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Liquid–liquid phase separation and morphologies in organic particles consisting of α-pinene and β-caryophyllene ozonolysis products and mixtures with commercially available organic compounds

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S1. Liquid-liquid phase separation in one and two organic species

Table S1. Summary of lower RH boundary for LLPS ($LLPS_{lower}$) and upper RH boundary for LLPS ($LLPS_{upper}$) for particles of one organic species with decreasing and increasing RH in this work. Uncertainties represent 2σ of multiple measurements and the uncertainty from the calibration. Also, morphologies of particles after occurrence of LLPS with increasing RH are included. "-" indicates one phase.

Compounds	O:C	Decreasing RH		Increasing RH		Morphologies after LLPS
		$LLPS_{lower}$	$LLPS_{upper}$	$LLPS_{lower}$	$LLPS_{upper}$	
β-caryophyllene aldehyde	0.13	96.1±2.2%	100±1.5%	94.1±1.9%	100±1.5%	Core-shell
β-caryophyllonic acid	0.20	94.9±2.3%	100±1.5%	95.8±2.6%	100±1.5%	Core-shell
Pinonaldehyde	0.20	93.0±1.9%	100±1.5%	94.0±1.7%	100±1.5%	Core-shell
β-nocaryophyllene aldehyde	0.21	93.8±2.7%	100±1.5%	94.7±2.6%	100±1.5%	Core-shell
β-nocaryophyllonic acid	0.29	92.1±1.6%	100±1.5%	95.7±1.7%	100±1.5%	Inclusions
β-caryophyllinic acid	0.29	81.1±3.2%	100±1.5%	84.6±2.1%	100±1.5%	Core-shell
Pinic acid	0.44	95.4±1.9%	100±1.5%	96.8±1.6%	100±1.5%	Core-shell
suberic acid monomethyl ester*	0.44	97.8±2.5%	100±1.5%	98.1±2.2%	100±1.5%	Core-shell
Polyethylene glycol-400 (PEG-400)*	0.56	No LLPS		No LLPS		-
Diethyl L-tartrate*	0.75	No LLPS		No LLPS		-
Pyruvic acid	1.00	No LLPS		No LLPS		-

*This result is consistent with a previous study of Song et al. (2018).

Table S2. Summary of lower RH boundary for LLPS ($LLPS_{lower}$) and upper RH boundary for LLPS ($LLPS_{upper}$) for particles of two organic species with decreasing and increasing RH in this work. Uncertainties represent 2σ of multiple measurements and the uncertainty from the calibration. Also, morphologies of particles after occurrence of LLPS with increasing RH are included. "-" indicates one phase.

Mixtures	Average O:C	|ΔO:C|	Decreasing RH		Increasing RH		Morphologies after LLPS
			$LLPS_{lower}$ (%)	$LLPS_{upper}$ (%)	$LLPS_{lower}$ (%)	$LLPS_{upper}$ (%)	
β-caryophyllene aldehyde / β-caryophyllonic acid	0.16	0.07	95.0±2.4%	100±1.5%	93.3±2.4%	100±1.5%	Core-shell
β-caryophyllene aldehyde / β-nocaryophyllene aldehyde	0.17	0.08	92.5±1.6%	100±1.5%	91.3±1.6%	100±1.5%	Core-shell
β-caryophyllene aldehyde / β-nocaryophyllonic acid	0.20	0.16	93.1±1.7%	100±1.5%	91.4±1.9%	100±1.5%	Core-shell
β-caryophyllonic acid / β-nocaryophyllene aldehyde	0.21	0.01	96.4±2.1%	100±1.5%	95.6±2.1%	100±1.5%	Core-shell
β-caryophyllonic acid / β-nocaryophyllonic acid	0.24	0.09	94.7±2.1%	100±1.5%	94.6±1.8%	100±1.5%	Core-shell, and partially engulfed
β-nocaryophyllonic acid / β-nocaryophyllene aldehyde	0.25	0.08	94.3±1.8%	100±1.5%	92.0±2.0%	100±1.5%	Core-shell

Mixtures	Average O:C	|ΔO:C|	Decreasing RH		Increasing RH		Morphologies after LLPS
			$LLPS_{lower}$ (%)	$LLPS_{upper}$ (%)	$LLPS_{lower}$ (%)	$LLPS_{upper}$ (%)	
β-caryophyllene aldehyde / suberic acid monomethyl ester	0.26	0.31	96.1±2.2%	100±1.5%	95.2±1.8%	100±1.5%	Core-shell
β-caryophyllene aldehyde / Polyethylene glycol-400	0.27	0.43	41.5±1.9%	100±1.5%	39.6±2.3%	100±1.5%	Core-shell
β-caryophyllonic acid / suberic acid monomethyl ester	0.30	0.24	94.0±1.9%	100±1.5%	92.1±1.8%	100±1.5%	Core-shell
β-nocaryophyllene aldehyde / suberic acid monomethyl ester	0.31	0.35	94.1±1.9%	100±1.5%	94.1±1.8%	100±1.5%	Core-shell
β-nocaryophyllonic acid / suberic acid monomethyl ester	0.35	0.27	95.6±1.5%	100±1.5%	94.2±1.7%	100±1.5%	Core-shell
β-caryophyllonic acid / Polyethylene glycol-400	0.35	0.36	82.7±2.5%	100±1.5%	82.4±2.7%	100±1.5%	Core-shell
β-nocaryophyllene aldehyde / Polyethylene glycol-400	0.36	0.35	86.8±2.2%	100±1.5%	86.5±1.7%	100±1.5%	Core-shell
β-caryophyllene aldehyde / Diethyl L-tartrate	0.36	0.62	80.1±2.2%	100±1.5%	81.1±2.8%	100±1.5%	Core-shell
β-nocaryophyllonic acid / Polyethylene glycol-400	0.41	0.27	87.7±3.0%	100±1.5%	87.3±2.7%	100±1.5%	Core-shell

Mixtures	Average O:C	|ΔO:C|	Decreasing RH		Increasing RH		Morphologies after LLPS
			$LLPS_{lower}$ (%)	$LLPS_{upper}$ (%)	$LLPS_{lower}$ (%)	$LLPS_{upper}$ (%)	
β-caryophyllonic acid / Diethyl L-tartrate	0.42	0.55	92.5±2.8%	100±1.5%	90.7±2.7%	100±1.5%	Core-shell
β-nocaryophyllene aldehyde / Diethyl L-tartrate	0.43	0.54	89.8±2.8%	100±1.5%	90.2±2.2%	100±1.5%	Core-shell
β-caryophyllene aldehyde / Pyruvic acid	0.44	0.87	67.1±2.7%	100±1.5%	63.1±2.9%	100±1.5%	Core-shell
β-nocaryophyllonic acid / Diethyl L-tartrate	0.48	0.46	93.1±1.5%	100±1.5%	92.2±2.5%	100±1.5%	Core-shell
β-caryophyllonic acid / Pyruvic acid	0.49	0.8	70.5±2.2%	100±1.5%	70.1±1.5%	100±1.5%	Core-shell
β-nocaryophyllene aldehyde / Pyruvic acid	0.50	0.79	67.1±2.8%	100±1.5%	63.0±2.9%	100±1.5%	Core-shell
β-nocaryophyllonic acid / Pyruvic acid	0.56	0.44	86.1±1.7%	100±1.5%	86.0±2.8%	100±1.5%	Core-shell
suberic acid monomethyl ester / Pyruvic acid	0.67	0.56	87.2±2.8%	100±1.5%	86.5±1.9%	100±1.5%	Core-shell
Polyethylene glycol-400 / Pyruvic acid	0.75	0.44	No LLPS		No LLPS		-
Diethyl L-tartrate / Pyruvic acid	0.87	0.25	No LLPS		No LLPS		-

S2. Morphologies of particle of β-caryophyllonic acid/β-nocaryophyllonic acid after occurrence of LLPS.

Particles of β-caryophyllonic acid/β-nocaryophyllonic acid showed both core-shell and partially engulfed morphologies after LLPS (Fig. S1). Out of 22 particles, 14 particles showed a core-shell morphology (Fig. S1a) while 8 particles showed a partially engulfed morphology (Fig. S1b).

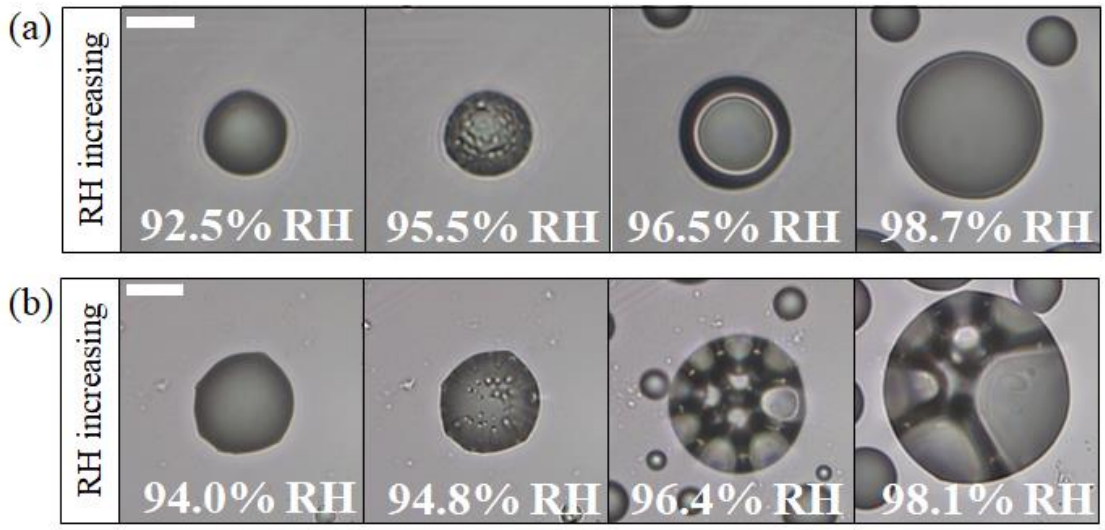

Figure S1. Optical images of particles of β-caryophyllonic acid/β-nocaryophyllonic acid for increasing RH: (a) a core-shell morphology after LLPS, (b) a partially engulfed morphology after LLPS. The scale bar is 20 µm.

S3. Parameterization of relative humidity of liquid-liquid phase separation

Parameterization of the $LLPS_{lower}$ and $LLPS_{upper}$ as a function of O:C ($0.0 \leq$ O:C < 0.68) was obtained using Sigmoidal–Boltzmann curve fits to data from Song et al. (2018) and this study at 291 ± 1K (Fig. 3b).

$$\text{RH of } \text{LLPS}_{\text{lower}}\ (\%) = (-17.2) + \left(\frac{105.8}{1 + \exp\left(\frac{(\text{the O:C ratio}) - 0.68}{dx}\right)}\right)$$

$$\text{RH of } \text{LLPS}_{\text{upper}}(\%) = \left(\frac{100}{1 + \exp\left(\frac{(\text{the O:C ratio}) - 0.68}{dx}\right)}\right)$$

References

Song, M., Ham, S., Andrews, R. J., You, Y. and Bertram, A. K.: Liquid-liquid phase separation in organic particles containing one and two organic species: importance of the average O:C, Atmos. Chem. Phys., doi:10.5194/acp-18-12075-2018, 2018.