio.

The dicarboxylic acids (DCA) mixture M5 acts as an antisolvent for NaCl and as a solvent for AS. At the eutonic composition of M5 with AS, the solubilities of the more acidic and hydrophilic DCA (i.e., malic, malonic and maleic acid) are increased compared with the purely organic system M5, the ones of the more hydrophobic and less acidic glutaric and methylsuccinic acids are decreased.[24] AS can therefore be considered a salting-in agent for malic, malonic and maleic acid, and a salting-out agent for glutaric and methylsuccinic acid, as listed in Table 1. The exact saturation concentrations of the individual dicarboxylic acids in the presence and absence of AS, AN, and NaCl are given in Table 2 of Marcolli et al.[24] Considering the pK_a values of the more acidic dicarboxylic acids, the enhanced solubility of AS in the presence of these substances might be at least partly due to an acid/base reaction leading to the bisulfate ion (pK_a = 1.99) and the dissociated dicarboxylic acid. On the basis of the first pK_a values of malic (3.40), malonic (2.83) and maleic acids (1.83), this effect should be strongest for maleic acid with a solubility increase of 145%, followed by malonic (15%) and malic acids (4%). The measured solubility increases for maleic, malonic, and malic acids of 64%, 43%, and 15%, respectively, indicate that the increase observed for maleic acid is driven by the dissociation reaction whereas for malonic and malic acid attractive interactions between the undissociated acid and the electrolyte also seem to be important. Literature data indicate that carboxylic acids are generally salted out by sulfates and chlorides: the relative volatility of acetic acid is increased in aqueous ternary systems containing sodium or potassium sulfates.[45] Similarly, all of the studied chlorides—including sodium, potassium, and ammonium chloride—were found to have a salting-out effect for acetic and propionic acids.[45−48] A salting-in effect of AS might therefore be restricted to the most hydrophilic and/or acidic organic acids, such as short-chain dicarboxylic acids.

AN is soluble in the investigated polyols with solubilities at 25 °C of 23.2, 5.9, 2.7, and 11.8 wt % in glycerol, 1,4-butanediol, 1,2-hexanediol, and PEG 400, respectively. Likewise, it is soluble in anhydrous methanol with 14.6 wt % and in absolute ethanol with 3.7 wt % at 20.5 °C.[49] On the other hand, the systems AN/ethanol/water and AN/2-propanol/water separate into two liquid phases at temperatures above 65.7 °C and at room temperature, respectively.[50,51] This behavior is in good correspondence with the one of the AN/1,2-hexanediol/water and AN/1,4-butanediol/water systems investigated in this study. One possible explanation for this combination of salting-in and salting-out properties is that AN forms contact ion pairs in anhydrous solutions whereas it completely dissociates into NH_4^+ and NO_3^- in rather dilute aqueous media. In this case,

TABLE 1: Organic/Electrolyte Interactions in Mixed Systems[a]

	NaCl	AS	AN
glycerol	antisolvent	antisolvent	solvent
1,4-butanediol	antisolvent	antisolvent/phase separation	solvent
1,2-hexanediol	antisolvent/phase separation	antisolvent/phase separation	solvent/phase separation
PEG 400	antisolvent	antisolvent/phase separation	solvent
dicarboxylic acids	antisolvent	solvent	solvent
malic acid	salting-in	salting-in	salting-in
malonic acid	salting-in	salting-in	salting-in
maleic acid	no effect	salting-in	salting-in
glutaric acid	salting-out	salting-out	salting-out
methylsuccinic acid	salting-out	salting-out	salting-out

[a] Organic substances are denoted as antisolvents when they decrease the aqueous solubility of the electrolyte and as solvents when they increase it. Dicarboxylic acids are salted-out/salted-in when their aqueous solubility is decreased/increased.

TABLE 2: Composition and Water Activity of the NaCl/Polyol/Water Mixtures Shown in Figures 1 and 4

composition of aqueous solutions (mol/kg of water)						composition of aqueous solutions (mol/kg of water)					
NaCl	glycerol	1,4-butanediol	1,2-hexanediol	PEG 400	a_w	NaCl	glycerol	1,4-butanediol	1,2-hexanediol	PEG 400	a_w
3.85^{a}	227.76				0.146	5.62^{b}			10.63		0.756
4.45^{a}	66.51				0.345	5.78^{b}			9.16		0.752
4.93^{a}	34.52				0.482	5.83^{b}			7.56		0.750
5.45^{a}	13.51				0.632	5.88^{b}			6.30		0.749
5.63^{a}	7.72				0.696	5.98^{b}			3.79		0.749
5.94^{a}	3.81				0.717	6.01^{b}			2.19		0.753
6.05^{a}	1.95				0.731	6.02^{b}			1.38		0.752
6.09^{a}	0.95				0.743	6.04^{b}			0.73		0.755
6.09^{a}	0.51				0.750	6.07^{b}			0.33		0.753
5.21^{d}	3.29				0.750	6.06^{b}			0.21		0.754
4.25^{d}	2.69				0.802	6.09^{a}			0.10		0.753
3.32^{d}	2.1				0.845	3.56^{c}			6.73		0.847
2.44^{d}	1.54				0.894	3.15^{c}			4.47		0.869
1.73^{d}	1.10				0.932	3.05^{c}			2.14		0.873
1.29^{d}	0.81				0.952	3.05^{c}			1.15		0.875
0.74^{d}	0.47				0.974	3.32^{c}			0.77		0.870
0.31^{a}		54.09			0.557	3.60^{c}			0.44		0.857
1.83^{a}		25.17			0.681	4.20^{c}			0.28		0.833
2.87^{a}		16.29			0.700	5.09^{c}			0.18		0.796
3.76^{a}		9.81			0.715	5.39^{e}			2.64		0.783
4.56^{a}		5.98			0.722	4.58^{e}			2.24		0.819
5.18^{a}		3.41			0.726	3.75^{e}			1.84		0.854
5.63^{a}		1.80			0.736	3.02^{d}			1.48		0.888
5.79^{a}		0.96			0.744	2.28^{d}			1.12		0.921
5.93^{a}		0.50			0.750	1.64^{d}			0.81		0.942
4.61^{d}		2.99			0.762	0.95^{d}			0.46		0.966
3.83^{d}		2.48			0.807	1.22^{a}				71.33^{f}	0.207
3.07^{d}		1.99			0.847	1.41^{a}				33.75^{f}	0.350
2.23^{d}		1.45			0.898	1.72^{a}				15.96^{f}	0.504
1.64^{d}		1.06			0.933	2.86^{a}				9.81^{f}	0.583
1.23^{d}		0.79			0.952	4.32^{a}				5.06^{f}	0.649
0.71^{d}		0.46			0.973	4.83^{a}				2.84^{f}	0.706
1.68^{a}			240.63		0.310	5.18^{a}				1.77^{f}	0.729
2.31^{a}			172.95		0.408	5.40^{a}				1.18^{f}	0.742
3.00^{a}			74.27		0.613	5.57^{a}				0.80^{f}	0.747
3.47^{a}			45.97		0.721	5.67^{a}				0.53^{f}	0.751
4.56^{a}			31.27		0.737	5.80^{a}				0.37^{f}	0.752
5.31^{a}			18.28		0.750	5.95^{a}				0.21^{f}	0.753
5.65^{a}			13.27		0.751	6.04^{a}				0.09^{f}	0.754

[a] At saturation in one-phase system. [b] At saturation in two-phase system. [c] Concentration at end point of two-phase system. [d] Undersaturated, one-phase system. [e] Undersaturated, two-phase system. [f] Assuming a molecular weight of 400 for PEG 400.

water is a good solvent for the ions, whereas the alcohols may only act as solvents for the contact ion pairs. On the basis of an infrared spectroscopic investigation, the formation of contact ion pairs has recently indeed been postulated for liquid AN particles at a relative humidity of 1%.[52] A large number of nitrates are appreciably soluble in acetic acid: thus AN exhibits a solubility of 39.08 wt % at 21.4 °C in anhydrous acetic acid.[53] Cryoscopic studies indicate that AN associates into at least binary ion pairs in anhydrous acetic acid.[54] These findings indicate that the good solubility of AN in organic solvents might in general be due to the formation of contact ion pairs.

3.2. Water Uptake of Bulk Samples. Water uptake curves for electrolyte/polyol mixtures with mixing ratios of 1:1 in terms of weight percent are shown as a function of relative humidity in Figures 4−6. The data shown in these figures as well as the ones from Figures 1−3 are listed in Tables 2−4. The data points below total deliquescence in Figures 4−6 were constructed from the measured water activities and solubilities shown in Figures 1−3 assuming that the undissolved salt does not contribute to the water uptake. The data points above total deliquescence were determined from water activity measurements of subsaturated solutions. Because the investigated polyols are hygroscopic

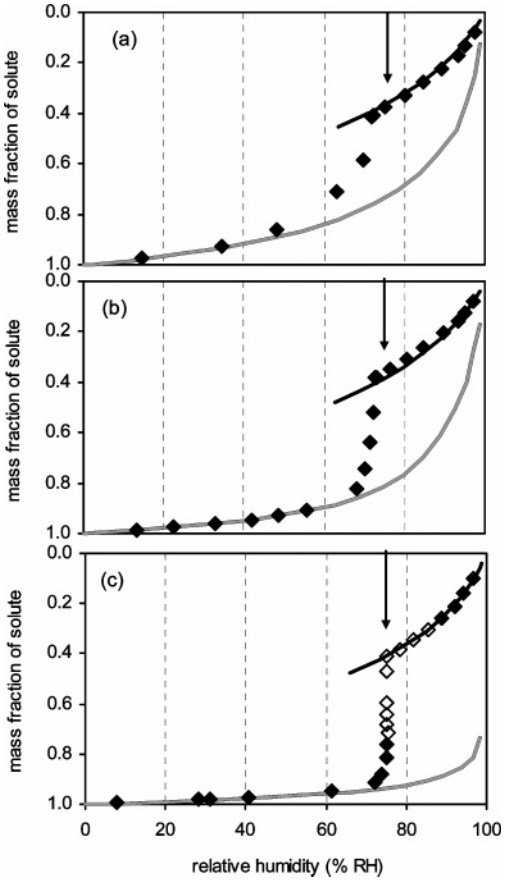

Figure 4. Water uptake curves based on bulk measurements (diamonds) and ZSR predictions (bold black line) for (a) NaCl/glycerol, (b) NaCl/1,4-butanediol, and (c) NaCl/1,2-hexanediol mixtures with mixing ratios of 1:1 in terms of weight percent. Key: arrows, DRH of pure NaCl; filled symbols, one liquid phase; open symbols, two liquid phases; gray lines, water uptake of the polyols assuming that NaCl is present as an inert mass.

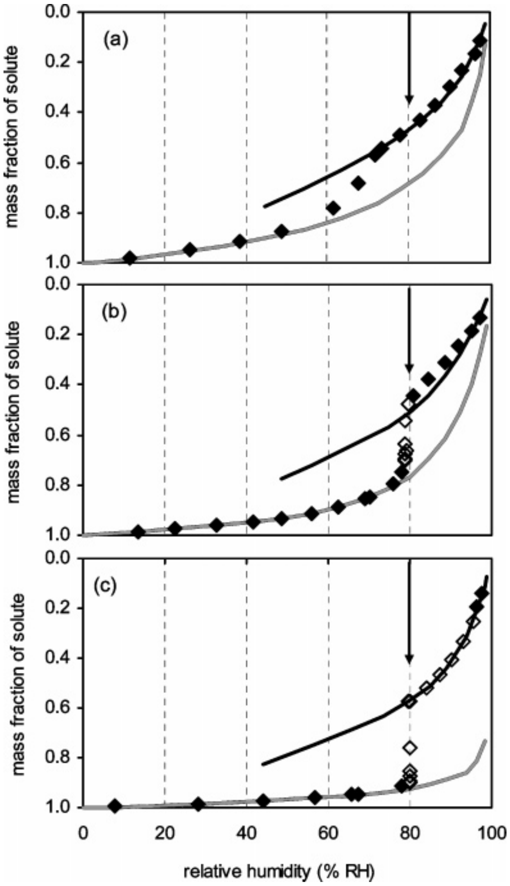

Figure 5. Water uptake curves based on bulk measurements (diamonds) and ZSR predictions (bold black line) for (a) AS/glycerol, (b) AS/1,4-butanediol, and (c) AS/1,2-hexanediol mixtures with mixing ratios of 1:1 in terms of weight percent. Key: arrows, DRH of pure AS; filled symbols, one liquid phase; open symbols, two liquid phases; gray lines, water uptake of the polyols assuming that AS is present as an inert mass.

liquids at 25 °C, they take up water continuously at any relative humidity. The gray lines in Figures 4−6 represent the water uptake of the polyols assuming that the salts are present as inert masses that are not hygroscopic. It can be seen that the water uptake at very low relative humidity is in good agreement with this assumption for all investigated mixtures. With 1,2-hexanediol as the organic component, the water uptake follows the gray line almost up to total deliquescence. We attribute a water uptake that exceeds the one of the organic component to the fraction of inorganic salt that is dissolved in the polyol/water mixtures. This fraction increases with increasing relative humidity and increasing water content. It is highest for the mixtures with glycerol and almost negligible for the ones with 1,2-hexanediol. In Figures 4−6, the deliquescence relative humidities of the pure salts are indicated by the black arrows. It can be seen that a large water uptake of the mixtures below total deliquescence goes along with a strong depression of the DRH*. This is most pronounced for the AN/glycerol system, which exhibits an almost continuous water uptake with no visible deliquescence step. On the other hand, for AS/1,2-hexanediol, the water uptake below total deliquescence is low and the DRH* corresponds exactly with the one of pure AS. This behavior is in accordance with the fact that 1,2-hexanediol is a strong antisolvent for AS and that two separate liquid phases are present at the DRH*.

The Zdanovskii−Stokes−Robinson (ZSR) approach[55] is based on the assumption that every substance in a mixture interacts with water independently. Using the single solute data of the components, we calculated the water uptake on the basis of the ZSR model for the electrolyte/polyol mixtures assuming completely liquid particles. It can be seen from Figures 4−6 that this approach is in good agreement for mixtures with glycerol and 1,2-hexanediol. A deviation between measurement and ZSR prediction is observed for the electrolyte/1,4-butanediol mixtures above the DRH*: for the mixtures with AN and AS the water uptake is ca. 5% higher than predicted. This means that water is bound more strongly by the mixture than by the individual components. The excellent agreement for the mixtures with 1,2-hexanediol is not astonishing because the organic substance and the electrolyte form two separate liquid phases that indeed interact with water independently.

Measurements of bulk samples can be directly applied to describe properties of aerosol particles that reflect thermodynamic equilibrium such as the water uptake and release of liquid aerosol particles in the accumulation and coarse mode. However, if properties such as the crystallization tendency and morphological effects of aerosol particles are concerned, conclusions based on bulk experiments are of limited use to predict the behavior of aerosol particles. We therefore complement the bulk measurements with the investigation of single particles levitated in an electrodynamic balance.

3.3. Single Particle Measurements in the Electrodynamic Balance.

Mixtures of Dicarboxylic Acids and Ammonium Sulfate. Micrometer sized particles tend to stay liquid up to high supersaturations and are less likely to crystallize than a bulk

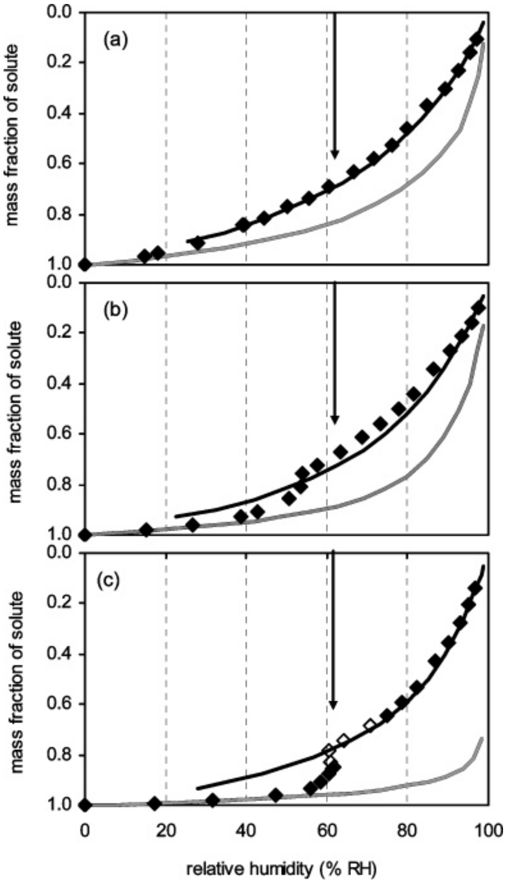

Figure 6. Water uptake curves based on bulk measurements (diamonds) and ZSR predictions (bold black line) for (a) AN/glycerol, (b) AN/1,4-butanediol, and (c) AN/1,2-hexanediol mixtures with mixing ratios of 1:1 in terms of weight percent. Key: arrows, DRH of pure AN; filled symbols, one liquid phase; open symbols, two liquid phases; gray lines, water uptake of the polyols assuming that AN is present as an inert mass.

sample of the same composition. In an atmosphere of increasing relative humidity, they are expected to take up water along the thermodynamic equilibrium curve. When exposed to decreasing relative humidity, liquid particles release water continuously until they crystallize. Micrometer sized particles consisting of one pure substance, undergo a sharp deliquescence at a relative humidity that matches well the water activity of the saturated bulk solution.[13,39,56] The height of the deliquescence step corresponds with the concentration of the saturated solution. Colberg et al.[39] have shown for single levitated NH_4HSO_4/H_2O aerosol particles that the morphology influences the deliquescence relative humidity: when a liquid is left after the crystallization of $(NH_4)_3H(SO_4)_2$, the particle's hygroscopicity depends on whether the liquid is shielded from the atmosphere by a surrounding shell or not. Such effects are not restricted to inorganic systems: Choi and Chan[12] investigated single levitated aerosol particles consisting of NaCl/glycerol and AS/glycerol mixtures. Although glycerol is a hygroscopic liquid, they did not observe any water uptake for effloresced particles at relative humidities below DRH*. They therefore suspected that a crystalline shell enclosed the liquid glycerol and prevented water uptake before deliquescence. Thus, for mixtures, the deliquescence and the efflorescence branch of the relative humidity cycle cannot be derived on the basis of bulk measurements alone. We therefore studied the water uptake and release of micrometer sized particles of mixtures of AS with DCA and with PEG 400 in an electrodynamic balance.

Figure 7 shows the relative humidity cycle of a single levitated particle consisting of the DCA mixture M5 with the composition given in Table 5. The relative abundance of the components corresponds to the one of the eutonic composition with a deliquescence relative humidity of 45.4%. The cycle started at 33% RH and the relative humidity was further reduced to 12% RH at an average rate of 0.4% RH/min. The water uptake proceeded at an average rate of 0.2% RH/min up to 92% RH followed by a relative humidity decrease at 0.3% RH/min down to 22% RH, thus closing the cycle. At these rates, a whole humidity cycle was completed within 12 h. Within these time scales no evaporation of the dicarboxylic acids was noted. However, when a particle of this composition was kept for several hours at low relative humidity, a continuous mass loss was observed. Partial evaporation of dicarboxylic acids and especially malonic acid has been observed by Choi and Chan[57] for single levitated particles. Because evaporation rates depend on the partial pressures of the dissolved dicarboxylic acids, they are higher at low relative humidity when the solution is more concentrated. Our own measurements of micrometer sized aqueous malonic acid particles in the electrodynamic balance gave evaporation rates of 4.5×10^{-7} μm/s for a particle with a radius of ~ 7 μm at 10% RH, and 3.3×10^{-9} μm/s for the particle with a radius of ~ 10 μm at 90% RH.[58] On the basis of the lack of a hysteresis between water uptake and release and the intensity fluctuation analysis (not shown), the particle remained liquid although it was exposed for 2 h to a relative humidity below 30%. Four of the five components of the mixture M5 have already been studied in an electrodynamic balance:[56,57] Malic and malonic acids were found to stay liquid at any relative humidity whereas maleic and glutaric acids effloresced at 48−51 and 28−30% RH, respectively. Crystallization of these two latter components was, however, suppressed in mixtures with malonic and malic acids. The absence of crystallization for M5 is therefore in agreement with crystallization suppression in dicarboxylic acid mixtures. The single-particle levitation experiments of the individual dicarboxylic acids by Choi and Chan[57] can be used for the prediction of the M5 water uptake based on the ZSR model.[24,55] It can be seen from Figure 7 that the ZSR prediction is in good agreement with our electrodynamic balance results and previous bulk measurements by Marcolli et al.[24]

We investigated two mixtures of M5 with AS in the electrodynamic balance, one with an organic-to-electrolyte ratio of 1:1 in terms of weight percent (M5AS1), the other one with a ratio of 1:4 (M5AS4). The exact compositions of the mixtures are given in Table 5. The relative abundance of the organic components corresponds with the one of the eutonic composition. In both samples, AS is present at a higher concentration than in the eutonic mixture, where it is at 15.4 wt %. According to bulk measurements[24] and assuming thermodynamic equilibrium, fully crystallized particles of compositions M5AS1 and M5AS4 start to deliquesce at 36.4% RH where all the DCA become liquid. AS gradually dissolves into the aqueous DCA solution until total deliquescence is reached at 73.3 and 78.3% RH, respectively.

Figure 8 shows the water uptake and release of M5AS1 for a faster and a slower relative humidity cycle. Please note that gas-phase diffusion does not limit the water uptake, as has been shown for inorganic salt particles.[40] The faster cycle started at 90% RH with decreasing relative humidity at an average rate of 0.4% RH/min down to 26% RH. In this cycle, an efflorescence step appeared at 28% RH. During the subsequent increase of RH at an average of 0.2% RH/min the water uptake

TABLE 3: Composition and Water Activity of the AS/Polyol/Water Mixtures Shown in Figures 2 and 5

composition of aqueous solutions (mol/kg of water)						composition of aqueous solutions (mol/kg of water)					
AS	glycerol	1,4-butanediol	1,2-hexanediol	PEG 400	a_w	AS	glycerol	1,4-butanediol	1,2-hexanediol	PEG 400	a_w
0.92^a	312.41				0.113	2.81^b			24.06		0.798
1.78^a	99.18				0.261	4.17^b			13.24		0.799
2.11^a	57.33				0.386	5.11^b			5.64		0.797
2.41^a	36.65				0.486	5.44^b			2.42		0.800
3.04^a	19.39				0.613	5.61^b			0.65		0.800
3.76^a	11.81				0.677	5.61^b			0.17		0.803
4.50^a	7.14				0.716	0.73^c			17.95		0.904
4.92^a	4.28				0.753	0.76^c			11.42		0.928
5.41^a	1.61				0.777	0.75^c			6.40		0.937
4.57^d	6.51				0.734	0.82^c			2.80		0.940
3.66^d	5.21				0.780	0.97^c			1.07		0.936
2.87^d	4.09				0.827	1.16^c			0.51		0.936
2.22^d	3.16				0.864	1.41^c			0.36		0.935
1.63^d	2.33				0.901	2.18^c			0.25		0.918
1.16^d	1.65				0.930	3.41^c			0.10		0.880
0.76^d	1.08				0.963	4.14^e			4.59		0.840
0.47^d	0.67				0.977	3.35^e			3.71		0.874
0.05^a		30.22			0.700	2.61^e			2.89		0.902
0.18^a		21.39			0.760	1.88^e			2.08		0.929
0.44^a		16.57			0.780	1.29^e			1.43		0.954
0.86^a		13.02			0.788	0.91^d			1.01		0.963
1.10^b		12.49			0.786	0.63^d			0.70		0.974
1.39^b		11.52			0.787	0.04^a				5.31^f	0.774
1.35^b		10.77			0.790	0.50^b				3.89^f	0.797
2.01^b		9.60			0.788	1.18^b				3.40^f	0.795
2.94^b		6.63			0.789	2.04^b				2.71^f	0.800
3.65^b		4.36			0.791	2.82^b				2.16^f	0.800
4.38^b		2.67			0.786	3.42^b				1.68^f	0.803
4.51^b		2.23			0.787	3.88^b				1.31^f	0.800
4.62^a		1.85			0.787	4.38^b				0.95^f	0.802
4.86^a		1.41			0.788	4.82^b				0.72^f	0.799
1.74^c		8.32			0.799	5.13^b				0.45^f	0.801
2.59^c		5.73			0.793	5.53^b				0.18^f	0.801
3.26^c		3.90			0.801	5.60^b				0.10^f	0.799
3.30^c		3.88			0.799	5.65^b				0.05^f	0.801
4.08^c		2.44			0.796	0.40^c				3.13^f	0.838
3.02^d		4.39			0.809	0.74^c				2.14^f	0.865
2.31^d		3.36			0.846	1.11^c				1.47^f	0.881
1.72^d		2.50			0.884	1.42^c				1.09^f	0.887
1.22^d		1.77			0.920	1.73^c				0.85^f	0.892
0.88^d		1.27			0.953	1.96^c				0.66^f	0.891
0.57^d		0.83			0.972	2.21^c				0.48^f	0.894
0.49^a			71.42		0.673	2.43^c				0.36^f	0.889
0.85^a			45.08		0.781	2.71^c				0.24^f	0.888
1.19^b			38.23		0.800	3.25^c				0.10^f	0.882
1.42^b			35.09		0.801	3.70^c				0.07^f	0.867
2.20^b			29.17		0.801	4.34^c				0.04^f	0.848

[a] At saturation in one-phase system. [b] At saturation in two-phase system. [c] Concentration at end point of two-phase system. [d] Undersaturated, one-phase system. [e] Undersaturated, two-phase system. [f] Assuming a molecular weight of 400 for PEG 400.

of the particle continuously increased and peaked at the DRH* at 75% RH. The second, slower RH cycle with average rates of 0.2 and 0.1% RH/min for decreasing and increasing relative humidity, respectively, directly followed the first one. During this second cycle, an efflorescence step occurred at 26% RH. Below 75% RH where total deliquescence was observed, the water uptake was lower than during the first cycle. Above 75% RH the water uptake and release of the first and second cycles agree.

For the mixture M5AS4 with a DCA/AS ratio of 1:4, we also performed two humidity cycles which are shown in Figure 9. The particle was injected into a dry atmosphere as a 5 wt % aqueous solution and crystallized completely. During the first deliquescence branch that we started at 41% RH and performed at an average rate of 0.2% RH/min, the water content of the particle rose by 6 wt % between 41 and 47% RH, followed by a first low but continuously increasing water uptake up to total deliquescence at 78% RH. During the subsequent decrease of RH down to 19% at an average rate of 0.4% RH/min, efflorescence occurred at 35% RH, followed by a further gradual water loss. The second deliquescence branch at an average rate of 0.2% RH/min differed in several respects from the first one: below 25% RH, the water content decreased slightly although RH was increased. The water uptake below full deliquescence at 78% RH fell behind the one of the first cycle and exhibited small deliquescence steps at 47, 61 and 63% RH. The efflorescence branch at an average rate of 0.2% RH/min showed again an efflorescence step at 35% RH.

For comparison, Figures 8 and 9 also show the water uptake curves based on bulk measurements and the ZSR prediction from single particle data of the pure components. The DRH* of the mixtures M5AS1 and M5AS4 at 75 and 78% RH are in fairly good agreement with the ones of the bulk measurements at 73.3 and 78.3% RH, respectively, proving that AS indeed underwent efflorescence and deliquescence in the mixed particles. We therefore assign the efflorescence steps at 26−28%

TABLE 4: Composition and Water Activity of the AN/Polyol/Water Mixtures Shown in Figures 3 and 6

composition of aqueous solutions (mol/kg of water)					
AN	glycerol	1,4-butanediol	1,2-hexanediol	PEG 400	a_w
81.21[a]	158.77				0.148
67.66[a]	118.65				0.180
44.53[a]	57.17				0.280
33.54[a]	28.8				0.389
27.96[a]	12.11				0.498
26.47[a]	6.49				0.550
25.99[a]	2.27				0.591
27.12[d]	23.48				0.444
21.24[d]	18.39				0.504
17.26[d]	14.95				0.554
13.85[d]	11.99				0.606
10.78[d]	9.33				0.666
8.53[d]	7.39				0.718
6.87[d]	5.95				0.761
5.40[d]	4.68				0.798
3.69[d]	3.19				0.847
2.70[d]	2.34				0.891
1.90[d]	1.64				0.924
1.18[d]	1.03				0.954
0.74[d]	0.64				0.971
30.34[a]		317.04			0.154
16.78[a]		135.60			0.267
14.56[a]		71.12			0.387
15.52[a]		54.30			0.430
15.78[a]		32.36			0.505
17.33[a]		23.41			0.536
19.09[a]		16.94			0.539
22.50[a]		8.52			0.559
23.56[a]		5.32			0.574
25.07[a]		2.19			0.589
16.11[d]		14.33			0.577
12.58[d]		11.20			0.634
9.94[d]		8.84			0.686
7.94[d]		7.06			0.733
6.30[d]		5.61			0.776
4.87[d]		4.33			0.814
3.25[d]		2.89			0.866
2.28[d]		2.03			0.907
1.70[d]		1.51			0.934
1.14[d]		1.02			0.957
0.70[d]		0.63			0.975
21.50[a]			439.78		0.174
19.27[a]			184.26		0.318
15.88[a]			95.19		0.474
15.75[a]			58.24		0.559
16.09[a]			42.73		0.586
17.98[a]			29.50		0.603
18.10[a]			25.56		0.615
19.10[b]			23.30		0.618
19.91[b]			20.63		0.607
22.29[b]			13.40		0.605
23.41[b]			7.89		0.608
24.69[b]			4.00		0.609
25.47[b]			2.24		0.611
25.32[b]			1.39		0.616
25.33[a]			0.71		0.617
17.06[c]			20.81		0.639
14.28[c]			14.27		0.692
12.28[c]			7.38		0.741
12.35[c]			4.20		0.749
12.57[c]			2.03		0.749
13.27[c]			1.29		0.742
14.69[c]			0.81		0.730
18.10[e]			12.15		0.644
13.59[e]			9.12		0.708
11.27[d]			7.56		0.751
9.13[d]			6.13		0.788
7.09[d]			4.76		0.823
4.74[d]			3.18		0.870
3.42[d]			2.30		0.903
2.42[d]			1.62		0.931
1.62[d]			1.09		0.952
0.98[d]			0.66		0.968
47.24[a]				44.90[f]	0.251
25.01[a]				15.85[f]	0.437
20.01[a]				8.55[f]	0.547
19.19[a]				5.13[f]	0.602
18.89[a]				3.80[f]	0.615
19.87[a]				3.28[f]	0.620
21.60[a]				2.85[f]	0.606
22.69[a]				1.95[f]	0.601
24.04[a]				1.14[f]	0.607
24.87[a]				0.48[f]	0.613

[a] At saturation in one-phase system. [b] At saturation in two-phase system. [c] Concentration at end point of two-phase system. [d] Undersaturated, one-phase system. [e] Undersaturated, two-phase system. [f] Assuming a molecular weight of 400 for PEG 400.

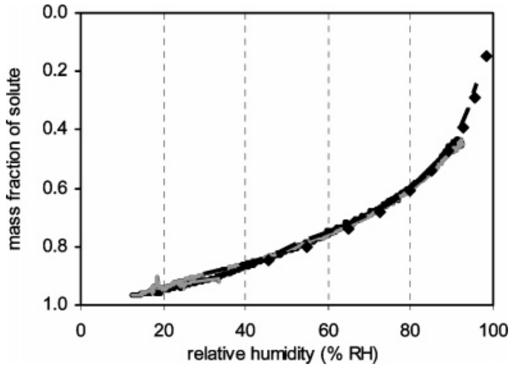

Figure 7. Water uptake and release of the mixture M5 (consisting of malic, malonic, maleic, glutaric, and methylsuccinic acid). Key: gray line, water release of the single levitated particle; black line: water uptake of the single levitated particle; dashed line, ZSR prediction; diamonds, bulk measurements.

TABLE 5: Composition of Mixtures for Electrodynamic Balance Experiments in Terms of wt %

	malic acid	malonic acid	maleic acid	glutaric acid	methylsuccinic acid	AS
M5	17	28	11	30	13	
M5AS1	9	18	8	11	4	50
M5AS4	3.4	7.4	3.5	4.1	1.6	80

RH for M5AS1 and at 35% RH for M5AS4 to AS crystallization. Pure micrometer sized AS particles have been observed to crystallize between 35 and 40% RH at 298 K.[19,59,60] Several authors have measured the crystallization relative humidity of AS particles internally mixed with different DCA. For a mole fraction ratio of 1:1, Parsons et al.[19] found a crystallization RH of 30% for AS/glutaric and no crystallization for AS/malic acid micrometer sized particles in an optical microscope. For mole fraction ratios of DCA/AS 1:4 the crystallization RH was at ∼34% for AS/glutaric and at ∼30% RH for AS/malic acid. Brooks et al.[14] measured in flow tube experiments a crystallization RH of around 30% for AS/maleic acid particles irrespective of the mixing ratio. The observed crystallization RH of 26−28% RH for M5AS1 (with an AS mole fraction of 0.47) and 35% RH for M5AS4 (with an AS mole fraction of 0.78) are in satisfactory agreement with the results of Parsons et al.[19] and Brooks et al.[14] Choi and Chan,[12] on the other hand, measured efflorescence relative humidities between 45 and 60% RH for AS/malonic acid and AS/glutaric acid 1:1 mixtures with an electrodynamic balance. This discrepancy might be due to

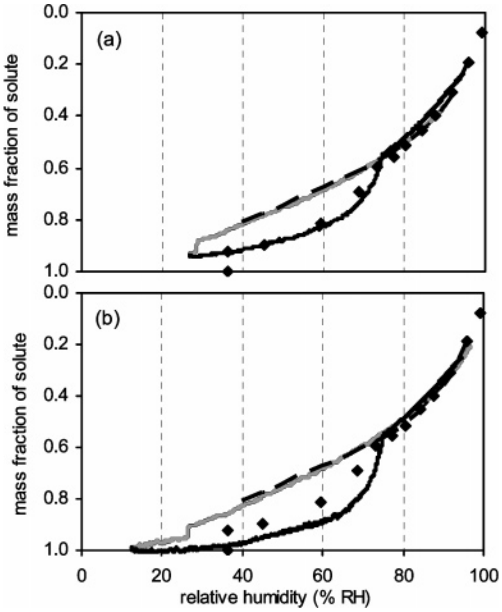

Figure 8. Water uptake and release of M5 and AS in a 50/50 wt % mixture: (a) fast cycle, (b) slow cycle. Key: black line, water uptake of the single levitated particle; gray line, water release of the single levitated particle; dashed line, ZSR prediction; diamonds, bulk measurements.

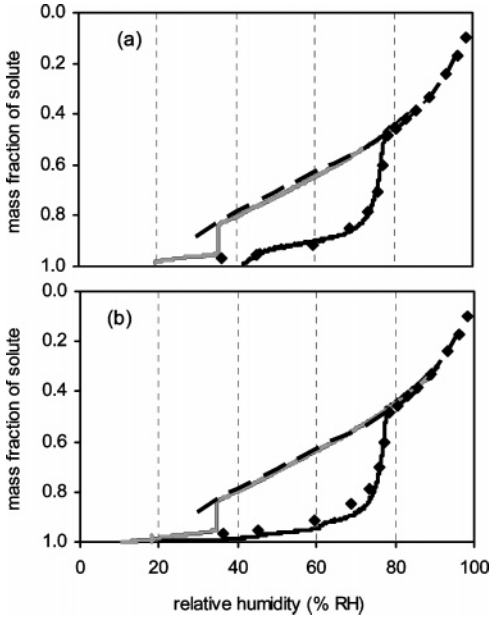

Figure 9. Water uptake and release of M5 and AS in a 20/80 wt % mixture: (a) fast cycle; (b) slow cycle. Key: black line, water uptake of the single levitated particle; gray line, water release of the single levitated particle; dashed line, ZSR prediction; diamonds, bulk measurements.

trace amounts of a contamination present in the Choi and Chan particles. Braban and Abbatt[61] in flow tube experiments and Prenni et al.[15] and Hämeri et al.[11] in HTDMA experiments observed much stronger or even complete crystallization suppression for AS/malonic acid particles, however, for considerably smaller particle sizes and shorter time scales.

Because the water content of the particles M5AS1 and M5AS4 still dropped continuously upon further reducing RH, we can infer that the particles crystallized only partly at the efflorescence step. When the relative humidity was increased again, M5AS1 showed no water uptake below 25% RH and M5AS4 even showed further water loss, indicating that at low RH at least a part of the DCA crystallized. Because no crystallization was observed for the mixture M5, this would imply that AS acts as a nucleus for DCA crystallization.

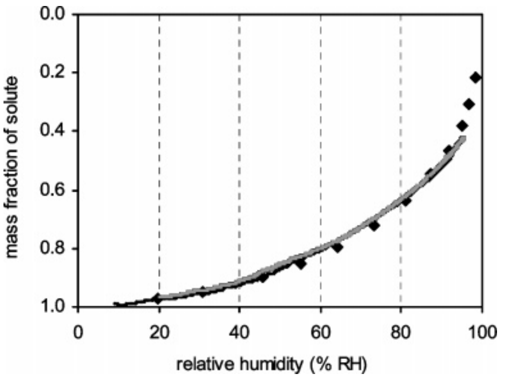

Figure 10. Water uptake and release of PEG 400. Key: black line, water uptake of the single levitated particle; gray line, water release of the single levitated particle; diamonds, bulk measurements, one liquid phase.

At RH above total deliquescence, the water uptake and release of the particles are in good agreement with the ones of the bulk samples given as diamonds in Figures 8 and 9. The water release of fully liquid particles is well described by the ZSR approach (dashed lines in Figures 8 and 9) based on single solute data from electrodynamic trap experiments.[56,57,62] Depending on the lowest RH that was reached during the preceding efflorescence branch, the water uptake of the particles below total deliquescence shows deviations from thermodynamic equilibrium: If the RH is decreased just below the efflorescence of AS so that the DCA most probably remain dissolved, as was the case for the first cycle of M5AS1, the water uptake follows quite well thermodynamic equilibrium. When the particles M5AS1 and M5AS4 are exposed to an RH below 30%, also the DCA seem to crystallize at least partly. In this case, a sharp deliquescence step is expected at 36.4% RH assuming thermodynamic equilibrium for the mixtures M5AS1 and M5AS4. Such a step is not observed during the second deliquescence branch. Instead, the water uptake remains below the one of the bulk samples and several small deliquescence steps well above the deliquescence relative humidity of the eutonic composition are observed. Interestingly, when the particle M5AS4 crystallized during injection, deliquescence started with a delay at 41% RH but then followed thermodynamic equilibrium much better than during the second cycle when the trapped particle effloresced in the electrodynamic balance. The rate of water loss, which is much higher during injection than during a humidity cycle, therefore seems to influence the morphology of the effloresced particle. We thus suspect that morphological differences are responsible for the varying water uptake before full deliquescence: the completely dried particles form a complex conglomerate of AS and DCA crystals. When these particles are exposed to an increasing relative humidity, the onset of deliquescence depends on the specific crystals confining the grain boundaries and veins rather than on the overall composition of the particles. If, e.g., crystals of AS, malic, and malonic acids are adjacent to each other in a vein of the particle, the deliquescence of this subsystem might occur without being influenced by the other components. The presence of a crystalline shell enclosing a remaining liquid can be excluded because the particles take up water over the whole relative humidity range.

Mixtures of PEG 400 and Ammonium Sulfate. PEG 400 is a liquid at room temperature and exhibits a continuously increasing water activity with increasing water content. Figure 10 shows

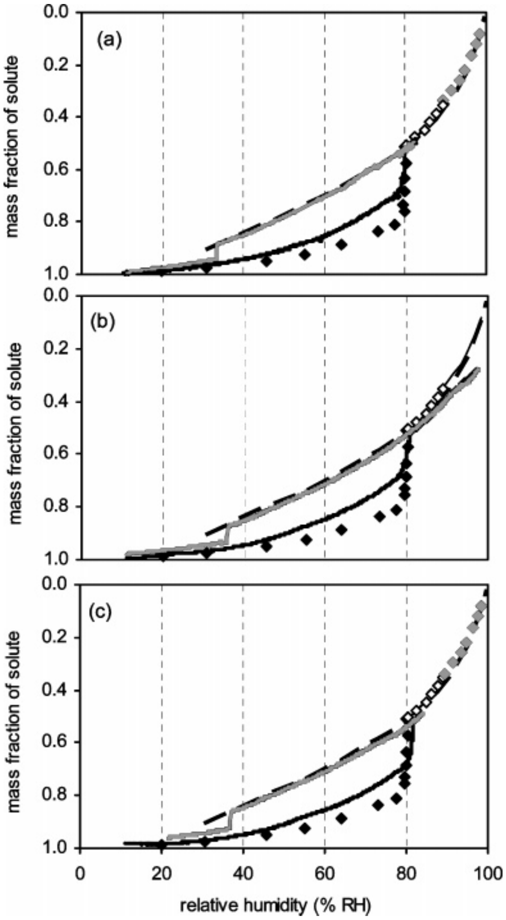

Figure 11. Water uptake and release of PEG 400 and AS in a 50/50 wt % mixture: (a)−(c) three subsequent cycles with the same particle. Key: black lines, water uptake of the single levitated particle; gray line, water release of the single levitated particle; dashed line, ZSR prediction; diamonds, bulk measurements (black, a solid and a liquid phase; white, two liquid phases, gray: one liquid phase).

the water uptake and release of a levitated particle at 290 K. As expected, there is no hysteresis between increasing and decreasing relative humidity. The slight mismatch between bulk and single particle data between 40 and 80% RH is at least partly due to the temperature dependence of the poly(ethylene glycol)/water interactions: as temperature increases, the PEG-H_2O interaction strength decreases which implies a decrease of the number of water molecules bonded to the PEG, a gain of free water and thus an increase of water activity.[63,64] A comparison of water activities of PEG 400/water bulk solutions at 290 and 298 K showed increases of water activity by 0.017 and 0.024 a_w for PEG 400 mass fractions of 0.905 and 0.83, respectively. This increase accounts for more than half of the observed difference between bulk and single particle measurements. Above 90% RH the relative humidity indicated by the sensor in the electrodynamic balance is not calibrated anymore, which explains the deviations between bulk and single particle data at these high relative humidities.

For the 50/50 wt % mixture of AS/PEG 400, we performed several humidity cycles with different particles at 290 K. Figure 11 shows the water uptake and release for three cycles with the same particle together with bulk data and ZSR predictions. At relative humidities above 80%, the bulk data is based on water activity measurements of solutions consisting of two (white diamonds) or one liquid phases (gray diamonds). Below 80% RH (black diamonds) it is constructed from the water activities of the saturated solutions, assuming that the undissolved AS does not contribute to the water uptake. The particle was injected into the electrodynamic balance at low relative humidity. It immediately effloresced and did not retain any appreciable amount of water. The three cycles started at low relative humidity and were performed at an average rate of approximately 0.1% RH/min. In the first and the third cycle (a and c), the efflorescence branch started from the two-phase region, in the second cycle from the one-phase region (b). For all three cycles DRH* of AS was observed between 80 and 82% RH, the efflorescence between 33 and 37% RH. These results are representative for all performed cycles with all particles and correspond quite well with the deliquescence/efflorescence relative humidities of pure AS. The deliquescence of AS is not or at least not substantially inhibited by the presence of PEG 400. The quite large scatter of the DRH* of 2% is the only sign of a slight inhibition. No dependence of the DRH* and the efflorescence RH on the way the cycles were run could be found. Between the efflorescence and the deliquescence steps the particle still showed a continuous water uptake and release indicating that the PEG 400 surrounds the solid AS as a coating. Above 80% RH, the fringe pattern and the glare spots of the elastically scattered light are in agreement with one liquid phase. The presence of two liquid phases can only be derived indirectly assuming that the thermodynamic properties established by bulk measurements are also valid for the particle. In the case of two liquid phases, the most probable morphology for the AS/PEG 400 system would be that the PEG 400 phase, as the one with the lower surface tension (surface tension of pure PEG 400: 44.5 mN/m), concentrically surrounds the AS phase. In the case of the 50/50 wt % mixture, the PEG coating exhibits a thickness of 15−17% of the particle's radius, the exact value depending on the relative humidity. One reason the presence of two phases was not observed experimentally could be that the two phases exhibit similar refractive indices: the PEG phase 1.39−1.41 (based on the values of the pure substances and using the Lorentz−Lorenz mixture rule[65]) and the AS phase 1.38−1.40 (from Figure 2 of Nemesure et al.[66])—the exact value depends again on the relative humidity. The similarity of the refractive indices was also noticed during the bulk measurements where the separation between the two phases could be easily overlooked.

There is a good agreement between bulk and single particle measurements at relative humidities above 80%, where the particle had fully deliquesced. The deviations above 90% RH are again due to the relative humidity sensor which at these high values is difficult to calibrate. The efflorescence branches of the relative humidity cycles are in good agreement with the Zdanovskii−Stokes−Robinson approach. This is not surprising for two liquid phases because in this case, PEG 400 and AS indeed take up water independently. However, between 40 and 80% RH the water uptake of the levitated particle is considerably higher than the one reconstructed from bulk sample data. The deviation was found very reproducibly for all investigated particles and cycles. For a given relative humidity, this corresponds to almost a doubling of the particle's water content, and for a given water content to a decrease of the water activity by 0.1 a_w compared with the bulk system. This means that the particle binds water more strongly than the corresponding saturated bulk solutions. A part of this difference (approximately 1/4) can be attributed to the temperature dependence of the poly(ethylene glycol)/water interactions. Moreover, the bulk data were constructed from measurements of saturated solutions in thermodynamic equilibrium and in the absence of undissolved AS. If AS did not crystallize fully at the efflorescence step or formed nanocrystals with a large surface area, this could lead to additional water in the particle that is not accounted for in the bulk experiment. Indeed, the small hysteresis between water uptake and release below 30% RH indicates that the precipitation of AS at the efflorescence step is followed by a slower crystallization or recrystallization process which is accompanied by a further water release. To clarify the phase behavior and water uptake of mixed AS/PEG 400 particles, further investigations are therefore necessary.

4. Conclusion and Outlook

Bulk solubility and water activity measurements of mixed aqueous solutions showed that polyols generally reduce the aqueous solubility of AS and NaCl and thus act as antisolvents. This effect is the stronger the lower the OH/CH_n ratio of the polyols is. On the other hand, the presence of dicarboxylic acids decreases the aqueous solubility of NaCl but increases the one of AS. Conversely, AN dissolves readily in anhydrous alcohols as well as in the aqueous mixture of DCA. All investigated salts induce a phase separation in the completely miscible 1,2-hexanediol/water system. NaCl can therefore be considered as a salting-out agent for alcohols and organic acids whereas AN and AS exhibit salting-in and salting-out tendencies depending on the nature and number of functional groups as well as on the concentration of the solution. The observed organic/electrolyte interactions influence the vapor pressure of the semivolatile constituents, the solubility of the inorganic salts, and the DRH*, whereas they hardly affect the overall water uptake of the fully liquid system.

To account for these interactions between organics and electrolytes, which are specific for the salt and the functional groups present in the organic molecule, a thermodynamic model is desirable. Because the number of potential compounds present in the tropospheric aerosol is much higher than the number of functional groups, this model should be parametrized preferably in terms of structural groups to describe the interactions of organic molecules with electrolytes. For organic acids, the explicit inclusion of pK_a values might also be crucial.

To complement the bulk experiments, single particles consisting of AS/DCA and AS/PEG 400 were investigated in an electrodynamic balance. Whereas the DRH* values as well as the water uptake and release of the fully deliquesced particles are in good agreement with the bulk results, the water uptake before full deliquescence is rather too low in the case of AS/DCA and too high in the case of AS/PEG 400. Whereas the low water uptake of AS/DCA particles can be accounted for by morphological effects, further investigations are necessary to explain the high water uptake of AS/PEG 400 mixtures.

It was shown that organic/electrolyte interactions in mixed organic/inorganic particles may induce liquid−liquid phase separations during humidity cycles: effloresced particles that are exposed to increasing relative humidity may deliquesce into two separate liquid phases that coexist until they become miscible as the particle takes up more water. When the particle is now exposed to decreasing relative humidity, kinetic and morphological effects might determine whether it directly effloresces or whether it passes through a two-liquid-phase state again. On the basis of the analytical tools that are available in the electrodynamic balance, it could not be decided empirically which sequence of phase changes occurred. Investigations that allow a more detailed analysis of the particles are therefore necessary to improve the understanding of the phase changes in tropospheric aerosols.

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