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Phase Behavior of Internal Mixtures of Hydrocarbon-like Primary Organic Aerosol and Secondary Aerosol Based on Their Differences in Oxygen-to-Carbon Ratios

Fabian Mahrt, Youzhuo Huang, Julia Zaks, Annesha Devi, Long Peng, Paul E. Ohno, Yi Ming Qin, Scot T. Martin, Markus Ammann, and Allan K. Bertram*

ABSTRACT: The phase behavior, the number and type of phases, in atmospheric particles containing mixtures of hydrocarbon-like organic aerosol (HOA) and secondary organic aerosol (SOA) is important for predicting their impacts on air pollution, human health, and climate. Using a solvatochromic dye and fluorescence microscopy, we determined the phase behavior of 11 HOA proxies (O/C = 0−0.29) each mixed with 7 different SOA materials generated in environmental chambers (O/C 0.4−1.08), where O/C represents the average oxygen-to-carbon atomic ratio. Out of the 77 different HOA + SOA mixtures studied, we observed two phases in 88% of the cases. The phase behavior was independent of relative humidity over the range between 90% and <5%. A clear trend was observed between the number of phases and the difference between the average O/C ratios of the HOA and SOA components (ΔO/C). Using a threshold ΔO/C of 0.265, we were able to predict the phase behavior of 92% of the HOA + SOA mixtures studied here, with one-phase particles predicted for ΔO/C < 0.265 and two-phase particles predicted for ΔO/C ≥ 0.265. The threshold ΔO/C value provides a relatively simple and computationally inexpensive framework for predicting the number of phases in internal SOA and HOA mixtures in atmospheric models.

KEYWORDS: air pollution, phase separation, organic aerosol particles, human health, oxygen-to-carbon ratio, secondary organic aerosol

INTRODUCTION

Atmospheric aerosol particles influence the climate,1,2 and contribute to air pollution and hence have an impact on human health.3−8 Organic aerosols constitute a substantial portion of these aerosols in both urban and remote areas,9−11 and are broadly classified as primary organic aerosol (POA) or secondary organic aerosol (SOA). POA denotes aerosols that are directly emitted into the atmosphere, whereas SOA denotes aerosols that are formed within the atmosphere by oxidation of precursor gases, including volatile organic compounds (VOCs), intermediate volatility organic compounds, and semivolatile organic compounds, followed by gas−particle partitioning of the lower volatility oxidation products.10,12−16 SOA is also formed from oxidation processes taking place directly within the condensed phase.17−19

Measurements with aerosol mass spectrometers have shown that a considerable fraction of atmospheric POA can be described as hydrocarbon-like organic aerosol (HOA).20−22 Engine lubricating oil from, for example, vehicle exhaust, which usually has O/C ratios around 0.02,23,24 has been shown to be a major component of HOA.25−27 HOA can also have higher O/C ratios depending on several factors, including combustion conditions26,28,29 and atmospheric aging (i.e., oxidation),30 often leading to HOA with O/C 0.02 ≤ O/C ≤ 0.29 in the atmosphere.

Despite the enormous chemical complexity of SOA,31−33 factor analysis of aerosol mass spectrometer measurements has identified two main subclasses of SOA, namely, semivolatile oxygenated organic aerosol (SV-OOA) and low-volatility oxygenated organic aerosol (LV-OOA),34,35 with the average O/C ratios spanning ranges of approximately 0.32−0.83 and 0.68−1.32, respectively.35 SV-OOA represents a fresh, less-oxidized secondary organic material, while LV-OOA describes a more atmospherically aged and hence more oxidized secondary organic material.

The O/C ratio of atmospheric SOA material depends on several factors, including the oxidation time, the oxidation mechanism, and the precursor gases. Precursors to SOA are emitted from both anthropogenic and biogenic sources,10 with
the latter dominating SOA formation globally.\textsuperscript{34,35} The major classes of biogenic VOCs that lead to SOA production in the atmosphere are isoprene (C\textsubscript{5}), monoterpenes (C\textsubscript{10}), and sesquiterpenes (C\textsubscript{15}).\textsuperscript{10} All three classes are emitted from vegetation.\textsuperscript{36,37} Examples of atmospherically relevant monoterpenes are \(\alpha\)-pinene and limonene, while the most abundant atmospherically relevant sesquiterpene is \(\beta\)-caryophyllene.\textsuperscript{10} Examples of anthropogenic precursors that can become oxidized to form SOA include aromatic compounds, such as xylene, cyclohexene, and toluene.\textsuperscript{38−41} Biomass burning and wildfires are other emission sources of VOCs that can lead to SOA. Catechol is an example of a VOC from biomass burning and wildfires that can lead to SOA.\textsuperscript{42−44}

Studies investigating the chemical composition of ambient organic aerosol particles have shown that the primary and secondary aerosol materials can be internally mixed in individual particles.\textsuperscript{45−48} The internally mixed POA and SOA, that is, individual particles containing both POA and SOA materials, which we refer to as POA + SOA particles hereafter, can form from a range of atmospheric processes, including coagulation, gas−particle partitioning, condensed phase aging, and cloud processing.\textsuperscript{49−51}

Whether the internally mixed POA + SOA particles contain a single condensed phase or two distinct phases is important for predicting their impact on air quality and climate.\textsuperscript{52−54} For instance, the number of phases influences the formation and mass concentration of ambient organic matter. In single-phase particles, the activities of the organic molecules, that is, their effective concentrations within the mixture,\textsuperscript{56} are lower than their activities in separate POA and SOA phases.\textsuperscript{56} As a result of the decreased activities and the associated reduction in equilibrium partial pressure, the thermodynamic gas−particle equilibrium shifts to the condensed phase. Thus, for SOA and POA materials that form a single phase in the internally mixed POA + SOA particles, the presence of POA seed particles causes an enhancement in SOA formation by allowing more gaseous SOA precursors to be taken up into the existing POA phase. In contrast, in the case of two-phase POA + SOA particles, such SOA mass enhancement is smaller and absent in the case of complete immiscibility of the POA and SOA materials.

The phase behavior of POA + SOA particles can also impact the multiphase and heterogeneous chemistry,\textsuperscript{57−59} for example, by affecting the uptake of reactive gas species, as has previously been observed for dinitrogen pentoxide (N\textsubscript{2}O\textsubscript{5})\textsuperscript{50,61} in phase-separated organic−inorganic particle systems, with consequences for the gas-phase concentration of pollutants such as ozone (O\textsubscript{3}) and nitrogen dioxide (NO\textsubscript{2}).\textsuperscript{62} The phase behavior and formation of multiple liquid phases at high relative humidity (RH) values can also impact the ability of POA + SOA particles to act as nuclei for clouds.\textsuperscript{63−67}

Recently, we used microscopy techniques to investigate the phase behavior of internal mixtures of hydrocarbon-like POA proxies and single-component SOA proxies.\textsuperscript{68} We showed that two liquid phases were almost always observed when POA proxies having O/C < 0.11 were mixed with SOA proxies having 0.3 ≤ O/C ≤ 1.0. In the same study, we also found that one or two liquid phases were observed when POA proxies with 0.11 ≤ O/C ≤ 0.29 were mixed with the same SOA proxies depending on the type of the proxies. Nevertheless, real SOA is considerably more complex\textsuperscript{31−35} than the single-component SOA proxies we used previously. Hence, studies with real SOA, that is, SOA collected in the atmosphere or generated in environmental chambers, are still needed to confirm the conclusions from our recent study.

Previous studies have also investigated the phase behavior of POA + SOA mixtures using POA proxies and SOA generated in environmental chambers, which usually contain thousands of different molecules.\textsuperscript{24,69−78} However, those studies were limited to (1) POA proxies with an O/C ratio below 0.1 or an O/C ratio of 0.166, (2) the SOA material mostly generated by oxidation of \(\alpha\)-pinene, and (3) the RH values mostly less than approximately 20\% (see Table S3). On the other hand, the O/C ratio of atmospheric hydrocarbon-like POA ranges from approximately 0 to around 0.29.\textsuperscript{20} The RH in the atmosphere is most often >20\%, and SOA in the atmosphere can be generated from many different types of precursors and oxidants.

In our present study, we used a solvatochromic dye and fluorescence microscopy to directly observe the phase behavior of internally mixed POA + SOA particles at RH values of 90, 45, and 0\%. We used 11 POA proxies and examined the phase behavior of each proxy when mixed with 7 different SOA materials generated in environmental chambers, resulting in 77 unique types of internal POA + SOA mixtures studied.\textsuperscript{36} The O/C ratios of the POA materials ranged from 0 to 0.29, covering the O/C range observed for atmospheric HOA.\textsuperscript{20} The O/C ratios of SOA ranged from 0.37 to 1.08, covering a large fraction of the O/C range observed for atmospheric SOA (0.32−1.32).\textsuperscript{20} The SOA materials were derived from oxidation of \(\alpha\)-pinene, \(\beta\)-caryophyllene, cyclohexene, limonene, xylene, catechol, and toluene. We use the O/C ratio of the SOA and POA materials to interpret our results, as we have done previously. The O/C ratio is a useful parameter to estimate the polarity and hydrophilicity of the organic material, that is, properties that are related to the phase behavior of organic mixtures.\textsuperscript{68−70} In addition, the O/C ratio of ambient and laboratory-generated organic aerosols can be readily measured using well-established techniques.\textsuperscript{20,80,81}


\section*{EXPERIMENTAL SECTION}

**POA Proxies.** The POA proxies used here, and their relevant properties, are listed in Table S1. All POA proxies are non-crystalline (based on melting temperatures or optical images of particles containing just the POA proxies) at room temperature and have low saturation vapor pressures. Choosing POA proxies with these properties minimizes the crystallization and evaporative losses during our phase behavior experiments. The POA proxies had O/C ratios ranging from 0 to 0.29 (Table S1), covering the typical range found in atmospheric HOA.\textsuperscript{20} Furthermore, these O/C ratios allowed us to mimic the hydrophobic HOA close to emission sources as well as the more oxidized HOA that results from atmospheric aging.\textsuperscript{82} Most of the POA proxies (9 out of 11 proxies) are commercially available single-component organic compounds purchased from either Sigma-Aldrich or Alfa Aesar with purities ≥98\% or binary mixtures of these single-component organic compounds. Some of these single-component proxies, for example, nonanoic acid and decanoic acid, have been identified in ambient organic aerosol.\textsuperscript{83} The partially oxidized POA proxies had carboxylic acid, ester, aromatic, or alcohol functional groups, all of which have been identified in the ambient organic aerosol material.\textsuperscript{84−86} Also included as POA proxies were two more complex organic mixtures, namely, engine lubricating oil (Pennzoil, 5W30) and jojoba oil (Ciganic) that were purchased in retail stores.
Jojoba oil is a vegetable oil containing mixtures of mostly high molecular weight, long-chain monoesters of straight fatty acids and alcohols. Jojoba oil is considerably different from triglyceride-based vegetable oils. Engine lubricating oil is mostly composed of cyclic and branched hydrocarbons and was selected because it has been shown to be a major component of urban HOA resulting from engine combustion processes.

**Generation of SOA Materials.** The different SOA types studied here were generated from oxidation of precursor gases by either ozonolysis or photooxidation. Specifically, α-pinene, β-caryophyllene, limonene, cyclohexene, and catechol SOA materials were generated by ozonolysis. In contrast, toluene and xylene SOA materials were generated by photooxidation. We did not use ozonolysis to generate SOA from toluene and xylene since the half-life for the ozonolysis reaction with toluene and xylene was considerably longer than the residence time for typical conditions used in our experiments.

The SOA materials were produced with mass concentrations ranging from 20 to 130 μg m\(^{-3}\) and at RH ≤ 1.5%, with the exception of the toluene SOA material that was produced at 40% RH. The details for producing the individual SOA materials and experimental setups are given in Section S2 of the Supporting Information. Irrespective of the experimental setup used to generate SOA, the SOA material was collected onto hydrophobic glass slides by inertial impaction. The inertial impaction resulted in SOA particles with diameters ranging from approximately 5 to 30 μm. After impaction, the SOA material was either used immediately or stored in a freezer in sealed containers at −20 °C until used for phase behavior analysis. Most SOA-containing glass slides were used for phase behavior analysis within several days of storage. The impact of SOA sample storage on phase behavior was tested for mixtures of squalane and α-pinene SOA material. A similar phase behavior was observed for hydrophobic glass slides with a fresh (unfrozen) SOA material and SOA-containing glass slides stored in the freezer for up to 3 months, suggesting that the sample storage had no impact on our results.

**Generation of Internally Mixed POA + SOA Particles.** Following collection on glass slides, the SOA material was mixed with the POA material. To add each POA proxy to the SOA particles collected on the hydrophobic glass slides, the following procedure was used: first, solutions of 1.75 wt % of each POA proxy were prepared in ethyl acetate (Sigma-Aldrich, ≥99.8% purity). Trace amounts of Nile red (9-diethylamino-5H-benzo[α]phenoxazine-5-one, Sigma-Aldrich) were added to each solution to achieve a final Nile red concentration of 10 mg L\(^{-1}\). Nile red is a solvatochromic dye that fluoresces at different wavelengths depending on the polarity of the surrounding chemical environment. This property enables discrimination of the different phases present in internally mixed POA + SOA particles by their fluorescence color and has been used previously to observe the phase behavior of aerosol particles. The solutions containing the POA proxies and Nile red were then nebulized (Meinhard, TR-30-C0.5, using pure nitrogen as carrier gas, 5.0 grade, Linde) onto the glass slides containing the SOA particles by placing the SOA-containing glass slide into the air stream (~1.5 L min\(^{-1}\) of N\(_2\)) of the nebulizer for ~3 s at a distance from the tip of the nebulizer of ~2 cm. This resulted in mixtures of the SOA material with POA and ethyl acetate. Previous work has shown that at least some types of SOA materials are soluble in ethyl acetate. The slides containing SOA, POA, and ethyl acetate were then placed into a fume hood for several minutes to allow the ethyl acetate to completely evaporate. This overall procedure resulted in internally mixed POA + SOA particles on the slides with diameters approximately between 40 and 120 μm. The formation of internal POA + SOA mixtures using this generation method was verified by observing two distinctly different fluorescence colors within individual particles (see below). Each slide produced with this method also contained particles consisting of only POA and only SOA material. The overall average SOA volume fraction (i.e., SOA volume to total particle volume) for particles containing both SOA and POA generated with this technique was approximately 0.24, based on the experiments with squalane as the POA. Furthermore, this average SOA volume fraction varied from approximately 0.11 to 0.4 in the individual experiments, and the SOA volume fraction in individual particles varied by approximately 0.01–0.73. Hence, in the individual experiments, we explored a range of SOA volume fractions. See Section S5 and Figure S12 for additional details on how average SOA volume fractions were determined and the variability in this value from experiment to experiment and particle to particle.

**Microscopy Analysis of POA + SOA Particle Phase Behavior.** The phase behavior of the POA + SOA particles was directly observed by fluorescence microscopy. The hydrophobic glass slide with the deposited POA + SOA particles containing Nile red was mounted in a RH-controlled flow cell (BioSurface Technologies Corp., model: FC 81) that was coupled to a fluorescence microscope (Olympus X70, MAG ×10k objective lens), following the method of our previous work. The fluorescence microscope was equipped with a mercury arc lamp as a light source, a U-MNIB filter cube (excitation wavelengths between 470 and 490 nm and emission wavelengths of ≥515 nm), and a colored charge-coupled device camera (Olympus, model DP80). The temperature of the flow cell was at T = 293 ± 2 K for all experiments, monitored by a thermocouple mounted to the flow cell (Type, Omega, Model FF-T-20-100). Previous studies have reported negligible effects of temperature on the phase behavior for mixed inorganic–organic particles. The water vapor mixing ratio in the flow cell was controlled by continuously passing a combination of dry and humidified nitrogen gas (5.0 grade, Linde) through the flow cell. The humidified nitrogen gas was obtained by passing a flow of nitrogen gas through a bubbler system mounted in a refrigerated bath (Thermo Fisher, Model RTE-140). Typical total volumetric flow rates through the flow cell were ~1.5 L min\(^{-1}\). The RH of the gas flow was determined in situ with a chilled mirror hygrometer (General Eastern, model: M4/E4) mounted ~10 cm downstream of the flow cell. The accuracy of the hygrometer was ±2.5% RH, verified by measuring the deliquescence RH of pure ammonium sulfate particles (Sigma-Aldrich, purity >99%) and comparing against literature values.

At the beginning of each experiment, the RH in the flow cell was set to ~90%, and the particles were allowed to equilibrate for ~5 min. The RH was then continuously decreased at a rate of about 0.5% RH min\(^{-1}\) by changing the temperature of the refrigerated bath controlled by the Nescom software (NESLAB, v2.02). Ramps were stopped at RH levels of 45% and 0%, and particles were allowed to further equilibrate for ~5 min prior to capturing images using the fluorescence microscope and the CellSens software (Olympus, Dimensions 3962 https://doi.org/10.1021/acs.est.1c07691 Environ. Sci. Technol. 2022, 56, 3960–3973
concentrations (60 generated using the same experimental setup and similar mass based on AMS measurements of the toluene SOA material the current experiments. For this case, we used a value of 1.08 O/C ratio of the toluene SOA material was not measured in types with conditions similar to our experiments.103

limonene, cyclohexene, and xylene are in good agreement with the O/C ratios found in previous studies for these SOA α determined here for

v1.23 and SQUIRREL 1.63I (Aerodyne Inc.) and applying the ToF-AMS data in Igor Pro 8 (Wavemetrics Inc.) using PIKA interferences. The O/C ratio was derived by analyzing the HR-ToF-AMS spectra of various SOA materials sampled periodically with the HR-ToF-AMS to correct for air fi beam blocked every 5 s for background subtraction. Particle-spectra were collected using the MS mode with the particle V-mode with a typical resolution of 2400 m/Δm. Mass spectra were collected using the MS mode with the particle beam blocked every 5 s for background subtraction. Particle-filtered (Whatman, 1851-047, grade QM-A) air was also sampled periodically with the HR-ToF-AMS to correct for air interferenc. The O/C ratio was derived by analyzing the HR-ToF-AMS data in Igor Pro 8 (Wavemetrics Inc.) using PIKA v1.23 and SQUIRREL 1.63I (Aerodyne Inc.) and applying the improved ambient method.20 Overall, the O/C ratios determined here for α-pinene, β-caryophyllene, catechol, limonene, cyclohexene, and xylene are in good agreement with the O/C ratios found in previous studies for these SOA types with conditions similar to our experiments.103–107 The O/C ratio of the toluene SOA material was not measured in the current experiments. For this case, we used a value of 1.08 based on AMS measurements of the toluene SOA material generated using the same experimental setup and similar mass concentrations (60–100 μg m⁻³) to those used in the current study.108

Figure 1. Examples of fluorescence microscopy images of particles composed of mixtures of the POA materials and SOA derived from (a) ozonolysis of α-pinene and (b) photooxidation of toluene. The POA type and the associated elemental oxygen-to-carbon (O/C) ratio are indicated below each image. All images are taken at a RH of 90%, and the scale bar applies to all images shown. The colors result from the fluorescence of trrace amounts of Nile red embedded into the particles. See text for details.

v1.18). For each POA + SOA mixture, between 2 and 18 individual particles were monitored within each experiment.

Determination of O/C Ratio. The O/C ratios of all the POA proxies were calculated from the molecular formula, except for the engine lubricating oil and jojoba oil, which were determined using an elemental analyzer (Thermo Fisher Scientific, model: Thermo Flash 2000). The O/C ratios of all the SOA materials except toluene SOA were determined using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Inc.) operated in the V-mode with a typical resolution of 2400 m/Δm. Mass spectra were collected using the MS mode with the particle beam blocked every 5 s for background subtraction. Particle-filtered (Whatman, 1851-047, grade QM-A) air was also sampled periodically with the HR-ToF-AMS to correct for air interferenc. The O/C ratio was derived by analyzing the HR-ToF-AMS data in Igor Pro 8 (Wavemetrics Inc.) using PIKA v1.23 and SQUIRREL 1.63I (Aerodyne Inc.) and applying the improved ambient method.20 Overall, the O/C ratios determined here for α-pinene, β-caryophyllene, catechol, limonene, cyclohexene, and xylene are in good agreement with the O/C ratios found in previous studies for these SOA types with conditions similar to our experiments.103–107 The O/C ratio of the toluene SOA material was not measured in the current experiments. For this case, we used a value of 1.08 based on AMS measurements of the toluene SOA material generated using the same experimental setup and similar mass concentrations (60–100 μg m⁻³) to those used in the current study.108

RESULTS AND DISCUSSION

Figure 1 shows examples of fluorescence microscopy images from our experiments recorded at 90% RH. Panel 1a shows images for all the POA proxies mixed with the SOA material derived from ozonolysis of α-pinene, and panel 1b shows images for all the POA proxies mixed with the SOA material derived from the photooxidation of toluene. These two SOA types are often used as laboratory model systems for biogenic and anthropogenic SOA, respectively. From these images, the morphology (see Section S3) and the number of phases in the POA + SOA particles can be determined. The number of phases can be determined because the fluorescence spectrum of Nile red, a solvatochromatic dye, is different (different emission wavelength and hence different color) when embedded in the different types of chemical phases.67,83 The color depends on the polarity of the surrounding phase,93,109 as well as to some degree on experimental conditions, including the water content in the particles,93,110 the pH of the organic phase,111 the aggregation of the solvatochromatic dye,112,113 and the fluorescent detector settings. In our experiments, the POA-dominated phase appeared mostly green for POA with a low O/C ratio and yellow to orange for POA with a higher O/C ratio. The SOA-dominated phase mostly appeared yellow to red or black (see Figure 1 and Section S2). In the following, we use the presence of multiple colors to indicate the presence of two phases in POA + SOA particles.

For the SOA material derived from α-pinene ozonolysis, two phases were observed at 90% RH when the O/C ratio of the POA material was low, whereas one- or two-phase particles were observed when the O/C ratio of the POA material was high (Figure 1a). In contrast, when the SOA material derived from photooxidation of toluene was mixed with the POA, we always observed phase-separated particles at 90% RH, regardless of the O/C ratio of the POA (Figure 1b). Note, in the case of phase-separated particles, the POA and SOA can be either partially or completely immiscible since these two scenarios cannot be distinguished in our experiments.

Shown in Figures S1–S7 are the fluorescence microscopy images of all 77 unique POA + SOA mixtures examined in this study. Here, we focus on the number of phases in the POA + SOA mixtures, while the particle morphology is discussed in Section S3. The number of phases determined from these images is summarized in Figure 2 (filled symbols) as a function of the O/C ratio of the POA proxy and the RH. For all the mixtures studied, the number of phases was independent of the RH levels (90, 45, and 0%) studied here. Out of the 77 different POA + SOA mixtures studied, we observed two phases in 88% of the cases. For toluene, catechol, and

Figure 1. Examples of fluorescence microscopy images of particles composed of mixtures of the POA materials and SOA derived from (a) ozonolysis of α-pinene and (b) photooxidation of toluene. The POA type and the associated elemental oxygen-to-carbon (O/C) ratio are indicated below each image. All images are taken at a RH of 90%, and the scale bar applies to all images shown. The colors result from the fluorescence of trrace amounts of Nile red embedded into the particles. See text for details.
limonene SOA materials, we observed two-phase mixtures regardless of the O/C ratio of the POA proxies. For α-pinene, β-caryophyllene, cyclohexene, and xylene SOA materials, we always observed two-phase particles when the O/C ratio of POA was low and one- or two-phase particles when the O/C ratio of POA was high.

The phases observed in our study were most likely non-crystalline since the mixed POA + SOA particles did not have irregular and jagged features that could be assigned to a crystalline material (Figures S1–S7). This is consistent with prior work indicating that crystallization is not expected for complex, multi-component atmospheric organic mixtures such as the SOA material studied here.114 Hence, the phases in our experiments were most likely liquid, semisolid, or glassy. For simplicity, we refer to them as liquid phases here.

Figure 2. Overview of the number of liquid phases formed in different internal mixtures of hydrocarbon-like POA and SOA (POA + SOA) as a function of RH for mixtures where the SOA material is derived from oxidation of (a) β-caryophyllene, (b) cyclohexene, (c) α-pinene, (d) limonene, (e) xylene, (f) catechol, and (g) toluene. In each panel, the filled triangles correspond to data from this study, while the open symbols denote data reported in the literature, as indicated in the legend. See Table S3 for details and for overlapping data points in the case of panel (a).

Figure 3 summarizes the number of liquid phases observed for all the POA + SOA mixtures studied here as a function of the average O/C ratios of the POA proxies (see Table S1) and
the average O/C ratio of the SOA materials (see Table 1). The different panels in Figure 3 correspond to the three different RH values tested here. When SOA had 0.40 < O/C ≤ 0.57, two-phase particles were observed if the POA had O/C ≤ 0.166, and one- or two-phase particles were observed when the POA had O/C ratios between 0.2 and 0.29. On the other hand, when SOA had 0.88 ≤ O/C ≤ 1.08, we always observed two-phase particles, independent of the O/C ratio of POA (0 ≤ O/C ≤ 0.29). As mentioned above, the phase behavior of each internal POA + SOA mixture was independent of RH across the studied range of 90%–0% (see Figure 2).

Figure 4 summarizes the number of phases as a function of the absolute difference in the average O/C ratios of the POA and SOA components, that is, \( \Delta O/C = O/C_{SOA} - O/C_{POA} \), where O/C_SOA and O/C_POA refer to the average O/C ratios of the POA and SOA materials, respectively, and for 0% ≤ RH ≤ 90%. A clear trend can be observed between the number of phases and the \( \Delta O/C \) values. In order to parameterize the phase behavior in terms of \( \Delta O/C \), we fit the phase behavior data with a sigmoidal Boltzmann function

\[
y = \frac{1}{2} + \frac{1}{2} \text{erf} \left( \frac{\Delta O/C - \Delta O/C_{\text{threshold}}}{m} \right)
\]

Here, the values of 1 and 2 indicate the physical boundaries of one- or two-phase POA + SOA particles, \( m \) denotes the slope of the sigmoidal function, and \( \Delta O/C_{\text{threshold}} \) corresponds to the threshold \( \Delta O/C \) for the formation of two phases (i.e., the \( \Delta O/C \) value at which we see a transition from one-phase to two-phase particles). We intentionally chose a steep slope (\( m = 4.85 \times 10^{-3} \), see Table S4) to approximate a step-like function to describe the switch from one- to two-phase POA + SOA particles, once a threshold \( \Delta O/C \) value is reached. We point out that eq 1 with \( \Delta O/C_{\text{threshold}} = 0.265 \) fits

Table 1. Summary of the Elemental Composition for SOA Obtained from AMS Analysis Showing the Average Elemental O/C Ratio, the Average Hydrocarbon-to-Oxygen Ratio (H/C), and the Average Carbon Oxidation State (OSC) for V-Mode AMS Data

| O/C          | H/C          | OSC       |
|--------------|--------------|-----------|
| cyclohexene + O3 (OFR-UBC) | 0.14 ± 0.14 (0.47–0.53) | 1.72              |
| \( \alpha \)-pinene + O3 (EC-UBC) | 0.50 ± 0.14 (0.47–0.53) | 1.58              |
| limonene + O3 (OFR-UBC) | 0.56 ± 0.16 (0.53–0.58) | 1.59              |
| xylene + OH (EC-UBC) | 0.57 ± 0.16 (0.54–0.59) | 1.59              |
| catechol + O3 (EC-UBC) | 0.88 ± 0.25 (0.81–0.94) | 1.21              |
| toluene + OH (OFR-HU) | 1.08 ± 0.30 (0.81–0.94) | 1.67              |

“Also indicated in parenthesis are the ranges of the average O/C, H/C, and OSC values observed over all experiments when the AMS was sampling from either the environmental chamber or the oxidation flow reactor for a given SOA type, reflecting a day-to-day variation in SOA properties. All values were obtained by analyzing the AMS data using the improved ambient method unless indicated otherwise. The associated uncertainties in the calculated average O/C and H/C ratios are 28 and 13% (average absolute value of relative error), respectively, based on the comparison to previously reported standards. The uncertainty in the OSC value determined with the improved ambient method is 0.5 OSC units. All the values are rounded to the second decimal point. EC-UBC: Environmental Chamber University of British Columbia; OFR-UBC: Oxidation Flow Reactor University of British Columbia; and OFR-HU: Oxidation Flow Reactor Harvard University. \( \Delta \)Values correspond to \( \alpha \)-pinene + O3 SOA chamber experiments performed for a different set of experiments, where 2-butanol rather than cyclohexene was used as an OH scavenger. \(^{19,20}\) Taken from Song et al.\(^{19,20}\) Also taken from Canagaratna et al.\(^{20}\)
our data well (the dashed line in Figure 4) and is able to predict the phase behavior of 92% of the POA + SOA mixtures studied. Our results are consistent with the observations of Gorkowski et al.,27 who suggested that the phase behavior of internally mixed organic aerosol will be dependent on the O/C ratio of the organic material, although they did not investigate the relationship between phase separation and the O/C values. The ΔO/C framework presented in Figure 4, including the fit curve to the data using eq 1, shows that ΔO/C can explain the phase behavior of a large fraction of our internal POA + SOA mixtures. Even though ΔO/C has substantial merits to predict the phase behavior of POA + SOA particles, we acknowledge that it cannot explain all our experimental results. For instance, the ΔO/C framework fails to explain the results for the POA proxy with O/C = 0.2 being mixed with cyclohexene, α-pinene, and xylene (see Figure 2). To explain the remaining variability, other factors beyond the difference in the average O/C ratios of the organic components, such as difference in functional groups, molecular weight, and molecular structure, are likely required. For instance, the enthalpy-based Hansen solubility parameter (HSP) framework might have more predictive power when estimating the number of phases in such internally mixed POA + SOA particles compared to the average O/C ratio or ΔO/C because it takes into account more chemical information of the organic species within a mixture, including intermolecular forces (dispersion force, dipole–dipole intermolecular forces, and hydrogen bonding).115 However, estimating the HSP requires either detailed molecular speciation of the main SOA components to predict the HSP using a functional group contribution method or requires information on the bulk H/C, O/C, and mole ratios of hydroxyl groups and carboxyl groups to estimate the HSP with empirical regression models,69 which is beyond the scope of this study. In addition, the HSP framework does not consider any entropy effects, which likely play a role for the phase behavior of POA + SOA particles.

**Comparison with Previous Studies Using Laboratory Generated SOA**

Also shown in Figure 2 are the results of phase behavior experiments from previous studies (open symbols) where the SOA material generated in environmental chambers was mixed with POA proxies that had O/C ratios equal to or below 0.166. A detailed list of the literature results shown in Figure 2 is compiled in Table S3. In the majority of the previous experiments (14 out of 17 experiments), two phases were assumed or inferred, consistent with our results for POA proxies with O/C ≤ 0.166.

The only three previous experiments that did not assume or infer two-phase particles when investigating the phase behavior of laboratory-generated SOA mixed with POA were carried out by Asa-Awuku et al.24 and Ye et al.70 The study by Ye et al.70 reported enhancement of the SOA material derived from α-pinene ozonolysis in the presence of hexadecanol (O/C = 0.0625) POA seed particles at 2–5% RH, suggesting either partial or complete miscibility between the POA and SOA materials. However, from their experiment, the number of phases could not be conclusively constrained since partial miscibility can result in either one- or two-phase particles (represented by the gray symbol in Figure 2c). In the study by Asa-Awuku et al.,24 a smog chamber was used to investigate the SOA material that was either derived from ozonolysis of α-pinene or β-caryophyllene, and which was mixed with POA from diesel engine exhaust, having an O/C ratio of 0.047. They observed strong mixing in both cases and concluded that single-phase POA + SOA particles were formed (blue, left pointing triangles in Figure 2a,c). These observations from Asa-Awuku et al.24 are not consistent with our results. However, we note that Ye et al.69 investigated the same internal mixture and reported no enhancement of the α-pinene + O3 SOA material in the presence of diesel engine exhaust POA particles. The latter suggests phase-separated POA + SOA particles and complete immiscibility of the POA and SOA materials, in line with our findings. We conclude that additional field and laboratory studies with diesel engine exhaust POA materials are needed to resolve the apparent discrepancies between our results and some previous studies, given that diesel engine exhaust POA particles denote an important HOA source in the atmosphere, and the properties of POA from diesel engines may be strongly different from engine to engine.

**Comparison with Previous Studies Using Single-Component SOA Proxies**

In our previous work, we used a set of 13 different POA proxies and 21 different single-component, commercially available SOA proxies to investigate the phase behavior of...
internally mixed POA + SOA particles. In Figure S9, we have replotted the data from our previous study and furthermore indicated the regions where mostly one- and two-phase POA + SOA particles were observed (red and blue hashed regions). Overall, the general trends observed in our previous studies are consistent with the general trends observed in the current study. Specifically, when the O/C ratio of the SOA proxy was high (>0.75), we always observed two phases, regardless of the O/C ratio of the POA proxy. In addition, when the O/C ratio of the SOA proxy was low (≤0.75), we always observed two phases if the O/C ratio of the POA proxy was low, and one or two phases if the O/C ratio of the POA proxy was high. Nevertheless, there were quantitative differences between our previous experiments and the current study. To explore these differences, we use ΔO/C.

Shown in Figure S10 are the number of phases as a function of ΔO/C from our previous study. Similar to the current experiments, a trend is observed between the number of phases and ΔO/C. In addition, this trend can be described by a sigmoidal Boltzmann function (eq 1), again using a steep slope to approximate a step-like function. The threshold ΔO/C values from the fits to the data from our previous experiments using POA and SOA proxies were ΔO/C_{threshold} = 0.38, 0.39, and 0.28 for RH values of <5%, 45%, and 90%, respectively (see Table S4). These threshold ΔO/C values are higher than the values observed using the SOA material generated in environmental chambers (ΔO/C_{threshold} = 0.265, see Table S4). A shift of ΔO/C_{threshold} to higher values when using single-component SOA proxies is not surprising. The molecules in the SOA material generated in environmental chambers are expected to have a distribution of O/C ratios contributing to the average O/C ratio. A distribution of O/C ratios for SOA should lead to a lower ΔO/C_{threshold} Value for the formation of two phases. This is because the SOA molecules with higher O/C ratios than the average, if sufficiently abundant, are more likely to favor phase separation (two-phase particle) compared to SOA molecules with O/C ratios similar to the average (i.e., having O/C ratios more similar to that of the HOA component). In contrast, the single-component SOA proxies have single, distinct O/C values, and hence, a higher ΔO/C_{threshold} for the formation of two phases is expected compared to SOA with a distribution of O/C values.

In the current experiments, the phase behavior was independent of RH, and hence, ΔO/C_{threshold} for the transition from one phase to two phases was independent of RH. On the other hand, ΔO/C_{threshold} was dependent on RH when using single-component SOA proxies in our previous study (Figure S10). This may suggest that some of the SOA proxies used in the previous experiments were more hygroscopic than the SOA material used in the current work. Additional studies are needed to understand why an RH dependence was observed in the previous experiments but not in the current experiments.

ATMOSPHERIC IMPLICATIONS

Knowledge on the phase behavior, that is, the number and type of phases formed in the internally mixed aerosol particles composed of HOA and SOA materials, is crucial to predict their role for air quality and climate. In the atmosphere, freshly emitted HOA particles in many cases have low O/C ratios (~0.02), similar to that of engine lubricating oil. Such HOA particles can then be oxidized in the atmosphere, causing the O/C ratio of the HOA particles to range from approximately 0.02 ≤ O/C ≤ 0.29 (horizontal gray bars in Figure 3). At the same time, SOA is likely a continuum of different species with a range of O/C values and with aging causing the O/C ratio to increase over time. Nevertheless, two main subclasses of atmospheric SOA material have been identified by factor analysis of AMS data, namely, SV-OOA and LV-OOA.

These two subclasses usually co-exist in the atmosphere. SV-OOA and LV-OOA have been reported to have average O/C ratios between 0.32 and 0.83 and between 0.68 and 1.32, respectively (vertical gray bars in Figure 3). Based on a comparison of these O/C ranges and our results (Figure 3), two phases are expected in the internal mixtures of LV-OOA and HOA. For SV-OOA, two phases are also expected when mixing with HOA having an O/C ratio between 0 and 0.166, while one or two phases are expected when internally mixing with HOA having an O/C ratio between 0.2 and 0.29.

Field measurements have shown that in urban environments close to HOA sources where HOA has a low O/C ratio, organic particle populations are often characterized by a bimodal mass size distribution, with HOA and SOA being found in separate size modes. This observation is consistent with our results that show HOA components with low O/C ratios form two phases when internally mixed with SOA. A two-phase HOA + SOA system would prevent the two size modes from mixing by gas–particle partitioning. The same field studies have found that this bimodality converges to a monomodal size distribution when going from urban to rural areas and after HOA has been partially oxidized (higher O/C) during transport. Our results showing that HOA and SOA can form single-phase particles when the O/C ratio of HOA is more similar to that of SOA.

When modeling the formation of SOA in the atmosphere, SOA and HOA are either assumed to form a single phase or instead two completely separate phases. Our results challenge this approach. Specifically, our results suggest that the number of phases assumed in atmospheric models for HOA + SOA particles should vary depending on the ΔO/C of the HOA and SOA components. As a first-order approximation, a threshold ΔO/C value of 0.265 can be used to predict the number of phases, with one-phase particles predicted for ΔO/C < 0.265 and two-phase particles for ΔO/C ≥ 0.265 at RH between 90% and 0%. In the case of single-phase particles, HOA seed particles cause enhancement of ambient SOA mass concentrations. This is a consequence of the reduced equilibrium partial pressure of an organic molecule in a single-phase internal HOA + SOA mixture, as compared to the higher equilibrium partial pressure of the same organic molecule in the respective pure HOA or pure SOA phases, ultimately enhancing the partitioning of gaseous SOA components into the condensed phase. In the case of two-phase particles, the enhancement of SOA mass will be less, if at all.

The threshold ΔO/C value provides a relatively simple and computationally inexpensive framework for predicting the number of phases in internal SOA and HOA mixtures in atmospheric models, an observation which we anticipate will contribute to improved predictive capabilities for the phase behavior of ambient HOA + SOA particles. Using a threshold ΔO/C of 0.265, we were able to predict the phase behavior of 92% of the HOA + SOA types studied here, with additional information being needed for high-accuracy predictions.

In the absence of information on the O/C ratio of the organic components, the internal mixtures of HOA and SOA are likely best represented by two-phase particles, given the
hence, the dependence of the threshold have some dependence on the SOA volume fraction, and depends on this ratio. It is likely that the threshold than supermicron particles apply to particles with diameters larger than 40 nm, while the phase behavior of particles larger than 40 nm is consistent with the results of supermicron particles. Based on these observations, we expect that the results of our phase behavior experiments using supermicron particles apply to particles with diameters larger than ~40 nm, that is, for a wide range of particle sizes observed in the atmosphere. Nonetheless, future experimental studies are needed to clarify the role of particle size on the phase behavior of HOA + SOA particles.

Another caveat is that our internally mixed HOA + SOA particles were limited to the average SOA volume fractions between approximately 0.11 and 0.4 in the individual experiments. Since we did not systematically vary the SOA volume fraction in our experiments, we were not able to determine if the phase behavior and the threshold ΔO/C depends on this ratio. It is likely that the threshold ΔO/C does have some dependence on the SOA volume fraction, and hence, the dependence of the threshold ΔO/C on the mass mixing ratio of the HOA and SOA components should be investigated in future work. Studies as a function of viscosity of SOA would also be interesting. Viscosity is not expected to limit the phase behavior at the highest RH used here since the viscosity of SOA is most often small at high RH values. On the other hand, at 0% RH and room temperature, viscosity can be large and could limit mixing of the organic material. Additional experiments are needed to investigate the effect of viscosity on the phase behavior of the POA + SOA particles at low RH values.

Future studies are also needed to investigate a more realistic, multi-component HOA material, as well as extending to other POA types including cooking organic aerosol and biomass burning aerosol that denote possible other local sources of POA. Additional studies are also needed to investigate how and on what timescales atmospheric aging affects the O/C ratio of POA and with that the resulting phase behavior of POA + SOA particles. Studies are furthermore needed to extend the work described here to particles containing mixtures of HOA, SOA, and secondary inorganic material (SIA). SIA is abundant in the atmosphere and can be internally mixed with HOA and SOA. Recently, we have shown that internal mixtures of squalane, ammonium sulfate (a SIA proxy), and single-component SOA proxies can form three non-crystalline phases over a wide range of RHs, when the O/C ratio of the SOA proxy was less than 0.8. These results, combined with the results presented here, suggest that three non-crystalline phases may co-exist in HOA + SOA + SIA particles if the average ΔO/C of the organic components is equal to or larger than 0.265 and the average O/C of SOA is less than 0.8. However, future studies are needed to fully elucidate the phase behavior of such mixtures.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c07691.

List of organic materials used as POA proxies, additional experimental details of SOA generation, fluorescence microscopy images of all POA + SOA mixtures, additional details of POA + SOA particle morphology, list of previous studies investigating the POA + SOA particle phase behavior, and additional details of phase volume fraction in POA + SOA particles (PDF)

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Author Contributions
F.M. prepared the manuscript with contributions from all authors. F.M. and A.K.B designed the experiments. Y.H., A.D., and F.M. conducted the phase behavior experiments and analyzed the measurements. Y.Q. and P.E.O. prepared the toluene samples. J.Z. sampled and analyzed the AMS data. L.P. performed confocal microscopy measurements. All authors discussed and interpreted the data and gave their approval for the final version of the manuscript. A.K.B. conceived the idea. A.K.B., M.A., and S.T.M. supervised the overall project.

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Notes
The authors declare no competing financial interest.

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ABBREVIATIONS
LLPS liquid–liquid phase separation
RH relative humidity
T temperature
POA primary organic aerosol
SOA secondary organic aerosol
HOA hydrocarbon-like organic aerosol
O/C elemental oxygen-to-carbon ratio
PM particulate matter
AMS aerosol mass spectrometer
H/C elemental hydrogen-to-carbon ratio

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