**Auxiliary Material**

# Liquid-liquid phase separation in aerosol particles: dependence on O:C, organic functionalities, and compositional complexity

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## 1. Experimental methods

The instrument operation, experimental procedure, and evaluation methods have been described in detail previously [*Song et al.*, 2012]. Micrometer-sized aqueous droplets were deposited on a hydrophobically coated glass slide using a droplet generator. The glass slide was mounted inside the flow-cell. Aqueous solutions for droplet injection were prepared with purified water (resistivity ≥ 18.0 MΩ cm). To change the relative humidity (RH) inside the flow-cell, the water vapor mixing ratio of a constant $N_2/H_2O$ flow (180 sccm) was varied. This flow was brought to 293.2 ± 0.1 K before entering the cell, which was also kept at 293.2 ± 0.1 K. RH was measured by a G-TUCN.34 sensor (U.P.S.I., France), which was calibrated by observing the deliquescence RH (DRH) for pure $(NH_4)_2SO_4$ (80.0 %), $NH_4NO_3$ (65.5 %) and NaI (38.0 %) crystals at 293 K. At the beginning of an experiment, the droplets were equilibrated at a RH of < ~100 % during 15 minutes and a single droplet was chosen for observation. The RH was decreased continuously from ~100 % down to 25 % if (partial) efflorescence was observed and to ~0 % in case of no efflorescence. Subsequently, RH was continuously increased to ~100 %. Typically, experiments were carried out twice, once at a rate of 0.14 % and once at a rate of 0.39 % RH $min^{-1}$. No variation of the results was observed with these rates. The morphological changes of the particle

were monitored optically with the microscope and recorded by a CCIR video camera with an acquisition frequency of 25 frames $s^{-1}$.

For the most volatile organic substances experiments were performed to test whether they show significant evaporation during a humidity cycle at 293 K. These semivolatile components are: pinonic acid, vapor pressure (VP) at 293 K: $7.90 \times 10^{-3}$ Pa, estimate by the EVAPORATION model [*Compernolle et al*., 2011]; 3-hydroxybenzoic acid, VP estimate at 293 K: $2.73 \times 10^{-4}$ Pa or $2.97 \times 10^{-5}$ Pa using the VP estimation model of *Nannoolal et al*. [2008] or *Moller et al.* [2008], respectively, from the E-AIM website http://www.aim.env.uea.ac.uk/aim/aim.php; and 2,4,5-trimethoxybenzoic acid (asaronic acid), VP estimate at 293 K: $3.85 \times 10^{-3}$ Pa [*Nannoolal et al*., 2008] or $9.11 \times 10^{-4}$ Pa [*Moller et al*., 2008]. Small crystals of these substances were deposited in the flow-cell and monitored during a humidity cycle. For none of these substances any change in shape was visible, evidencing that there was no appreciable evaporation occurring. Furthermore, we checked whether the more hydrophobic (low O:C ratio) substances would spread on the substrate by measuring the contact angle of droplets with O:C = 0.33 (consisting of 1,2-hexanediol) and O:C = 0.50 (1,2-butanediol) on the substrate. They exhibited contact angles of 55° and 68°, respectively, and did not spread on the substrate.

## 2. O:C calculation

In this study, we mixed various organic components with ammonium sulfate (AS) in water, and determined the mixture's O:C ratio by the following equation:

$$\mathrm{O{:}C} = \frac{\sum_{k=1}^{n} \frac{\mathrm{mf}_k}{\mathrm{MW}_k} \times \mathrm{O}_k}{\sum_{k=1}^{n} \frac{\mathrm{mf}_k}{\mathrm{MW}_k} \times \mathrm{C}_k}$$

*n*: number of organic components in the mixture

$k$: organic component

$mf_k$: mass fraction of component $k$ in the mixture

$MW_k$: molecular weight of component $k$

$O_k$: number of oxygen atoms in a molecule of component $k$

$C_k$: number of carbon atoms in a molecule of component $k$

## 3. Parameterization of average onset RH of liquid-liquid phase separation

A parameterization of the average onset RH of LLPS (SRH) in the range of AS dry mass fraction ($mf_d(AS)$), $0.1 < mf_d(AS) < 0.9$, as a function of O:C was obtained by fitting a three-parameter sigmoid function to data from this study and the literature [*Marcolli and Krieger*, 2006; *Ciobanu et al*., 2009; *Bertram et al*., 2011; *Song et al*., 2012] at temperatures between 290 and 298 K.

$$\mathrm{SRH}\ (\%) = \frac{10^{1.76}}{10^{1.76} + 0.11 \times 10^{3.45 \times (O:C)}} \times 100\ \%$$

## 4. Supporting Tables

List of investigated organic/AS/$H_2O$ model mixtures, namely "complex organic mixture (COM)" (Table S1), "oxidized aromatic compound (OAC) + dicarboxylic acid (DCA)" (Table S2), "Polyol+DCA" (Table S3), "OAC" (Table S4), "Polyol" (Table S5), "multi-functional compound (MFC)" (Table S6) and "DCA" (Table S7). Each mixture consists of an organic fraction and AS with different organic-to-inorganic dry mass ratios (OIR). The Tables give the organic components in terms of organic dry mass fraction ($mf_d$(org) (%)), the O:C and H:C ratios, the occurrence of LLPS: present ("yes") or absent ("no"), and the onset RH of LLPS (%) (SRH) for OIR = 2:1, 1:2 and 1:6 ("0" = no LLPS, "-" = no experiment performed). The uncertainty in the SRH was typically 1.5 % RH.

**Table S1. COM/AS/$H_2O$**

| | COM1 | COM2 | COM3 | COM4 |
|---|---|---|---|---|
| Components (O:C) | $mf_d$(org) (%) | $mf_d$(org) (%) | $mf_d$(org) (%) | $mf_d$(org) (%) |
| Diethylmalonic acid (0.57) | 12.5 | 0.0 | 0.0 | 0.0 |
| Methylmalonic acid (1.00) | 0.0 | 12.5 | 0.0 | 12.5 |
| Malonic acid (1.33) | 0.0 | 0.0 | 12.5 | 12.5 |
| Glutaric acid (0.80) | 0.0 | 0.0 | 0.0 | 12.5 |
| 2-methylglutaric acid (0.67) | 12.5 | 12.5 | 12.5 | 0.0 |
| 3-methyladipic acid (0.57) | 12.5 | 12.5 | 12.5 | 0.0 |
| Malic acid (1.25) | 12.5 | 12.5 | 12.5 | 12.5 |
| Levoglucosan (0.83) | 12.5 | 12.5 | 12.5 | 12.5 |
| Pinonic acid (0.30) | 3.125 | 3.125 | 3.125 | 3.125 |
| Pinolic acid (0.30) | 3.125 | 3.125 | 3.125 | 3.125 |
| 3-hydroxybenzoic acid (0.43) | 6.25 | 6.25 | 6.25 | 6.25 |
| 3,5-dihydroxybenzoic acid (0.57) | 12.5 | 12.5 | 12.5 | 12.5 |
| 1,2,7,8-octanetetrol (0.50) | 12.5 | 12.5 | 12.5 | 12.5 |
| O:C | 0.63 | 0.68 | 0.70 | 0.77 |
| H:C | 1.57 | 1.50 | 1.53 | 1.44 |
| LLPS | yes | yes | yes | no |
| SRH for OIR = 2:1; 1:2; 1:6 | 74.6; 84.5; 71.9 | 0; 80.9; 72.0 | 0; 79.4; 73.3 | 0; 0; 0 |

**Table S2. OAC+DCA/AS/$H_2O$**

| | OAC+DCA1 | OAC+DCA2 | OAC+DCA3 |
|---|---|---|---|
| Components (O:C) | $mf_d$(org) (%) | $mf_d$(org) (%) | $mf_d$(org) (%) |
| 3-hydroxybenzoic acid (0.43) | 6.25 | 6.25 | 6.25 |
| 4-hydroxybenzoic acid (0.43) | 6.25 | 6.25 | 6.25 |
| 2,5-dihydroxybenzoic acid (0.57) | 12.5 | 18.75 | 18.75 |
| 2,6-dihydroxybenzoic acid (0.57) | 6.25 | 6.25 | 6.25 |
| 3,4-dihydroxybenzoic acid (0.57) | 6.25 | 6.25 | 6.25 |
| 3,5-dihydroxybenzoic acid (0.57) | 37.5 | 43.75 | 43.75 |
| Malonic acid (1.33) | 12.5 | 6.25 | 0.0 |
| Malic acid (1.25) | 12.5 | 6.25 | 0.0 |
| Diethylmalonic acid (0.57) | 0.0 | 0.0 | 6.25 |
| 2-methylglutaric acid (0.67) | 0.0 | 0.0 | 6.25 |
| O:C | 0.68 | 0.61 | 0.56 |
| H:C | 0.95 | 0.90 | 0.95 |
| LLPS | no | no | no |
| SRH for OIR = 2:1; 1:2; 1:6 | -; 0; - | -; -; 0 | -; 0; 0 |

**Table S3. Polyol+DCA/AS/$H_2O$**

| | Polyol+DCA1 | Polyol+DCA2 |
|---|---|---|
| Components (O:C) | $mf_d$(org) (%) | $mf_d$(org) (%) |
| Levoglucosan (0.83) | 20 | 0.0 |
| Glutaric acid (0.80) | 20 | 0.0 |
| 2-methylglutaric acid (0.67) | 0.0 | 30 |
| Diethylmalonic acid (0.57) | 20 | 30 |
| Sorbitol (1.00) | 20 | 20 |
| 1,2,7,8-octanetetrol (0.50) | 20 | 20 |
| O:C | 0.72 | 0.65 |
| H:C | 1.90 | 1.92 |
| LLPS | yes | yes |
| SRH for OIR = 2:1; 1:2; 1:6 | 70.7; 81.4; 73.6 | 85.2; 87.0: 78.0 |

**Table S4. OAC/AS/$H_2O$**

| | OAC1 | OAC2 | 2,5-dihydroxybenzoic acid | 2,6-dihydroxybenzoic acid |
|---|---|---|---|---|
| Components (O:C) | $mf_d$(org) (%) | $mf_d$(org) (%) | $mf_d$(org) (%) | $mf_d$(org) (%) |
| 2,4,5-trimethoxybenzoic acid (0.50) | 35 | 0.0 | 0.0 | 0.0 |
| 3,5-dihydroxybenzoic acid (0.57) | 35 | 70 | 0.0 | 0.0 |
| 2,5-dihydroxybenzoic acid (0.57) | 30 | 30 | 100 | 0.0 |
| 2,6-dihydroxybenzoic acid (0.57) | 0.0 | 0.0 | 0.0 | 100 |
| O:C | 0.55 | 0.57 | 0.57 | 0.57 |
| H:C | 0.98 | 0.86 | 0.86 | 0.86 |
| LLPS | yes | no | yes | yes |
| SRH for OIR = 2:1; 1:2; 1:6 | 92.6; 95.3; 87.0 | -; 0; 0 | -; 68.5; - | -; 91.5; - |

**Table S5. Polyol/AS/$H_2O$**

| | Polyol1 | Polyol2 |
|---|---|---|
| Components (O:C) | $mf_d$(org) (%) | $mf_d$(org) (%) |
| Sorbitol (1.00) | 50 | 60 |
| 1,2,7,8-octanetetrol (0.50) | 50 | 40 |
| O:C | 0.71 | 0.76 |
| H:C | 2.29 | 2.29 |
| LLPS | yes | no |
| SRH for OIR = 2:1; 1:2; 1:6 | 62.6; 69.4; 59.0 | - ; 0; 0 |

**Table S6. MFC/AS/$H_2O$**

| | MFC1 | MFC2 | MFC3 |
|---|---|---|---|
| Components (O:C) | $mf_d$(org) (%) | $mf_d$(org) (%) | $mf_d$(org) (%) |
| 2-oxoglutaric acid (1.00) | 0.0 | 0.0 | 30 |
| Maleic acid (1.00) | 20 | 50 | 30 |
| 3,4-Dihydro-2,2-dimethyl-4-oxo-2H-pyran-6-carboxylic acid (0.50) | 20 | 10 | 5 |
| Itaconic acid (0.80) | 20 | 15 | 15 |
| Dehydroacetic acid (0.50) | 20 | 10 | 5 |
| Kojic acid (0.67) | 20 | 15 | 15 |
| O:C | 0.67 | 0.79 | 0.84 |
| H:C | 1.09 | 1.06 | 1.10 |
| LLPS | yes | yes | no |
| SRH for OIR = 2:1; 1:2; 1:6 | 79.3; 76.6; 76.5 | 0; 59.0; 0 | -; 0; 0 |

**Table S7. DCA/AS/$H_2O$**

| | DCA(C7) | DCA(C6) | DCA(C5) | DCA(C5+C6+C7) |
|---|---|---|---|---|
| Components (O:C) | $mf_d$(org) (%) | $mf_d$(org) (%) | $mf_d$(org) (%) | $mf_d$(org) (%) |
| 3-methyladipic acid (0.57) | 33.3 | 0.0 | 0.0 | 11.1 |
| 3,3-dimethylglutaric acid (0.57) | 33.3 | 0.0 | 0.0 | 11.1 |
| Diethylmalonic acid (0.57) | 33.3 | 0.0 | 0.0 | 11.1 |
| 2-methylglutaric acid (0.67) | 0.0 | 33.3 | 0.0 | 11.1 |
| 3-methylglutaric acid (0.67) | 0.0 | 33.3 | 0.0 | 11.1 |
| 2,2-dimethylsuccinic acid (0.67) | 0.0 | 33.3 | 0.0 | 11.1 |
| Glutaric acid (0.80) | 0.0 | 0.0 | 33.3 | 11.1 |
| Methylsuccinic acid (0.80) | 0.0 | 0.0 | 33.3 | 11.1 |
| Dimethylmalonic acid (0.80) | 0.0 | 0.0 | 33.3 | 11.1 |
| O:C | 0.57 | 0.67 | 0.80 | 0.67 |
| H:C | 1.71 | 1.67 | 1.60 | 1.67 |
| LLPS | yes | yes | no | yes |
| SRH for OIR = 2:1; 1:1; 1:2; 1:6 | 89.6; -; 87.8; 88.3 | 74.1; -; 72.7; 73.8 | 0; -; 0; - | 70.3; 74.0; -; - |

## References


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