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HYGROSCOPIC BEHAVIORS OF AMMONIUM SULFATE/ORGANIC MIXTURES INCLUDING DICARBOXYLIC ACID AND OLIGOMER

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INTRODUCTION

The hygroscopicity represents the ability of the particle to uptake water from the surrounding air. It depends mainly on the size and the phase state, and therefore influences several physicochemical properties of the particles including optical properties, CCN activity, atmospheric lifetime, chemical reactivity, especially with respect to the heterogeneous chemical reactivity and, respiratory tract deposition (Swietlicki et al., 2008; Varutbangkul et al., 2006). Atmospheric aerosol particles are typically complex mixtures of organic and inorganic species. In many regions, organic aerosol dominates the ambient aerosol mass (Kanakidou et al., 2005). It is well established that high-molecular-weight organic compounds like oligomer with molecular masses ranging from 200 to 1600 g mol⁻¹, represent an important fraction in atmospheric aerosols (Hodas et al., 2016; Kanakidou et al., 2005), but their interactions with other inorganic/organic, and atmospheric water vapor are not well understood. Moreover, single particle measurements suggest that organic and inorganic constituents are internally mixed in particulate matter (Murphy et al., 2006). Therefore, non-ideal interactions between the organic and inorganic aerosol fractions affect water uptake and solubility and, may induce liquid-liquid phase separation (LLPS) into an organic-rich and an aqueous electrolyte phase (Zuend et al., 2011).

Here, the hygroscopic behavior of submicron particles composed of ammonium sulfate (AS), dicarboxylic acids (including oxalic acid (OA), malonic acid (MA)), and oligomer Poly(ethylene glycol) (PEG-300 (-CH₂OCH₂-)_n) is investigated with a Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA), under relative humidity (RH) below 100%. The aerosol systems were varied in their complexity and ranged from single-component to more complex systems (2, 3 and 4 components). The experimental data are compared with predictions from Zdanovskii-Stokes-Robinson (ZSR) mixing rule (Stokes and Robinson, 1966) and the thermodynamic model "Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients" (AIOMFAC) (Zuend et al., 2011).

EXPERIMENTAL SETUP

The schematic of the HTDMA system is shown in Fig. 1. The HTDMA setup consists in the aerosol's generation and drying section, humidity control section and the particle size selection and detection system. The wet polydisperse sub-micrometer particles were generated using a constant output atomizer from aqueous solution prepared from reagent-plus grade chemicals. The solution was prepared with deionized water (18

MΩ.cm). Liquid water in the particles is removed by passing them through a diffusion drier to obtain internally mixed dry particles RH<5%. After being charged by the neutralizer, the dry polydisperse aerosol particles were transformed into quasi-monodisperse particles with a mobility diameter of 100 nm by the first differential mobility analyzer (DMA1). The size-selected particles were exposed to a given RH (10-90%) in the humidified section using Nafion conditioner tubes. Size distribution for the wet particles was measured using the second differential mobility analyzer (DMA2) and a condensation particle counter (CPC, TSI, 3022A). The ratio of sheath air to aerosol flow rate was maintained at 12:1 for both DMAs. For dehydration cycles, the nearly monodispersed particles selected by DMA1 firstly pass through a nafion membrane humidifier (Saturator) at 30°C, in which the particles are exposed to high-RH conditions ~98% to be sure that all particles are completely in liquid state. The RH at the inlet of DMA2 is measured for both aerosol sample flow and sheath flow using ROTRONIC HydroClip humidity sensors. The total residence time in the HTDMA is approximately 25s. The raw data obtained by the HTDMA were inverted using an automatic off-line algorithm TDMAinv developed by Gysel et al. (2009). Particle hygroscopicity can be expressed by the particle growth factor (GF) from the mobility diameters $D_{wet}(RH, DMA2)$ and $D_{dry} (<5\%, DMA1)$ as follows:

$$GF = \frac{D_{wet}(RH, DMA2)}{D_{dry}(RH < 5\%, DMA1)}$$

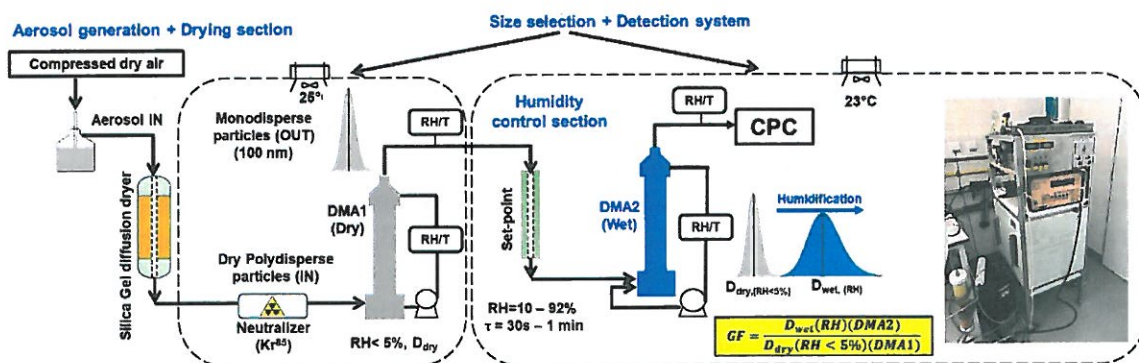


Fig. 1: Schematics of HTDMA.

RESULTS AND CONCLUSIONS

Fig.2 shows the hygroscopic behavior of pure component used on this study. The hygroscopic growths curve of AS typically exhibits the characteristic of crystalline solids with deliquescence relative humidity (DRH) and efflorescence relative humidity (ERH) at ~80% and ~37% during the hydration and dehydration cycles, respectively, in good agreement with the previous studies and thermodynamic model predictions (Choi and Chan, 2002). However, OA particles showed a non hygroscopic behavior. This suggested that OA particles generated during the drying process correspond to dehydrate crystalline stat (Mikhailov et al., 2009). In the other hand, MA and PEG-300 particles showed continuous water uptake without sharp phase transition in good agreement with the previous studies and thermodynamic models (Jing et al., 2016).

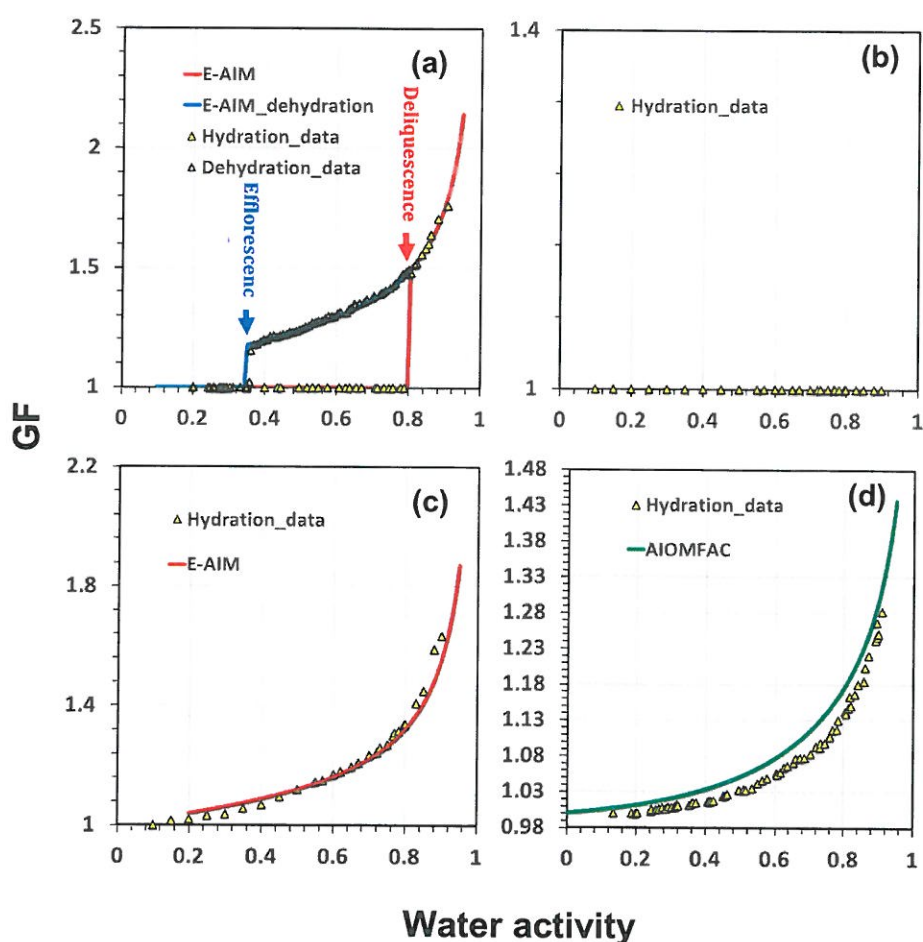


Fig. 2: Hygroscopic growth factors of (a) AS, (b) oxalic acid, (c) malonic acid, and (d) PEG-300 particles (100 nm) as a function of water activity.

As seen in Fig. 3, the mixed particles PEG-OA and PEG-MA showed slow and gradual continuous water-uptake behavior under hydration and dehydration cycles. The disagreement between the hygroscopic growth curves and AIOMFAC calculations may indicate a partial crystallization of organic acids probably present in solid-liquid equilibrium with PEG-OA and PEG-Ma aqueous solution. Note that all organic compounds are assumed to be in liquid-like state all for AIOMFAC predictions. The presence of solid organic acids in the mixture is supported by the comparison measurements-ZSR predictions (see Fig. 3a). In Fig. 3a, the measured GFs are between the values determined from ZSR on the basis of liquid and solid OA. For mixed PEG/organic acid/AS particles (See Fig. 4), in general, under hydration cycles, all the mixed particle systems showed small but gradual water uptake before the full deliquescence, followed by a deep increase in the diameter of the particles around the deliquescence point of AS (~80%). However, more gradual and continuous water uptake was observed prior to the full deliquescence compared to PEG/OA/AS and PEG/MA/AS, since organics may suppress the crystallization of OA and MA in the system and enhance the dissolution of AS (Mikailov et al., 2009; Jing et al., 2016).

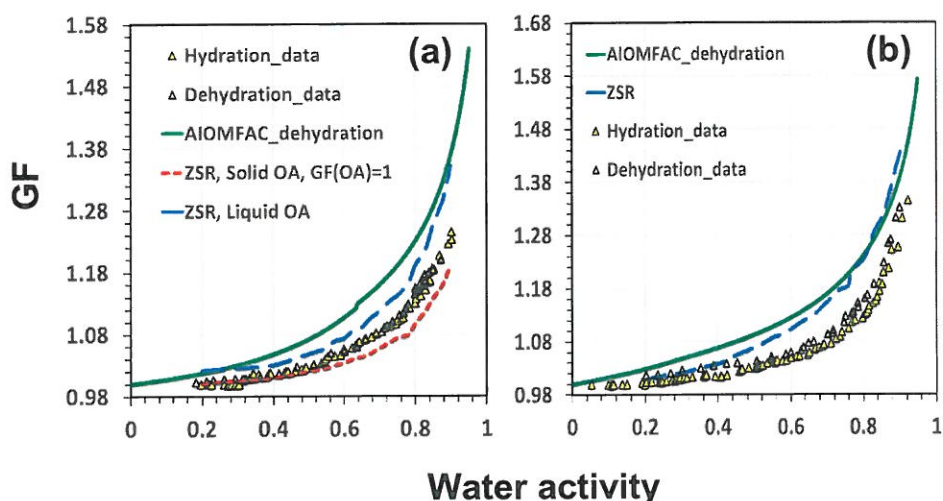


Fig. 3: shows the measured and AIOMFAC and ZSR predicted hygroscopic growth factors: (a) PEG-OA, (b) PEG-MA, with different dry mass ratios of 1:1.

Upon dehydration, all the mixed systems release water gradually without clear efflorescence phase transitions. The disagreement experimental results-AIOMFAC predictions suggest: (i) the presence of organic solids, probably the partial crystallization of organic acids, (ii) and/or that the equilibrium growth was not achieved in the 25s residence time in the HTDMA humidify section, may be caused by the presence of viscosity enhancing aerosol components such the PEG-300, which may affect the kinetic of water transport with the particles (Wang et al., 2017). The comparison between measurements ZSR supports the presence of organic acids in the mixed systems (see Fig. 4a and 4c). This strongly suggests the partial crystallization of organic acids in the mixed particles. In addition, the agreement between experimental results-AIOMFAC under dehydration, and with AIOMFAC and ZSR (based on liquid OA) above the full deliquescence, confirms that all the particles are in thermodynamic equilibrium on the timescale of 25s. AIOMFAC predicts a LLPS at RHs of 89.52, 82.50 and 87.57 for PEG/OA/AS, PEG/MA/AS and PEG/OA/MA/AS. After the full deliquescence, the particles are expected to separate into two phases, an electrolyte-rich phase α composed mainly of ammonium sulfate, OA and/or MA as a core, coated by an organic-rich phase β composed mainly of PEG300. The two phases are supposed to merge to one phase at the RH of the LLPS.

In this study we have studied the hygroscopic behaviors of different mixtures of particles containing AS, PEG, OA and MA. We have shown that the hygroscopic behavior of the different mixtures is well described by AIOMFAC and ZSR models as long as all components are completely liquid. However, we observed even more discrepancies compared to what is expected from models where a solid component is present.

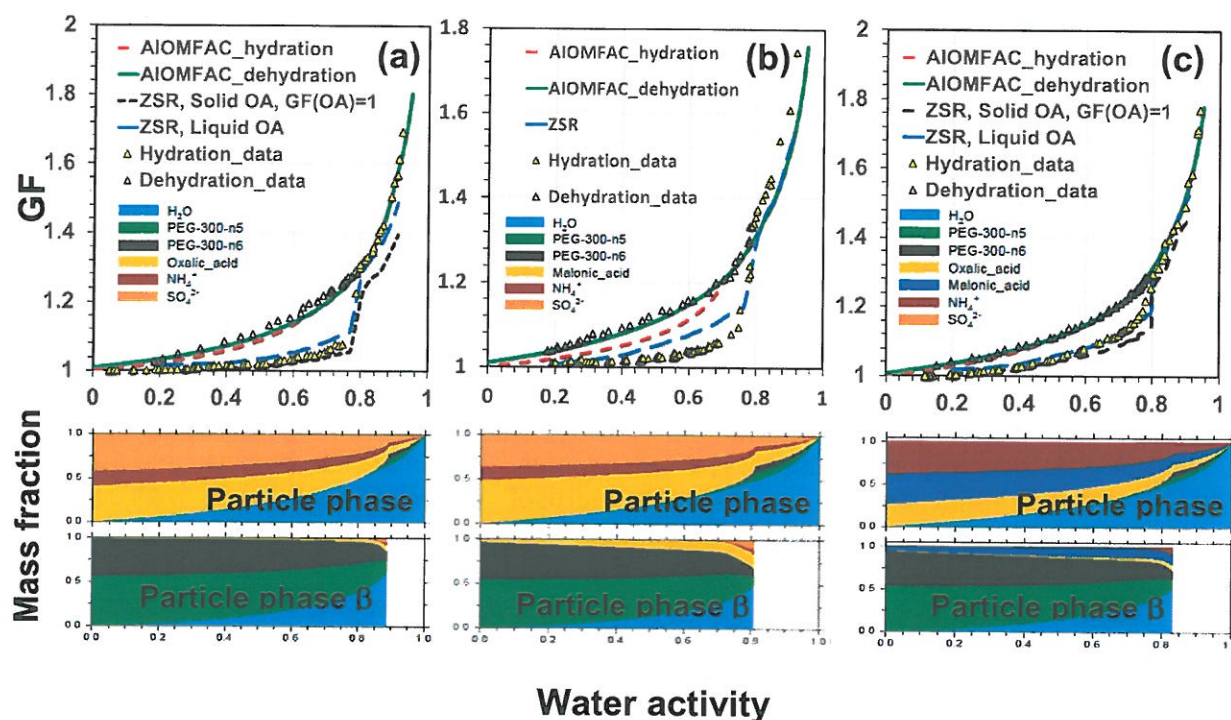


Fig. 4: shows the measured and AIOMFAC and ZSR predicted hygroscopic growth factors: (a) PEG-OA-AS, (b) PEG-MA-AS, (c): PEG-OA MA-AS with different dry mass ratios of 1:1:1, 1:1:1, and 1:1:1, respectively. Panels below illustrate RH-dependent hygroscopic growth curves showing AIOMFAC predictions of the number of phases and corresponding composition at thermodynamic equilibrium during dehydration cycles.

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