Atmospheric
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Climate-relevant physical properties of molecular constituents for isoprene-derived secondary organic aerosol material

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Abstract. Secondary organic aerosol (SOA) particles, formed from gas-phase biogenic volatile organic compounds (BVOCs), contribute large uncertainties to the radiative forcing that is associated with aerosols in the climate system. Reactive uptake of surface-active organic oxidation products of BVOCs at the gas–aerosol interface can potentially decrease the overall aerosol surface tension and therefore influence their propensity to act as cloud condensation nuclei (CCN). Here, we synthesize and measure some climate-relevant physical properties of SOA particle constituents consisting of the isoprene oxidation products α-, δ-, and *cis*- and *trans*-β-IEPOX (isoprene epoxide), as well as *syn*- and *anti*-2-methyltetraol. Following viscosity measurements, we use octanol–water partition coefficients to quantify the relative hydrophobicity of the oxidation products while dynamic surface tension measurements indicate that aqueous solutions of α- and *trans*-β-IEPOX exhibit significant surface tension depression. We hypothesize that the surface activity of these compounds may enhance aerosol CCN activity, and that *trans*-β-IEPOX may be highly relevant for surface chemistry of aerosol particles relative to other IEPOX isomers.

1 Introduction

Secondary organic aerosol (SOA) particles make up a substantial fraction of tropospheric aerosol and are known to lead to negative radiative forcing (Kanakidou et al., 2005; Carlton et al., 2009; Williams et al., 2011), yet their formation ranks among the least understood processes in the at-

mosphere (Kanakidou et al., 2005; Goldstein and Galbally, 2007; Galbally et al., 2007; Riipinen et al., 2011; Hallquist et al., 2009). Many studies (Kroll and Seinfeld, 2008; Lin et al., 2012; Worton et al., 2013; Kourtchev et al., 2014; Ehn et al., 2014; Carlton et al., 2009; Claeys et al., 2004b; Hallquist et al., 2009) support the idea that the gas-phase oxidation products of biogenic volatile compounds can either (a) partition to existing particles due to reduced volatility compared to the parent compounds or (b) dissolve in aerosol or cloud water and participate in aqueous phase reactions to form low-volatility material. Surface tension is expected to be of particular importance for SOA formation and growth as it involves processes occurring at the interface between the SOA particle phase and the gas phase (Wang and Wexler, 2013; Djikaev and Tabazadeh, 2003). Moreover, atmospheric particles, once formed, can contain thousands of organic compounds or surfactants that can decrease the surface tension and thereby change aerosol particle properties such as cloud droplet formation, reactivity, and ice nucleation (Schwier et al., 2013; McNeill et al., 2014; Aumann and Tabazadeh, 2008; Tabazadeh, 2005; Taraniuk et al., 2007, 2008). Specifically, it has been reported that organic surfactants can influence the propensity of atmospheric aerosol particles to act as cloud condensation nuclei (CCN) by depressing the surface tension at the moment of activation (Facchini et al., 1999, 2000; Kiss et al., 2005; Shulman et al., 1996; Asa-Awuku et al., 2008; Novakov and Penner, 1993; Sareen et al., 2013; Salma et al., 2006; Hitzenberger et al., 2002). Lower surface tension values result in decreases in the water vapor supersaturation required for cloud droplet activation, depending on ionic content, pH, temperature, and
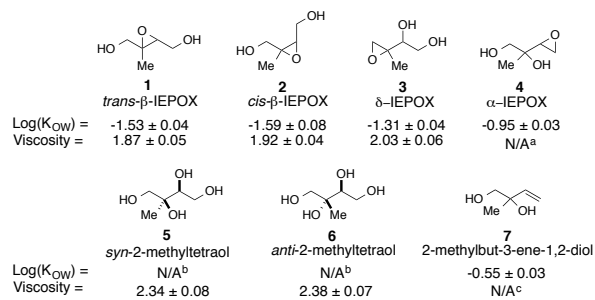
meteorological conditions. McNeill and coworkers recently showed that volatile surfactant species such as methylglyoxal and acetaldehyde can suppress surface tension at the gas–aerosol interface beyond predictions based on bulk surface tension measurements, leading to significantly enhanced CCN activity (Sareen et al., 2013). Chemical reactions at the surface and in the bulk of the particle between aerosol components may also influence overall surface tension and thus impact the dependence of CCN activity on the presence of surfactants. Yet, surface tension effects of many compounds relevant for SOA particle formation remain largely uncharacterized (McNeill et al., 2014; Woo et al., 2013).

Given their importance for global SOA particle formation (Carlton et al., 2009; Paulot et al., 2009; Claeys et al., 2004a), we report here surface tension values, measured using pendant drop tensiometry, of suspended drops of deionized water and 1.0 M ammonium sulfate solutions containing 0.1 to 30 mM concentrations of synthetically prepared isoprene-derived SOA particle constituents. Specifically, we studied the isoprene oxidation products α-, δ-, and *cis*- and *trans-β*-isoprene epoxide (IEPOX) (Fig. 1, 1–4), and *syn*- and *anti*-2-methyltetraol (5, 6). We are motivated by a recent study by Wennberg and coworkers reporting that *cis-β*-IEPOX (2) and *trans-β*-IEPOX (1) are produced in much higher yield than α-IE0POX (4) during isoprene oxidation by hydroxyl radicals with a ratio of α-IEPOX (4) to *cis-β*-IEPOX (2) to *trans-β*-IEPOX (1) of 1 : 20.5 : 27.9 (Bates et al., 2014). The δ-IEPOX (3) isomer was not detected in this study. We report octanol–water partitioning coefficients (K_{ow}) and viscosities of the compounds under investigation. These studies reveal that α-IEPOX (4) significantly decreases surface tension in water (19 % at 30 mM) and in 1.0 M (NH$_4$)$_2$SO$_4$ (30 % at 30 mM). The *trans-β*-IEPOX (1) isomer also decreases surface tension substantially with an overall decrease of 15 % in water and in 1.0 M (NH$_4$)$_2$SO$_4$ at a concentration of 30 mM. Surface tension results indicate that these compounds may enhance aerosol CCN activity, although further studies will be necessary to verify this experimentally.

2 Experimental

2.1 Synthesis of isoprene-derived SOA particle precursors

Synthesis of all compounds studied here are described in previous work (Ebben et al., 2014). The alkene diol (7) was prepared in order to examine the impact of the epoxide functional group on K_{ow} values. Purity of synthesized compounds was determined based on NMR spectra. Surface tension measurements performed in this work are most likely insensitive to impurities below the detection limit of NMR spectroscopy due to the higher concentrations of IEPOX and tetraols used in this study (above micromolar amounts).

1 *trans*-β-IEPOX	**2** *cis*-β-IEPOX	**3** δ–IEPOX	**4** α–IEPOX
Log(K_{OW}) = −1.53 ± 0.04	−1.59 ± 0.08	−1.31 ± 0.04	−0.95 ± 0.03
Viscosity = 1.87 ± 0.05	1.92 ± 0.04	2.03 ± 0.06	N/A[a]

5 *syn*-2-methyltetraol	**6** *anti*-2-methyltetraol	**7** 2-methylbut-3-ene-1,2-diol
Log(K_{OW}) = N/A[b]	N/A[b]	−0.55 ± 0.03
Viscosity = 2.34 ± 0.08	2.38 ± 0.07	N/A[c]

a. α-IEPOX (4) was insoluble in dH$_2$O at higher concentrations used for viscosity experiments b. 2-methyltetraols (5,6) had concentrations in octanol below the detection limit c. Viscosity for alkene diol (7) was not measured due to its increased hydrophobicity relative to α–IEPOX (4) observed during partitioning experiments.

Figure 1. Octanol–water partition coefficients and viscosity values for epoxides 1–4 and tetraols 5 and 6.

2.2 Partition experiments

The octanol water partition coefficient, K_{ow}, was gas-chromatographically determined after thorough mixing of the two phases to reach the equilibrium using the shake flask method (mass balance approach). For the IEPOX (1–4) and alkene diol (7) compounds, stock solutions ($\sim$ 45 mM) were prepared in high purity analytical grade 1-octanol (Sigma Aldrich), presaturated with water. Equal volumes of stock solutions and deionized water were mixed in three separate 15 mL propylene conical tubes. Due to the limited solubility of the 2-methyltetraol compounds in octanol, stock solutions ($\sim$ 45 mM) of the tetraol compounds were prepared in deionized water. Equal volumes of stock solution and 1-octanol presaturated with water were mixed in three separate 15 mL polypropylene conical tubes. In all cases, phases of the solvent systems were mutually saturated by shaking for $\sim$ 24 h on a mechanical shaker at room temperature. The three mixtures for each compound were subsequently centrifuged for 5 min at 3000 rpm to ensure complete phase separation. Three aliquots of the octanol phase were taken to determine the concentration of the IEPOX compounds (1–4), the tetraols (5, 6), and the alkene diol (7) compound.

The concentration of the compounds from the octanol phase for the epoxides and tetraols were determined using an Agilent 5973 gas chromatograph mass spectrometer with a FFAP column (length 30 m, inner diameter 0.25 mm, film thickness 0.25 μm) and a quadrupole analyzer and EI ionization. The injector and detector temperatures were 260 °C and 250 °C, respectively. For the alkene diol and IEPOX compounds, the oven had an initial temperature of 40 °C and a final temperature of 200 °C with a ramp rate of 15 °C min^{-1}. For the tetraol compounds, the oven had an initial temperature of 150 °C and a final temperature of 220 °C with a ramp rate of 30 °C min^{-1}. The gas flow rate was 1.0 mL min^{-1}.

For IEPOX and alkene diol compounds, the quantity of the compound present at equilibrium in the aqueous phase was calculated from the difference between the quantity of

the compound originally introduced and the quantity in the octanol phase determined using the mass balance technique.

2.3 Viscosity studies

All viscosities were measured using solutions of $0.325\,\mathrm{g\,mL^{-1}}$ of the compound of interest and $0.1625\,\mathrm{g\,mL^{-1}}$ $(NH_4)_2SO_4$. Viscosity measurements are relative to a control solution ($0.1625\,\mathrm{g\,mL^{-1}}$ $(NH_4)_2SO_4$ in deionized H_2O) and were determined using a technique similar to a Cannon-Fenske viscometer, by measuring the time taken for the solutions to pass through a 1 mL plastic syringe as reported by Drozd and McNeill (2014).

2.4 Dynamic surface tension measurements

Pendant drop tensiometry (PDT) was used to measure surface tension over time for all solutions in this study on a FTA125 goniometer. Solutions were prepared in $d\mathrm{H_2O}$ or with $1.0\,\mathrm{M}$ $(NH_4)_2SO_4$. The pH of solutions containing $(NH_4)_2SO_4$ ranged from approximately 5.0 to 6.0 while pH ranged from approximately 6.0 to 7.0 in $d\mathrm{H_2O}$. All solutions fell within the bounds of atmospherically relevant pH for aerosols in the troposphere (pH 0–8) (Zhang et al., 2007; Keene, 2004). Solutions containing 100 mM IEPOX compounds in 1 M $(NH_4)_2SO_4$ were allowed to stir at room temperature for one week and monitored by NMR. No conversion into the organosulfate or tetraols was observed during this time. All solutions for surface tension experiments were measured within a week of their formation and were stored in glass vials at $\sim 4\,^\circ\mathrm{C}$ in between measurements in order to further reduce the probability of conversion of IEPOX compounds into the organosulfate or tetraol products. Concentrations of compounds in solutions ranged from 0–30 mM although in some cases higher concentrations (50 mM, 100 mM) were also analyzed. All surface tension experiments were performed at ambient temperature and pressure. Relative humidity ranged from 15 to 45 %, and the laboratory temperature ranged from 20 to 23 $^\circ\mathrm{C}$.

Droplets of sample solutions were formed at the tip of a flat stainless steel needle 1 mL syringe mounted on the instrument and inserted $\sim 1\,\mathrm{cm}$ into a quartz cuvette containing 0.5 mL of $d\mathrm{H_2O}$. All droplets were approximately 7 μL in volume and varied between 2.1 and 2.4 mm in diameter. After formation, the droplet was allowed to stabilize and images were captured $\sim 5\,\mathrm{s}$ after droplet formation. Images were taken every 0.3 s for 10 min, resulting in 1500 images for each experiment and measurements were repeated 5–7 times for each solution. Recent dynamic surface tension studies using the extracted total surfactant component of the PM_{10} size fraction of aerosol particles collected in an urban setting reported similar equilibration times (Noziere et al., 2014). Surface tension for each image was determined by fitting the shape of the drop to the Young–Laplace equation, which relates interfacial tension to drop shape as described by Adamson and Gast (1997):

$$\Delta\rho g h = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right), \tag{1}$$

where $\Delta\rho$ is the difference in densities of the drop and the surrounding media, g is acceleration due to gravity, h is the height generally measured from the apex of the drop, γ is the surface tension, and R_1 and R_2 are the radii of curvature. To calculate the surface tension of the drop, images were captured using a RS170 CCD camera equipped with a microscope lens. FTA32 v2.0 software fit each drop profile and determined distances analytically. A regression then obtains the best overall fit to the Young–Laplace equation with the fitting parameter being interfacial tension with units of $\mathrm{mN\,m^{-1}}$.

3 Results and discussion

3.1 Partitioning and viscosity studies

The octanol water partition coefficient, K_{ow}, is defined as the ratio between the concentrations of a compound of interest in octanol to the one in water once equilibrium is established (Leo et al., 1971). Experimental values of K_{ow} serve as a measure of hydrophobicity while also allowing for the prediction of other physical values relevant to cloud formation that can be more difficult to experimentally measure (Finizio et al., 1997; Klopffer et al., 1982; Meylan and Howard, 2005). Since particles can undergo liquid–liquid phase separation and often contain an aqueous and an organic-rich phase (Yuan et al., 2012), K_{ow} values indicate the phase these compounds will preferentially partition to. Our gas-chromatographically determined K_{ow} values are listed in Fig. 1.

In general, K_{ow} values followed the expected trends in hydrophobicity for each of the compounds. The *trans*- and *cis*-β-IEPOX compounds 1 and 2 were found to have the most negative K_{ow} values, which is consistent with the presence of two primary hydroxyl groups. These compounds also displayed the longest GC retention times (~ 16.5 min) with nearly identical fragmentation patterns (Fig. S1 in the Supplement). δ-IEPOX (3), with its secondary and primary hydroxyl groups, had a slightly higher partition coefficient. α-IEPOX (4) proved to be the most hydrophobic epoxide with the least negative K_{ow} value of all the epoxides. These results are consistent with α-IEPOX (4) having the least accessible hydroxyl groups of the epoxides due to the placement of the methyl group and possibly indicate that α-IEPOX (4) would be the isomer most likely to partition into the organic-rich phase of particles. Replacement of the epoxide group in α-IEPOX (4) with a simple alkene (7) shifted the $\log(K_{ow})$ upward by about 0.4 units. This demonstrates that removal of the polar epoxide group significantly increases hydrophobicity.
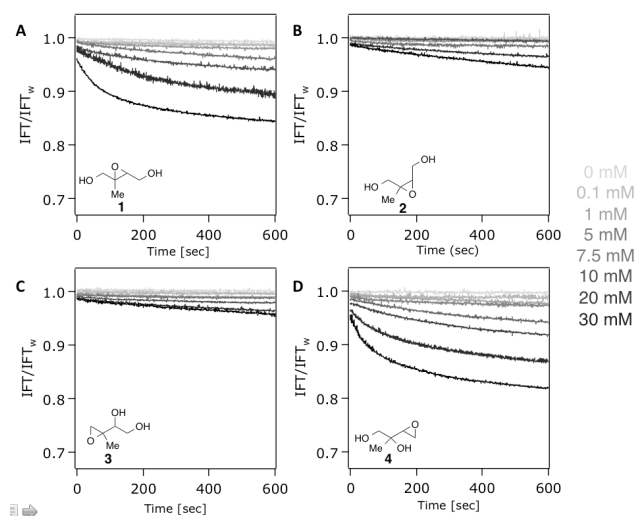
Figure 2. Dynamic surface tension measurements for IEPOX compounds in dH$_2$O. **(a)** trans-β-IEPOX (1) **(b)** cis-β-IEPOX (2) **(c)** δ-IEPOX (3) and **(d)** α-IEPOX (4).

Figure 3. Dynamic surface tension measurements for IEPOX compounds in 1 M (NH$_4$)$_2$SO$_4$. **(a)** trans-β-IEPOX (1) **(b)** cis-β-IEPOX (2) **(c)** δ-IEPOX (3) and **(d)** α-IEPOX (4).

The exact K_{ow} values of the two tetraol diastereomers (5 and 6) could not be determined, possibly due to their very limited solubility in octanol. GC traces of the octanol fraction in tetraol partitioning experiments showed that concentrations of the tetraols in the octanol fractions were below the detection limit. This indicates that the log(K_{ow}) values for tetraol compounds 5 and 6 would be much more negative than the values found for the IEPOX compounds.

Relative viscosities are listed in Fig. 1. The substances tested are all viscous liquids from room temperature down to $-40\,^\circ$C. The epoxides (1–3) have a viscosity similar to glycerol (1.98 ± 0.03), whereas the 2-methyltetraols (5, 6) are slightly more viscous and almost gelatinous.

3.2 Dynamic surface tension measurements

Based on the relevance of surface tension measurements in the prediction of new particle formation and aerosol CCN properties, the effect of concentration on surface tension over time was measured for the four epoxide isomers (1–4) and the two tetraol diastereomers (5, 6) in dH$_2$O and in 1.0 M (NH$_4$)$_2$SO$_4$. As shown in Fig. 2, results in dH$_2$O showed that the α-IEPOX (4) is by far the most surface active of the epoxide compounds. At the highest concentration measured (30 mM), interfacial tension for α-IEPOX (4) was lowered by 5 % at $t = 0$ s and decreased an additional 14 % over the course of 10 min relative to dH$_2$O. While some of this decrease may be due to evaporation, the majority of the effect is most likely due to the migration of α-IEPOX (4) to the surface of the droplet. Based on partitioning coefficients, α-IEPOX (4) is the most hydrophobic of the epoxides and therefore would be more likely to partition from the bulk of the aqueous droplet to the surface.
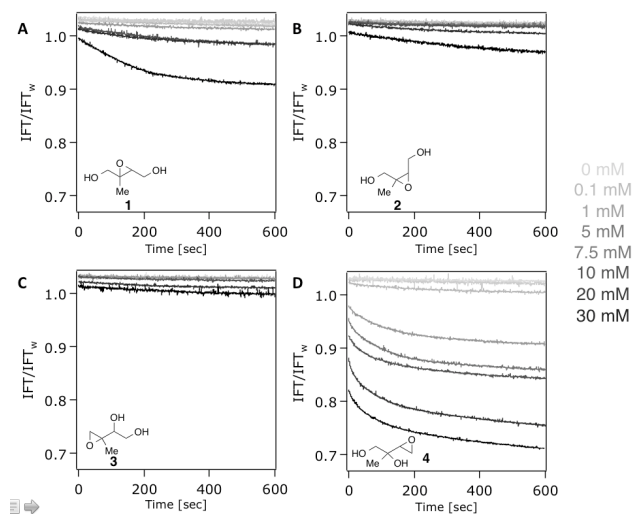
As shown in Fig. 3, the surface tension lowering effect of α-IEPOX (4) was greatly enhanced by the presence of 1.0 M (NH$_4$)$_2$SO$_4$. The presence of 1.0 M (NH$_4$)$_2$SO$_4$ in water raises the surface tension of the droplets by approximately 3 %. Addition of 30 mM α-IEPOX (4) to the 1.0 M (NH$_4$)$_2$SO$_4$ solution prompted a 20 % drop in surface tension at $t = 0$ s and decreased an additional 10 % over the course of 10 min (resulting in an overall 30 % decrease compared to interfacial tension of dH$_2$O). The presence of inorganic salt most likely decreased the solubility of α-IEPOX (4) in water, increasing the concentration of α-IEPOX (4) at the surface of the droplet due to "salting out". These types of nonreactive salt–organic interactions may have a significant influence of surface tension of atmospheric aerosols (Li et al., 1998; Matijevic and Pethica, 1958; Schwier et al., 2012; Sareen et al., 2010; Li et al., 2011). *Trans-β*-IEPOX (1) also demonstrated significant surface activity. However, addition of 1.0 M (NH$_4$)$_2$SO$_4$ did not appear to greatly enhance these surface tension lowering effects. Both with and without inorganic salt, a solution of 30 mM *trans-β*-IEPOX (1) resulted in an overall decrease of 15 % in surface tension relative to dH$_2$O after 10 min. δ-IEPOX (3) and *cis-β*-IEPOX (2) both showed minimal surface tension-lowering effects. A more concentrated solution of 100 mM δ-IEPOX (3) was required in order to achieve the 15 % surface tension depression seen for the 30 mM *trans-β*-IEPOX (1) solution. Addition of 1.0 M (NH$_4$)$_2$SO$_4$ also did not appear to greatly enhance the surface tension lowering effects of either δ-IEPOX (3) or *cis-β*-IEPOX (2).

Regarding the tetraols, Fig. 4 shows a sharp drop in surface activity between 20 mM and 10 mM *anti*-2-methyltetraol (6) solutions in dH$_2$O. Specifically, *anti*-2-methyltetraol (6) showed surface activity comparable to *trans-β*-IEPOX (1) at
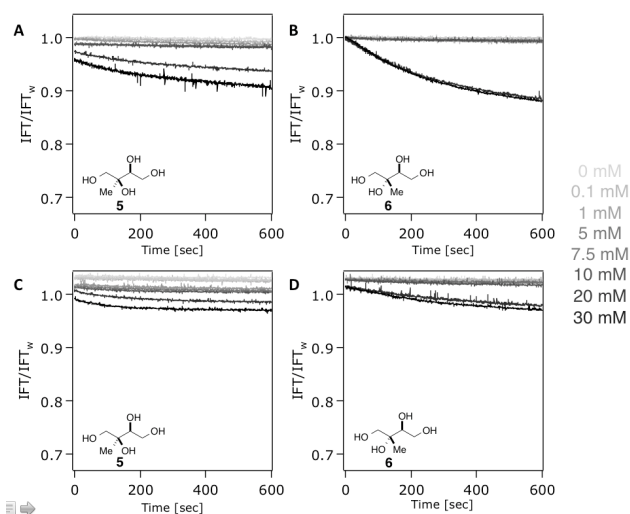
Figure 4. Dynamic surface tension measurements for 2-methyltetraol compounds in dH$_2$O **(a, b)** and 1 M (NH$_4$)$_2$SO$_4$ **(c, d)**. **(a, c)** syn-2-methyltetraol (5) and **(b, d)** anti-2-methyltetraol (6).

30 mM in dH$_2$O. The syn-2-methyltetraol (5) showed less surface activity compared to the $anti$-2-methyltetraol (6) but did exhibit a similar increase in surface activity between the 20 mM and 10 mM solutions in dH$_2$O. This phenomenon was also observed for the $anti$-2-methyltetraol (6) in 1.0 M (NH$_4$)$_2$SO$_4$ solutions but was less pronounced for the syn-2-methyltetraol (5) under the same conditions. This result could be an indication of the increased solubility of the 2-methyltetraol diastereomers in water and therefore a smaller concentration of the 2-methyltetraols at the surface of the droplet. We conclude that the 2-methyltetraol diastereomers may be completely soluble with little effect on droplet surface tension until a critical concentration above 10 mM is reached.

Droplets of pure water and 1.0 M (NH$_4$)$_2$SO$_4$ were also exposed to the vapor pressure over neat IEPOX compounds, however, no change in the surface tension of the droplets was observed on a timescale of 20 min. We caution here that the partial pressure of IEPOX used in these experiments was much higher than its typical pressure in the atmosphere, and that gas and particle phase diffusion limitations for this experiment would also differ for submicron-sized aerosol particles: a recent chamber study of methylglyoxal demonstrated enhanced CCN activity for ammonium sulfate aerosols exposed to methylglyoxal and/or acetaldehyde over 3–5 h, but not when exposure occurred in an aerosol flow tube on a timescale of seconds or minutes (Sareen et al., 2013).

Taken together, our surface tension and partitioning studies reveal that α-IEPOX (4) is both the most hydrophobic and most surface active of all the compounds studied. However, there does not appear to be a consistent correlation between hydrophobicity/viscosity and surface activity of the compounds studied here. For example, cis-β-IEPOX (2) and

$trans$-β-IEPOX (1) were found to possess nearly identical K_{ow} values and therefore similar levels of hydrophobicity but $trans$-β-IEPOX (1) demonstrated greater surface activity relative to cis-β-IEPOX (2). The difference in surface activity of $trans$-β-IEPOX (1) and cis-β-IEPOX (2) may be a reflection of the different relative orientations of the two hydroxyl and the single epoxide groups in cis- and $trans$-β-IEPOX (1, 2) as well as the difference in their propensity to form hydrogen bonds with water molecules inside the water droplet. The greater surface tension depression of $trans$-β-IEPOX (1) may indicate that this compound forms fewer hydrogen bonds than cis-β-IEPOX (2), which could be verified through computational chemistry, such as molecular dynamics simulations.

4   Implications for atmospheric chemistry

Experimental and field studies have shown that surface tension depression by organic compounds is a critical component of predicting aerosol particle behavior (Cruz and Pandis, 1997, 1998; Ekstrom et al., 2009; Corrigan and Novakov, 1999; Henning et al., 2005; Prenni et al., 2001; Raymond, 2003, 2002; Liu et al., 1996; Facchini et al., 2000; Broekhuizen et al., 2004; Kumar et al., 2003; Djikaev and Tabazadeh, 2003; Tabazadeh, 2005; Taraniuk et al., 2007, 2008). These studies have demonstrated that the amount of solute present in an aerosol particle (known as the dry diameter) as well as the surface tension of the droplet can alter its propensity to act as a cloud condensation nucleus. Köhler theory describes cloud droplet activation and growth from soluble particles (Kohler, 1936; Seinfeld and Pandis, 1998). The Köhler curve is given by
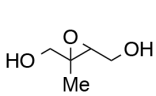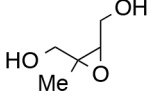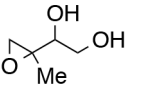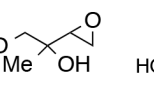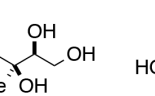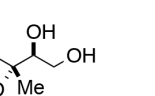
$$s = \frac{A}{D_p} - \frac{B}{D_p^3} \qquad (2)$$

with

$$A = \frac{4M_w\sigma}{RT\rho_w} \text{ and } B = \frac{6n_sM_w}{\pi\rho_w}, \qquad (3)$$

where s is the supersaturation, D_p is the diameter of the aqueous droplet, M_w is the molecular weight of water and ρ_w its density, R is the gas constant, T is temperature, σ is surface tension, and n_s is the number of moles of solute. A decrease in surface tension due to the presence of surfactants would therefore decrease parameter A and result in increased CCN activation. If the bulk solute content of the particle remains constant, the effect of organic surfactants on equilibrium CCN activity can be assumed to be purely surface tension based. This assumption is valid based on the fact that gas-phase isoprene oxidation products will be continuously taken up at the gas–aerosol interface as they are consumed in heterogeneous reactions within the bulk and at the surface of the aerosol (Sareen et al., 2010). Using this assumption,

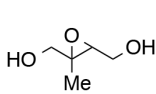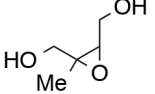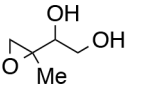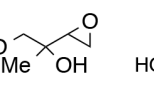**Table 1.** Equilibrium surface tension (at $t = \infty$) for IEPOX (1–4) and 2-methyltetraols (5, 6).
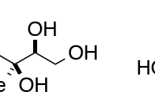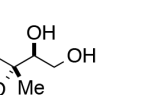
Concentration (mM)	1	2	3	4	5	6
0	71.8 (73.87)	72.73 (74.38)	72.84 (74.85)	72.4 (74.59)	72.48 (75.01)	72.47 (74.67)
0.1	71.4 (74.63)	72.59 (74.28)	72.3 (74.63)	71.96 (74.0)	72.06 (74.54)	72.36 (74.69)
1	71.68 (73.81)	72.31 (74.25)	72.46 (74.4)	70.7 (73.01)	71.8 (74.2)	71.30 (74.72)
5	71.20 (73.56)	72.32 (74.17)	71.96 (74.80)	70.69 (66.09)	71.68 (73.47)	71.70 (74.27)
7.5	68.72 (73.49)	71.67 (74.14)	71.85 (74.32)	67.64 (62.70)	71.48 (73.18)	71.27 (74.37)
10	67.87 (71.11)	71.7 (74.00)	71.09 (74.39)	65.95 (61.45)	71.1 (73.09)	71.34 (73.74)
20	64.57 (71.39)	69.01 (72.93)	69.31 (73.46)	62.99 (55.14)	67.78 (71.72)	61.45 (70.36)
30	61.62 (65.89)	65.5 (69.21)	67.4 (72.09)	59.46 (51.89)	65.35 (70.64)	60.96 (69.97)

Surface tension values at $t = \infty$ for solutions of IEPOX (1–4) and 2-methyltetraols (5, 6) in dH$_2$O based on exponential fits. All values have units of mN m^{-1}.
Values in parentheses denote surface tension values in 1 M (NH$_4$)$_2$SO$_4$.
Error in exponential fit varied from 0.01 to 0.2 for IEPOX 1–3 and syn-2-methyltetraol 5, from 0.01 to 0.1 for IEPOX 4, and from 0.01 to 0.06 for $anti$-2-methyltetraol 6.

Table 2. Supersaturation ratios for IEPOX (1–4) and 2-methyltetraols (5, 6).

Concentration (mM)	1	2	3	4	5	6
0	1.0 (1.02)	1.00 (1.0)	1.00 (1.04)	1.0 (1.04)	0.99 (1.05)	0.99 (1.04)
0.1	1.0 (1.04)	1.00 (1.03)	1.0 (1.04)	0.98 (1.0)	0.99 (1.0)	0.99 (1.04)
1	0.98 (1.02)	0.99 (1.03)	0.99 (1.0)	0.9 (1.00)	1.0 (1.0)	0.97 (1.04)
5	0.97 (1.02)	0.99 (1.03)	0.98 (1.04)	0.96 (0.86)	0.98 (1.01)	0.98 (1.03)
7.5	0.92 (1.01)	0.98 (1.03)	0.98 (1.03)	0.90 (0.80)	0.97 (1.00)	0.97 (1.03)
10	0.90 (0.96)	1.0 (1.02)	0.96 (1.03)	0.86 (0.78)	1.0 (1.00)	0.97 (1.02)
20	0.84 (0.97)	0.9 (1.00)	0.93 (1.01)	0.80 (0.66)	0.90 (0.98)	0.78 (0.95)
30	0.78 (0.86)	0.9 (0.93)	0.9 (1.0)	0.74 (0.60)	0.85 (0.96)	0.77 (0.94)

Supersaturation ratios (s_c^*/s_c) for solutions of IEPOX (1–4) and 2-methyltetraols (5, 6) in dH$_2$O.
Values in parentheses denote supersaturation ratios (s_c^*/s_c) in 1 M (NH$_4$)$_2$SO$_4$. Errors in ratios varied from 0.01 to 0.2 for IEPOX 1–3 and syn-2-methyltetraol 5, from 0.01 to 0.1 for IEPOX 4, and from 0.01 to 0.09 for $anti$-2-methyltetraol 6.

the critical supersaturation for particles of a given size can be described as follows:

$$s_c^* = \left(\frac{\sigma}{\sigma_w} \right)^{3/2} s_c. \tag{4}$$

Here, s_c^* is the critical supersaturation, σ_w and σ are the surface tension of water and the particle, respectively, and s_c is the critical supersaturation of particle with the surface tension of water (72.8 mN m^{-1}) (Engelhart et al., 2008). For all IEPOX and 2-methyltetraol compounds, dynamic surface tension measurements were fit to exponential curves in order to determine the equilibrium surface tension at $t = \infty$ (Table 1). The equilibrium surface tension was used in Eq. (4) to calculate the critical supersaturation ratio (s_c^*/s_c), which are listed in Table 2.

While there is some uncertainty regarding the in-particle concentrations of IEPOX and its reaction products, we can make reasonable estimates of these values based on field and modeling studies. Seinfeld and coworkers (Chan et al., 2010) reported up to 24 ng m^{-3} of IEPOX in Yorkville, GA, during the August 2008 Mini-Intensive Gas and Aerosol Study (AMIGAS). During that period, they also measured 33.4 mg m^{-3} of PM$_{2.5}$. Therefore, the observed IEPOX loading corresponds to an in-particle concentration of ~ 7 mM, assuming 1.2 g cm^{-3} for the particle density. The McNeill group's coupled gas–aqueous aerosol chemistry model, Gas Aerosol Model for Mechanism Analysis (GAMMA) (McNeill et al., 2012), has been updated to include the latest aqueous phase IEPOX chemistry and physical parameters (Nguyen et al., 2014), GAMMA 1.4 simulations predict in-particle concentrations of unreacted IEPOX between 2 and 23 mM in a rural scenario (see Supplement). Therefore, we take here 7.5 mM as an example of an atmospherically relevant IEPOX in-particle concentration and find that α-IEPOX (4) exhibited the largest decrease in s_c^*/s_c

(9 %), with an even larger decrease observed (23 %) in 1.0 M $(NH_4)_2SO_4$. *Trans-β*-IEPOX (1) was also observed to lower surface tension and therefore is also expected to lead to decreased supersaturation ratios and enhanced CCN activity. The potential of *trans-β*-IEPOX to enhance CCN activity is particularly significant based on recent studies demonstrating that *trans-β*-IEPOX is the most abundantly produced isomer relative to other IEPOX isomers during isoprene oxidation (Bates et al., 2014). At 10 mM, s_c^*/s_c for *trans-β*-IEPOX (1) is predicted to decrease by 8 % in dH$_2$O and in $(NH_4)_2SO_4$. Surface tension depression, and therefore the predicted impact on CCN activity, was less significant for *cis-β*-IEPOX (2), δ-IEPOX (3) and the 2-methyltetraols (5, 6). On a permole basis, surface tension depression by *trans-β*-IEPOX is similar to that observed for methylglyoxal in bulk solutions (Sareen et al., 2010). The Henry's Law constant for IEPOX is several orders of magnitude higher than that of methylglyoxal (Nguyen et al., 2014), leading to a greater potential for suppression of aerosol surface tension by these species via bulk effects. That being said, as demonstrated by McNeill and coworkers (Sareen et al., 2013), bulk absorption of surface-active gases is apparently not a requirement for surface tension depression and enhanced CCN activity. In fact, while reactive uptake may be important in other systems, and is certainly important for SOA particles, it is not relevant for our aqueous model experiments, as complementary NMR studies discussed in Sect. 2.4 show no hydrolysis of the epoxides in ammonium sulfate solution over the course of one week. Our results thus set the stage for future investigations of the effects of *trans-β*-IEPOX on the CCN activity of aqueous aerosols.

5   Conclusions

In conclusion, we report dynamic surface tension measurements, using pendant drop tensiometry, of synthetically prepared isoprene-derived SOA particle constituents. Specifically, we studied the isoprene oxidation products α-, δ- and *cis-* and *trans-β*-isoprene epoxide (IEPOX) (1–4) and *syn-* and *anti-*2-methyltetraol (5, 6) compounds. In addition, we experimentally determined octanol–water partitioning coefficients (K_{ow}) and viscosities of these compounds. Results these experiments revealed that α-IEPOX (4) is the most hydrophobic and surface active of the compounds studied here; however, the hydrophobicity of these compounds did not coincide with surface activity for all compounds. Calculation of supersaturation ratios from surface tension values demonstrated that *trans-β*-IEPOX (1) lowers supersaturation ratios significantly while the largest decrease in supersaturation ratios was calculated for α-IEPOX (4). Other compounds measured, *cis-β*-IEPOX (2), δ-IEPOX (3), and the 2-methyltetraols (5, 6), demonstrated less significant surface activity and therefore minimal decreases in supersaturation ratios at higher concentrations.

The enhanced surface activity of *trans-β*-IEPOX (1) and its potential to significantly decrease supersaturation ratios is particularly important based on its correlation with recent sum frequency generation (SFG) spectroscopy studies towards the identification of molecular constituents on the surfaces of isoprene-derived SOA particles (Ebben et al., 2014). This surface specific study identified *trans-β*-IEPOX (1) as the closest match to the SFG spectra of isoprene-derived SOA surfaces, which coupled with surface tension experiments presented here, strongly indicates that *trans-β*-IEPOX (1) may be present in higher concentrations at the surface of aerosol particles relative to other IEPOX isomers. This conclusion is also supported by the study by Wennberg and coworkers where *trans-β*-IEPOX (1) was found to be produced in higher yields relative to other IEPOX isomers during isoprene oxidation by hydroxyl radicals (Bates et al., 2014). Reactive uptake of IEPOX compounds into aerosol particles by acid-catalyzed epoxide ring opening can also lead to formation of organosulfate and organonitrate derivatives (Surratt et al., 2007, 2010; Darer et al., 2011) so future studies will involve synthesizing these derivatives and analyzing their surface activity and other atmospherically relevant properties.

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