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Liquid–liquid phase separation in particles containing organics mixed with ammonium sulfate, ammonium bisulfate, ammonium nitrate or sodium chloride

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Abstract

As the relative humidity varies from high to low values in the atmosphere, particles containing organics and inorganic salts may undergo liquid–liquid phase separation. The majority of the laboratory work on this subject has used ammonium sulfate as the inorganic salt. In the following we studied liquid–liquid phase separation in particles containing organics mixed with the following salts: ammonium sulfate, ammonium bisulfate, ammonium nitrate and sodium chloride. In each experiment one organic was mixed with one inorganic salt and the liquid–liquid phase separation relative humidity (SRH) was determined. Since we studied 23 different organics mixed with four different salts, a total of 92 different particle types were investigated. Out of the 92 types, 49 underwent liquid–liquid phase separation. For all the inorganic salts, liquid–liquid phase separation was never observed when the oxygen-to-carbon elemental ratio (O : C) was ≥ 0.8 and was always observed for $O:C < 0.5$. For $0.5 \leq O:C < 0.8$, the results depended on the salt type. Out of the 23 organics investigated, the SRH of 20 organics followed the trend: $(NH_4)_2SO_4 \geq NH_4HSO_4 \geq NaCl \geq NH_4NO_3$. This trend is consistent with previous salting-out studies and the Hofmeister series. Based on the range of O : C values found in the atmosphere and the current results, liquid–liquid phase separation is likely a frequent occurrence in both marine and non-marine environments.

1 Introduction

A large fraction of atmospheric particles contain both organic material and inorganic salts (Murphy et al., 1998, 2006; Zhang et al., 2007; Pratt and Prather, 2010). The number of possible inorganic salts is relatively small with ammonium sulfate, ammonium bisulfate, ammonium nitrate and sodium chloride thought to be important (Seinfeld and Pandis, 2006; Finlayson-Pitts and Pitts, 2000). In contrast, the number of organic species can be in the 100s to 1000s (Goldstein and Galbally, 2007; Hamilton et al., 2004) while only around 10 % of these organic species have been identified at the molecular level (Hallquist et al., 2009).

As the relative humidity cycles in the atmosphere, particles containing a mixture of organic material and inorganic salts can undergo a range of phase transitions including deliquescence, efflorescence and liquid–liquid phase separation (Martin, 2000; Clegg et al., 2001; Pankow, 2003; Marcolli and Krieger, 2006; Buajarern et al., 2007a; Chang and Pankow, 2006; Zuend et al., 2010; Bertram et al., 2011; Song et al., 2012a; Ciobanu et al., 2009; Brooks et al., 2002; Braban and Abbatt, 2004; Erdakos et al., 2006a; Erdakos and Pankow, 2004; Reid et al., 2011; Anttila et al., 2007). Knowledge of these phase transitions is required for predicting the roles of aerosol particles in air quality and climate. For example partitioning of organic molecules between the gas and particle can depend on the phase of atmospheric particles (Chang and Pankow, 2006; Zuend et al., 2010). Particle phase can also influence the reactive uptake of gas-phase species, the optical properties of particles, and ice nucleation properties of particles, all of which can influence air quality or climate (Anttila et al., 2006; Folkers et al., 2003; Riemer et al., 2009; Escoreia et al., 2010; You et al., 2012; Thornton et al., 2003; Wise et al., 2010 ; Abbatt et al., 2006; Zuberi et al., 2002; Martin, 2000; Martin et al., 2004; Adams et al., 2001; IPCC, 2007).

Many studies on phase transitions of mixed organic-inorganic salt particles of atmospheric relevance have focused on deliquescence and efflorescence (see for example Marcolli and Krieger, 2006; Salcedo, 2006; Pant et al., 2004; Parsons et al., 2004a; Treuel et al., 2009; Choi and Chan, 2002; Ling, 2008; Chan, 2003; Wise et al., 2003; Bertram et al., 2011; Parsons et al., 2006; Braban and Abbatt, 2004; Badger et al., 2006; Brooks et al., 2002, 2003; Smith et al., 2012). These studies have shown that when liquid–liquid phase separation does not occur, the addition of organics to inorganic salts lowers the deliquescence and efflorescence relative humidities of the salts. As a result, some atmospheric particles may remain in a single homogeneous liquid state for the full range of relative humidities found in the atmosphere.

More recent studies on phase transitions of mixed organic-inorganic salt particles of atmospheric relevance have focused on liquid–liquid phase separations (Song et al., 2012a, b; Bertram et al., 2011; Ciobanu et al., 2009; Marcolli and Krieger, 2006; Zuend et al., 2010; Smith et al., 2011; Prisle et al., 2010; Anttila et al., 2007; You et al., 2012; Clegg et al., 2001; Chang and Pankow, 2006; Erdakos et al., 2006b; Pankow, 2003; Reid et al., 2011; Kwamena et al., 2010; Buajarern et al., 2007a, b; Smith et al., 2013). The majority of the laboratory work on this subject has used ammonium sulfate as the inorganic salt.

In the following we studied liquid–liquid phase separation in particles containing organics mixed with the following salts: ammonium sulfate, ammonium bisulfate, ammonium nitrate and sodium chloride. In each experiment one organic was mixed with one inorganic salt and the liquid–liquid phase separation relative humidity (SRH) was determined. Since we studied 23 different organics mixed with four different salts, a total of 92 different particle types were investigated. These studies provide insight into the effect of salt type on liquid–liquid phase separation in atmospheric particles.

2 Experimental

Shown in Table 1 is the list of the organics studied. The organics investigated had a wide range of oxygen-to-carbon elemental ratios (O : C) (from 0.29 to 1.33), covering the range of O : C often observed in atmospheric particles (approximately 0.1 to 1.0) (Jimenez et al., 2009; Heald et al., 2010; Takahama et al., 2011; Aiken et al., 2008; Ng et al., 2010; DeCarlo et al., 2008; Chen et al., 2009; Hawkins et al., 2010). The organics studied herein also included several functional groups observed in atmospheric samples (e.g. carboxylic acids, alcohols, esters, ethers and aromatics) (Russell et al., 2011; Liu et al., 2009; Day et al., 2009; Seinfeld and Pandis, 2006; Finlayson-Pitts and Pitts, 1997; Decesari et al., 2006; Hallquist et al., 2009; Gilardoni et al., 2009; Takahama et al., 2011; Russell et al., 2009; Saxena and Hildemann, 1996; Rogge et al., 1993; Fu et al., 2011). All organic compounds studied herein were purchased from

Sigma–Aldrich with purities ≥ 98 %, with the exception of suberic acid monomethyl ester and 1,2,6-hexanetriol, which were purchased from Sigma–Aldrich with a purity of 97 %, and glycerol, which was obtained from Thermo Fisher Scientific with a purity of 99.9 %. All organics were used without further purification. The organic-to-inorganic mass ratio (OIR) in the particle was fixed at 2.0 ± 0.1 for most of the experiments. This value is in the range of OIR values observed in many field studies (Zhang et al., 2007; Jimenez et al., 2009).

Particles were generated by nebulizing (Meinhard) a solution of one organic compound and one salt, prepared in high purity water (Millipore, 18.2 kΩ) or in a mixture of water and methanol if the water solubility of the organic compound was low, and the droplets were deposited on a hydrophobic glass slide. As the droplets impacted on the slide surface, they coagulated into supermicron droplets. The water or the water/methanol mixture was then evaporated to generate organic–inorganic salt particles with lateral dimensions ranging from 10 to 35 µm.

The glass slide was mounted to a temperature and relative humidity controlled flow cell, which was coupled to an optical reflectance microscope (Zeiss Axiotech; 50× objective) (Koop et al., 2000; Pant et al., 2006; Parsons et al., 2004b; Bodsworth et al., 2010). The temperature of the cell was held constant at 290 ± 1 K in all the experiments described here. To control the relative humidity in the flow cell, a combination of dry and humidified nitrogen gas was continuously passed through the cell. The total flow rate was approximately 1.5 $\mathrm{L\,min^{-1}}$. The relative humidity of the gas was determined using a chilled mirror hygrometer (General Eastern), which was calibrated by measuring the deliquescence relative humidity of ammonium sulfate particles.

At the beginning of an experiment the RH in the flow cell was first set to nearly 95 % and particles were allowed to equilibrate for about 15 min. The RH was then ramped down at a rate of 0.4–0.6 % per minute, and images of the particles were captured approximately every 10 s until one of the following conditions occurred: liquid–liquid phase separation was observed, the particles effloresced, or an RH of ≤ 0.5 % was reached. For each different type of organic-inorganic salt particle, experiments were

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀| |▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

typically repeated at least three times. Roughly 5 particles were monitored in each experiment. For particles containing diethyl sebacate or suberic acid monomethyl ester, experiments started at RH = 100 ± 2.5 % since the RH of liquid–liquid phase separation was greater than 95 %.

While the RH was decreased, liquid–liquid phase separation could be identified from the recorded images. To illustrate this point we have included images and movies of particles containing 2-methylglutaric acid mixed with different inorganics salts as the relative humidity was decreased (Fig. 1a–d and Movies S1–S4). The images and movies show that all particle types containing 2-methylglutaric acid at an OIR of 2.0 ± 0.1 underwent liquid–liquid phase separation.

3 Results and discussion

3.1 Effect of H : C (hydrogen-to-carbon elemental ratio), O : C, and inorganic salt type on liquid–liquid phase separation

Listed in Table 2 are the measured SRH values for the different particle types investigated. Out of 92 particle types, 49 underwent liquid–liquid phase separation between 100 % and ≤ 0.5 % RH. These results are summarized in Fig. 2, which shows the dependence of observed liquid–liquid phase separation on the O : C and H : C (hydrogen-to-carbon elemental ratios) of the organic components of the particles. No trend with H : C is apparent for any of the salts studied. However, a trend with O : C is apparent: for all salts, liquid–liquid phase separation was never observed for O : C ≥ 0.8 and was always observed for O : C < 0.5. For 0.5 ≤ O : C < 0.8, the results depended on the salt type. For ammonium sulfate, phase separation was always observed for 0.5 ≤ O : C < 0.57 and phase separation was frequently observed for 0.57 ≤ O : C < 0.8. For the other three salts, phase separation was frequently observed for 0.5 ≤ O : C < 0.8.

To further investigate the effect of O : C on liquid–liquid phase separation, the measured SRH values are plotted as a function of O : C in Fig. 3. Although the results for each inorganic salt do not fall perfectly on a single line, a correlation between O : C and SRH is observed. This suggests that O : C is a useful parameter for estimating, to a first approximation, the relative humidity for liquid–liquid phase separation, as shown previously for particles containing organics with ammonium sulfate (Bertram et al., 2011; Song et al., 2012a, b). For high accuracy predictions, additional information such as the organic functional groups is required (Song et al., 2012b).

Marcolli and Krieger recently measured SRH in bulk solutions containing one organic mixed with ammonium nitrate or sodium chloride (Marcolli and Krieger, 2006). Organics studied were 1,2-hexanediol (O : C = 0.33), 1,4-butanediol (O : C = 0.5), polyethylene glycol (MW = 400 and O : C = 0.56) and glycerol (O : C = 1). Only one of these organics, glycerol, was investigated in the current study (see Table 1). The SRH data from Marcolli and Krieger (2006) is included in Fig. 3 as a function of O : C (red triangles), together with the results of this study. The overlap between the current data and the data from Marcolli and Krieger (2006) suggest good agreement between the particle studies and the bulk studies.

SRH results shown in Fig. 3 do not vary drastically with the type of inorganic salt. Shown in Fig. 4a are the SRH results of the organics (20 out of the 23 investigated) that followed the trend $(NH_4)_2SO_4 \geq NH_4HSO_4 \geq NaCl \geq NH_4NO_3$. The colors of the symbols and lines represent different O : C. Early in the last century, Randall and Failey showed the following trends for the salting-out efficiencies of ions relevant to our work: $Na^+ > NH_4^+ > H^+$ and $SO_4^{2-} > Cl^- > NO_3^-$ (Randall and Failey, 1927). In addition, the Hofmeister series, which consists of a ranking of cations and anions in terms of their ability to salt-out proteins follows the same trend (i.e. $Na^+ > NH_4^+$ and $SO_4^{2-} > Cl^- > NO_3^-$) (Kunz et al., 2004; Hofmeister, 1887, 1888). Based on these early salting-out studies, we would expect the SRH of $(NH_4)_2SO_4$ to be greater than NH_4HSO_4, and the SRH of $(NH_4)_2SO_4$ to be greater than SRH of NH_4NO_3. These expectations are roughly consistent with the trends observed for 20 out of the 23 organics investigated (Fig. 4a).

Three organics (2,5-dihydroxybenzonic acid, α,4-dihydroxy-3-methoxybenzeneacetic acid, and 2,2-dimethylsuccinic acid) were inconsistent with the SRH trend $(NH_4)_2SO_4 \geq NH_4HSO_4 \geq NaCl \geq NH_4NO_3$ when using an OIR of 2.0 ± 0.1. The results from these organics are illustrated in Fig. 4b. Interestingly, Bertram et al. also measured SRH values for these organics mixed with ammonium sulfate and found that the SRH values for these organics varied with the OIR of the particles. In fact, the SRH of these three organics were the only ones observed to vary with OIR out of the 13 organics studied by Bertram et al. (2011). To investigate this further we have measured SRH for these three organics mixed with the different salts using OIR values lower than 2.0 ± 0.1. The results from these measurements as well as the results from Bertram et al. (2011) are shown in Fig. 5 and are summarized in Table 3.

Figure 5a shows that for $OIR \leq 0.5$, SRH of 2,2-dimethylsuccinic acid followed the trend of $(NH_4)_2SO_4 \geq NH_4HSO_4 \geq NaCl \geq NH_4NO_3$, consistent with the 20 organics shown in Fig. 4a. Hence the anomaly at $OIR = 2$ for 2,2-dimethylsuccinic acid is absent at an OIR of ≤ 0.5. In other words, the trend for 2,2-dimethylsuccinic acid is consistent with the other 20 organics as long as the OIR is in a range where particles undergo liquid–liquid phase separation.

Figure 5b and c show that α,4-dihydroxy-3-methoxybenzeneacetic acid and 2,5-dihydroxybenzonic acid do not follow the trend of $(NH_4)_2SO_4 \geq NH_4HSO_4 \geq NaCl \geq NH_4NO_3$ regardless of the OIR studied. Note out of all organics studied, these two organics are the only two organics which contained aromatic functional groups. One possible reason for the differences in trends of SRH observed for these organics may be due to strong cation-pi interactions (Song et al., 2012b; Ma and Dougherty, 1997; Kumpf and Dougherty, 1993). Previous work by Song et al. has suggested that cation-pi interactions may decrease the salting-out effect of the ammonium cations, thereby influencing SRH values in particles containing ammonium salts and aromatic compounds (Song et al., 2012b).

Recent work has shown that chloride anions may react with organic acids in the particle phase to form organic salts (Laskin et al., 2012). This type of reaction potentially could occur in our studies. However, if such reactions are occurring in our studies, they do not appear to drastically affect the occurrence of liquid–liquid phase separation.

3.2 Atmospheric implications

A large fraction of submicron particles in the atmosphere contain organics mixed with some combination of ammonium (NH_4^+), protons (H^+), sulfate (SO_4^{2-}) and nitrate (NO_3^-) (Adams et al., 1999; Lee et al., 2003; Martin et al., 2004; Murphy et al., 2006; Pratt and Prather, 2010; Seinfeld and Pandis, 2006; Tolocka et al., 2005; Zhang et al., 2007). As a result the inorganic salts ammonium sulfate, ammonium bisulfate and ammonium nitrate, are thought to be important. As mentioned in the introduction, most of the previous laboratory work on liquid–liquid phase transitions of atmospheric importance have used $(NH_4)_2SO_4$ as the inorganic salt, even though sulfate is not always fully neutralized in atmospheric particles and NO_3^- can make up a large fraction of the inorganic anions under certain conditions (Dibb et al., 1996; Murphy et al., 2006; Pratt and Prather, 2010; Tolocka et al., 2005; Zhang et al., 2007; Huebert et al., 1998). To address this disconnect, we have carried out liquid–liquid phase separation experiments with particles containing organics mixed with $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3. The results from these studies show that in all cases, liquid–liquid phase separation is a common occurrence when O : C is < 0.8 and always observed when O : C is < 0.5. These ranges of O : C values are frequently observed in the atmosphere, suggesting that liquid–liquid phase separation is a common process in atmospheric particles, regardless of the identity of the salt.

In the marine boundary layer, supermicron particles containing NaCl make up a large fraction of the particulate mass (Quinn and Bates, 2005; Seinfeld and Pandis, 2006). These particles, which are produced from by a bubble bursting mechanism (Woodcock et al., 1953; Blanchard and Woodcock, 1957), can often contain relatively low O : C organics such as sterols, fatty acids and fatty alcohols (Schneider and Gagosian, 1985;

Kawamura et al., 2003; Peltzer and Gagosian, 1987; Sicre et al., 1990). Based on the liquid–liquid phase separation results for NaCl containing particles presented here and the O : C of sterols, fatty acids and fatty alcohols (O : C less than approximately 0.5) thought to be present in the marine boundary layer, liquid–liquid phase separation is also expected to be a common occurrence in marine environments.

4 Conclusions

Out of 92 types of particles studied, 49 underwent liquid–liquid phase separation. For all the inorganic salts, liquid–liquid phase separation was never observed when $O:C \geq 0.8$ and was always observed for $O:C < 0.5$. For $0.5 \leq O:C < 0.8$, the results depended on the salt type. In addition, a correlation between O : C and the separation relative humidity (SRH) was observed for all inorganic salts, suggests that O : C is a useful parameter for estimating, to a first approximation, the relative humidity for liquid–liquid phase separation, although additional information will be required for predictions with high accuracy.

Out of the 23 organics investigated, the SRH of 20 organics had the following trend: $(NH_4)_2SO_4 \geq NH_4HSO_4 \geq NaCl \geq NH_4NO_3$. The trend is consistent with previous salting-out studies and the Hofmeister series. Based on the range of O : C values found in the atmosphere and the current results, liquid–liquid phase separation is likely a common occurrence in marine and non-marine environments.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/13/20081/2013/acpd-13-20081-2013-supplement.zip.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

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Table 1. Summary of different organics used in the liquid–liquid phase separation experiments.

Compounds	Formula	Molecular weight	O : C	H : C	Functional group(s)
Diethyl sebacate	$C_{14}H_{26}O_4$	258.4	0.29	1.86	ester
2,5-hexanediol	$C_6H_{14}O_2$	118.2	0.33	2.33	alcohol
Poly (propylene glycol)	$C_{3n}H_{6n+2}O_{n+1}$	425	0.38	2.10	alcohol, ether
Suberic acid monomethyl ester	$C_9H_{16}O_4$	188.2	0.44	1.78	carboxylic acid, ester
Poly (ethylene glycol) diacrylate	$C_{2n+6}H_{4n+6}O_{n+3}$	575	0.50	1.77	ester, ether, C-C double bond
1,2,6-hexanetriol	$C_6H_{14}O_3$	134.2	0.50	2.33	alcohol
α,4-dihydroxy-3-methoxybenzeneacetic acid	$C_9H_{10}O_5$	198.2	0.56	1.11	alcohol, aromatic, carboxylic acid, ether
2,5-hydroxybenzoic acid	$C_7H_6O_4$	154.2	0.57	0.86	alcohol, aromatic, carboxylic acid
Diethylmalonic acid	$C_7H_{12}O_4$	160.2	0.57	1.71	carboxylic acid
3,3-dimethylglutaric acid	$C_7H_{12}O_4$	160.2	0.57	1.71	carboxylic acid
Poly (ethylene glycol) 300	$C_{2n}H_{4n+2}O_{n+1}$	300	0.58	2.17	alcohol, ether
Poly (ethylene glycol) 200	$C_{2n}H_{4n+2}O_{n+1}$	200	0.63	2.25	alcohol, ether
Poly (ethylene glycol) bis (carboxymethyl) ether	$C_{2n+2}H_{4n+6}O_{n+5}$	600	0.63	1.92	ester, ether, carboxylic acid
2,2-dimethylsuccinic acid	$C_6H_{10}O_4$	146.2	0.67	1.67	carboxylic acid
2-methylglutaric acid	$C_6H_{10}O_4$	146.1	0.67	1.67	carboxylic acid
Diethyl-L-tartrate	$C_8H_{14}O_6$	206.2	0.75	1.75	alcohol, ether
Glutaric acid	$C_5H_8O_4$	132.1	0.80	1.6	carboxylic acid
Levoglucosan	$C_6H_{10}O_5$	162.1	0.83	1.67	alcohol, ether
Maleic acid	$C_4H_4O_4$	116.1	1.00	1	carboxylic acid, C-C double bound
Glycerol	$C_3H_8O_3$	92.1	1.00	2.67	alcohol
Citric acid	$C_6H_8O_7$	192.1	1.17	1.33	alcohol, carboxylic acid
Malic acid	$C_4H_6O_5$	134.9	1.25	1.5	alcohol, carboxylic acid
Malonic acid	$C_3H_4O_4$	104.1	1.33	1.33	carboxylic acid

Table 2. Summary of SRH results for an organic-to-inorganic mass ratio (OIR) of 2.0 ± 0.1. Uncertainties represent 2σ of multiple SRH measurements and the uncertainty from the calibration.

Organics	$(NH_4)_2SO_4$		NH_4HSO_4		NaCl		NH_4NO_3	
	OIR	SRH (%)	OIR	SRH (%)	OIR	SRH (%)	OIR	SRH (%)
Diethyl sebacate	2.0	100.0 ± 2.5	2.0	100.0 ± 2.5	2.0	100.0 ± 2.5	2.0	100.0 ± 2.5
2,5-hexanediol	2.0	88.8 ± 3.7	2.1	81.0 ± 3.7	2.0	72.4 ± 2.6	2.1	63.9 ± 4.1
Poly (propylene glycol)	2.0	94.1 ± 3.2	2.0	90.3 ± 3.1	2.0	89.6 ± 2.7	2.0	77.6 ± 2.5
Suberic acid monomethyl ester	2.0	100.0 ± 2.5	2.0	100.0 ± 2.5	1.9	100.0 ± 2.5	2.1	100.0 ± 2.5
Poly (ethylene glycol) diacrylate	2.0	94.7 ± 2.5	2.0	91.0 ± 2.9	2.0	87.0 ± 2.7	2.0	69.4 ± 4.4
1,2,6-hexanetriol	2.1	76.7 ± 2.5	2.0	Not observed [a]	2.0	Not observed	2.1	Not observed
α,4-dihydroxy-3-methoxybenzeneacetic acid	2.0	72.6 ± 2.6	2.0	38.2 ± 2.7	1.9	63.1 ± 2.9	1.9	Not observed
2,5-dihydroxybenzoic acid	2.0	Not observed	1.9	Not observed	2.0	65.5 ± 3.1	2.0	Not observed
Diethylmalonic acid	2.0	89.2 ± 3.0	2.0	88.1 ± 2.6	1.9	87.4 ± 3.0	2.1	74.1 ± 3.7
3,3-dimethylglutaric acid	2.0	89.1 ± 3.4	2.0	88.7 ± 5.0	2.1	85.6 ± 2.6	2.0	60.5 ± 2.6
Poly (ethylene glycol) 300	2.0	86.7 ± 2.8	1.9	Not observed	2.0	Not observed	2.0	Not observed
Poly (ethylene glycol) 200	2.0	79.8 ± 4.1	2.0	Not observed	2.0	Not observed	2.0	Not observed
Poly (ethylene glycol) bis (carboxymethyl) ether	2.0	92.0 ± 2.7	2.0	53.6 ± 3.1	2.0	49.0 ± 2.6	2.0	Not observed
2,2-dimethylsuccinic acid	2.0	Not observed	2.0	61.4 ± 2.5	2.1	58.9 ± 2.6	1.9	40.0 ± 3.2
2-methylglutaric acid	2.0	75.3 ± 2.8	2.0	64.5 ± 4.4	2.1	60.1 ± 2.5	2.0	34.5 ± 3.0
Diethyl-L-tartrate	2.1	90.2 ± 3.0	2.1	65.2 ± 4.1	2.0	52.5 ± 2.5	2.0	28.7 ± 5.6
Glutaric acid	2.0	Not observed	1.9	Not observed	2.0	Not observed	2.0	Not observed
Levoglucosan	2.0	Not observed	1.9	Not observed	1.9	Not observed	1.9	Not observed
Maleic acid	2.0	Not observed	2.0	Not observed	2.0	Not observed	1.9	Not observed
Glycerol	2.0	Not observed	1.9	Not observed	2.0	Not observed	2.1	Not observed
Citric acid	2.0	Not observed	2.0	Not observed	1.9	Not observed	1.9	Not observed
Malic acid	2.1	Not observed	1.9	Not observed	1.9	Not observed	1.9	Not observed
Malonic acid	2.0	Not observed	2.0	Not observed	2.0	Not observed	2.0	Not observed

[a] Not observed means liquid–liquid phase separation was not observed for the range of relative humidities probed. In some cases SRH was not probed below 20–40 % RH since at RH values less than this value, efflorescence of the salts occurred.

Table 3. Summary of SRH results as a function of the organic-to-inorganic (OIR) mass ratio for following organics: 2,2-dimethylsuccinic acid; α,4-dihydroxy-3-methoxybenzeneacetic acid; and 2,5-dihydroxybenzonic acid. Included are results from both the current studies and results from Bertram et al. (2011). Uncertainties represent 2σ of multiple SRH measurements and the uncertainty from the calibration.

Organics	$(NH_4)_2SO_4$		NH_4HSO_4		NaCl		NH_4NO_3	
	OIR	SRH (%)	OIR	SRH (%)	OIR	SRH (%)	OIR	SRH (%)
2,2-dimethylsuccinic acid	2.0	Not observed[a]	2.0	61.4 ± 2.5	2.1	58.9 ± 2.6	1.9	40.0 ± 3.2
	0.3[b]	63.8 ± 2.5[b]	0.5	61.2 ± 2.5	0.5	60.0 ± 3.1	0.5	41.4 ± 2.7
	0.5[b]	61.5 ± 2.5[b]						
	1.0[b]	Not observed[b]						
	1.2[b]	Not observed[b]						
	1.5[b]	Not observed[b]						
α,4-dihydroxy-3-methoxybenzeneacetic acid	2.0	72.6 ± 2.6	2.0	38.2 ± 2.7	1.9	63.1 ± 2.9	1.9	Not observed
	0.4[b]	80.1 ± 2.5[b]	0.5	46.3 ± 3.0	0.5	62.6 ± 2.6	0.5	Not observed
	1.0[b]	81.3 ± 2.5[b]						
	6.0[b]	Not observed[b]						
2,5-dihydroxybenzoic acid	2.0	Not observed	1.9	Not observed	2.0	65.5 ± 3.1	2.0	Not observed
	0.2[b]	61.6 ± 2.5[b]	0.5	Not observed	0.5	65.2 ± 2.6	0.5	Not observed
	0.3[b]	64.2 ± 2.5[b]						
	0.5[b]	62.9 ± 2.5[b]						
	0.8[b]	Not observed[b]						
	1.0[b]	Not observed[b]						
	1.5[b]	Not observed[b]						

[a] Not observed means liquid–liquid phase separation was not observed for the range of relative humidities probed. In some cases SRH was not probed below 20–40 % RH since at RH values less than these values efflorescence of the inorganic salt occurred.

[b] Data from previous study of Bertram et al. (2011).

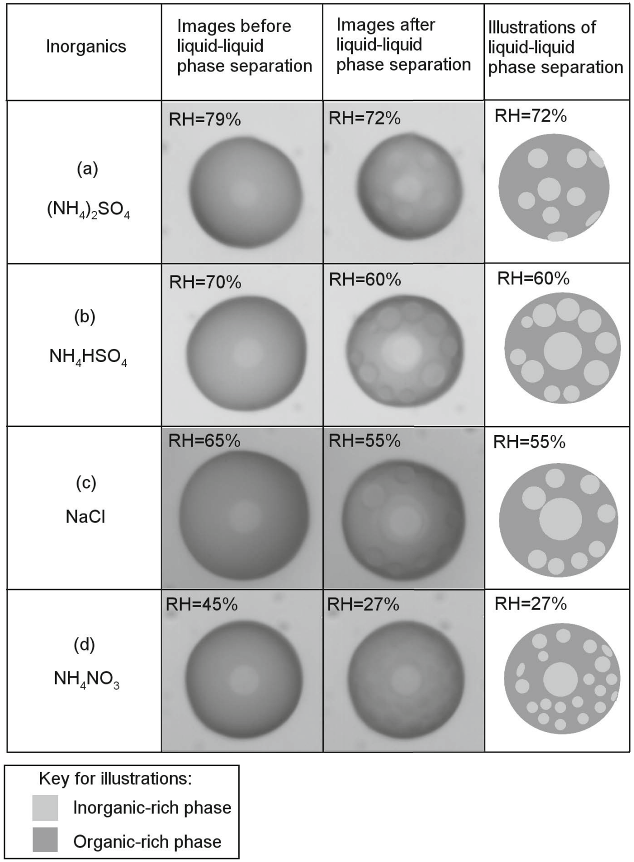

Fig. 1. Optical images and illustrations of particles containing 2-methylglutaric acid and one of the inorganic salts with OIR = 2.0 ± 0.1. Shown in the images and illustrations are the relative humidities at which the images were recorded. The inorganic salts studied were ammonium sulfate (row **a**), ammonium bisulfate (row **b**), sodium cholride (row **c**) and ammonium nitrate (row **d**). The diameter of the particles shown ranged from 28 to 34 µm.

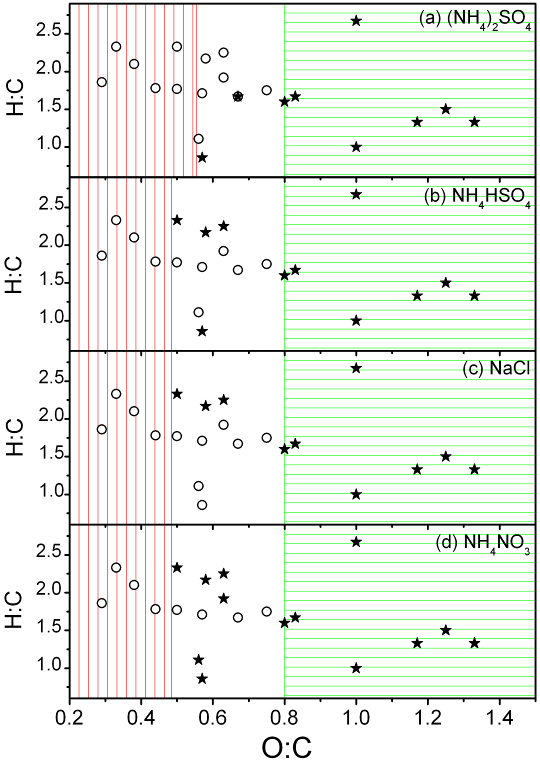

Fig. 2. Van Krevelen Diagram for the different mixed organic-inorganic salt particles (OIR = 2.0 ± 0.1) studied: **(a)** organic-ammonium sulfate particles, **(b)** organic-ammonium bisulfate particles, **(c)** organic-sodium chloride particles and **(d)** organic-ammonium nitrate particles. Circles indicate that liquid–liquid phase separation was observed, while stars indicate that liquid–liquid phase separation was not observed. The vertical red hatched regions correspond to the H : C and O : C conditions when liquid–liquid phase separation was always observed and the horizontal green hatched regions correspond to the H : C and O : C conditions when liquid–liquid phase separation was never observed.

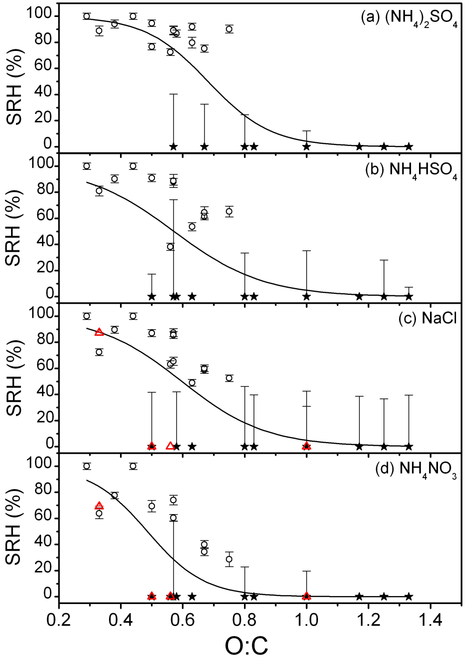

Fig. 3. Summary of SRH results (OIR = 2.0 ± 0.1) as a function of oxygen-to-carbon elemental ratio (O : C): **(a)** organic-ammonium sulfate particles, **(b)** organic-ammonium bisulfate particles, **(c)** organic-sodium chloride particles and **(d)** organic-ammonium nitrate particles. Circles represent the relative humidity at which separation occurred. Error bars associated with the circles represent 2σ of multiple SRH measurements and the uncertainty from the calibration. Stars indicate that liquid–liquid phase separation was not observed. The error bars corresponding to the stars indicate that liquid–liquid phase separation could potentially occur within the range indicated by the error bars, but could not be detected due to the occurrence of efflorescence in the particles. The curves in the panels are Sigmoidal-Boltzmann fits to the data and are added to guide the eye. Red triangles represent the results of liquid–liquid phase separation in bulk solution from Marcolli and Krieger (2006).

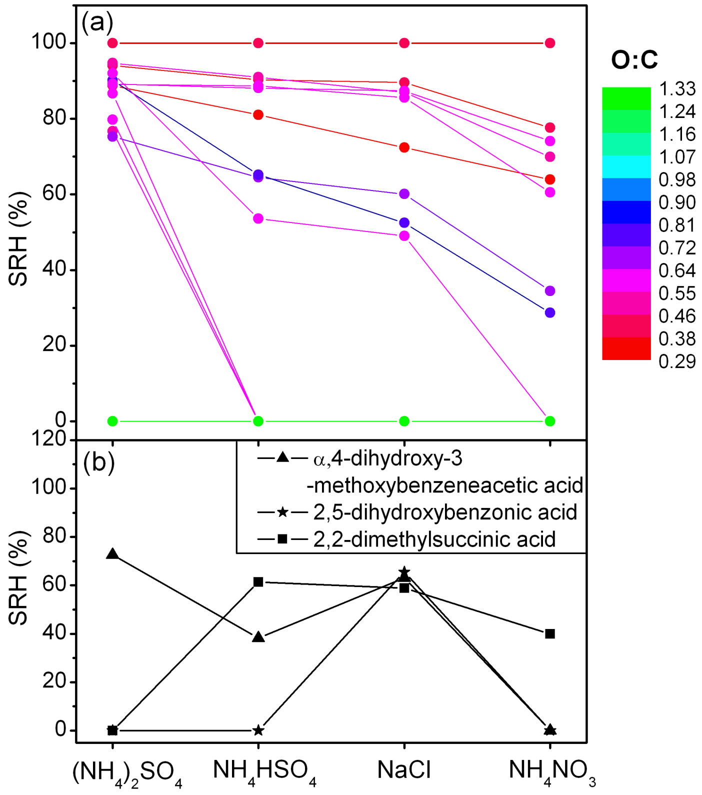

Fig. 4. Summary of trends of SRH of particles (OIR = 2.0 ± 0.1) as a function of inorganic salt type: **(a)** the SRH of the organics (20 in total) that followed the trend $(NH_4)_2SO_4 \geq NH_4HSO_4 \geq NaCl \geq NH_4NO_3$ and **(b)** the SRH for 2,5-dihydroxybenzonic acid, α,4-dihydroxy-3-methoxybenzeneacetic acid, and 2,2-dimethylsuccinic acid. In panel a, colors represent the O : C of individual organics. The organics shown in panel b did not follow the trend $(NH_4)_2SO_4 \geq NH_4HSO_4 \geq NaCl \geq NH_4NO_3$. Uncertainties in the SRH measurements have been left off for clarity.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀▌ ▐▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

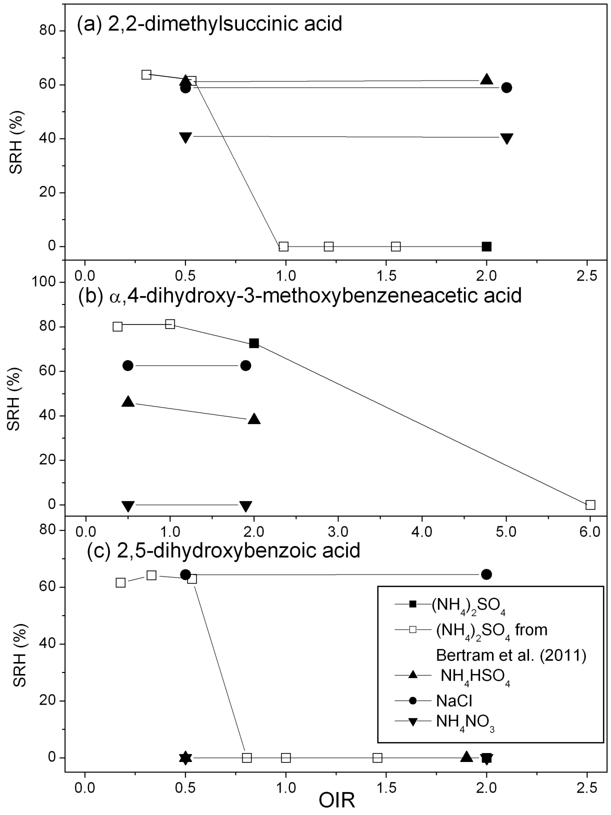

Fig. 5. Summary of SRH results as a function of OIR for the following types of particles: **(a)** 2,2-dimethylsuccinic acid and inorganic salts, **(b)** *α*,4-dihydroxy-3-methoxybenzeneacetic acid and inorganic salts, and **(c)** 2,5-dihydroxybenzonic acid and inorganic salts. Closed symbols represent results from the current study, while open squares represent results from previous studies by Bertram et al. (2011). Uncertainties in the SRH measurements have been left off for clarity.