

Supplementary of

**Liquid–liquid phase separation in organic particles consisting of α -
pinene and β -caryophyllene ozonolysis products and mixtures with
5 highly oxidized organic compounds**

Young-Chul Song et al.,

Correspondence to: Mijung Song (mijung.song@jbnu.ac.kr)

10 **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.

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Compounds	O:C	Increasing RH		Decreasing RH	
		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%
β-caryophyllonic acid	0.20	94.9±2.3%	100±1.5%	95.8±2.6%	100±1.5%
Pinonaldehyde	0.20	93.0±1.9%	100±1.5%	94.0±1.7%	100±1.5%
β-nocaryophyllene aldehyde	0.21	93.8±2.7%	100±1.5%	94.7±2.6%	100±1.5%
β-nocaryophyllonic acid	0.29	92.1±1.6%	100±1.5%	95.7±1.7%	100±1.5%
β-caryophyllinic acid	0.29	81.1±3.2%	100±1.5%	84.6±2.1%	100±1.5%
Pinic acid	0.44	95.4±1.9%	100±1.5%	96.8±1.6%	100±1.5%
suberic acid monomethyl ester*	0.44	97.8±2.5%	100±1.5%	98.1±2.2%	100±1.5%
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.

20 Uncertainties represent 2 σ of multiple measurements and the uncertainty from the calibration.

Mixtures	Average O:C	Δ O:C	Increasing RH		Decreasing RH	
			LLPS _{lower} (%)	LLPS _{upper} (%)	LLPS _{lower} (%)	LLPS _{upper} (%)
β -caryophyllene aldehyde / β -caryophyllonic acid	0.16	0.07	95.0 \pm 2.4%	100 \pm 1.5%	93.3 \pm 2.4%	100 \pm 1.5%
β -caryophyllene aldehyde / β -nocaryophyllene aldehyde	0.17	0.08	92.5 \pm 1.6%	100 \pm 1.5%	91.3 \pm 1.6%	100 \pm 1.5%
β -caryophyllene aldehyde / β -nocaryophyllonic acid	0.20	0.16	93.1 \pm 1.7%	100 \pm 1.5%	91.4 \pm 1.9%	100 \pm 1.5%
β -caryophyllonic acid / β -nocaryophyllene aldehyde	0.21	0.01	96.4 \pm 2.1%	100 \pm 1.5%	95.6 \pm 2.1%	100 \pm 1.5%
β -caryophyllonic acid / β -nocaryophyllonic acid	0.24	0.09	94.9 \pm 1.6%	100 \pm 1.5%	93.7 \pm 1.6%	100 \pm 1.5%
β -nocaryophyllonic acid / β -nocaryophyllene aldehyde	0.25	0.08	94.3 \pm 1.8%	100 \pm 1.5%	92.0 \pm 2.0%	100 \pm 1.5%
β -caryophyllene aldehyde / suberic acid monomethyl ester	0.26	0.31	96.1 \pm 2.2%	100 \pm 1.5%	95.2 \pm 1.8%	100 \pm 1.5%
β -caryophyllene aldehyde / Polyethylene glycol-400	0.27	0.43	41.5 \pm 1.9%	100 \pm 1.5%	39.6 \pm 2.3%	100 \pm 1.5%
β -caryophyllonic acid / suberic acid monomethyl ester	0.30	0.24	94.0 \pm 1.9%	100 \pm 1.5%	92.1 \pm 1.8%	100 \pm 1.5%
β -nocaryophyllene aldehyde / suberic acid monomethyl ester	0.31	0.35	94.1 \pm 1.9%	100 \pm 1.5%	94.1 \pm 1.8%	100 \pm 1.5%
β -nocaryophyllonic acid / suberic acid monomethyl ester	0.35	0.27	95.6 \pm 1.5%	100 \pm 1.5%	94.2 \pm 1.7%	100 \pm 1.5%
β -caryophyllonic acid / Polyethylene glycol-400	0.35	0.36	82.7 \pm 2.5%	100 \pm 1.5%	82.4 \pm 2.7%	100 \pm 1.5%
β -nocaryophyllene aldehyde / Polyethylene glycol-400	0.36	0.35	86.8 \pm 2.2%	100 \pm 1.5%	86.5 \pm 1.7%	100 \pm 1.5%

Mixtures	Average O:C	ΔO:C	Increasing RH		Decreasing RH	
			LLPS _{lower} (%)	LLPS _{upper} (%)	LLPS _{lower} (%)	LLPS _{upper} (%)
β-caryophyllene aldehyde / Diethyl L-tartrate	0.36	0.62	80.1±2.2%	100±1.5%	81.1±2.8%	100±1.5%
β-nocaryophyllonic acid / Polyethylene glycol-400	0.41	0.27	87.7±3.0%	100±1.5%	87.3±2.7%	100±1.5%
β-caryophyllonic acid / Diethyl L-tartrate	0.42	0.55	92.5±2.8%	100±1.5%	90.7±2.7%	100±1.5%
β-nocaryophyllene aldehyde / Diethyl L-tartrate	0.43	0.54	89.8±2.8%	100±1.5%	90.2±2.2%	100±1.5%
β-caryophyllene aldehyde / Pyruvic acid	0.44	0.87	67.1± 2.7%	100±1.5%	63.1± 2.9%	100±1.5%
β-nocaryophyllonic acid / Diethyl L-tartrate	0.48	0.46	93.1±1.5%	100±1.5%	92.2±2.5%	100±1.5%
β-caryophyllonic acid / Pyruvic acid	0.49	0.8	70.5± 2.2%	100±1.5%	70.1±1.5%	100±1.5%
β-nocaryophyllene aldehyde / Pyruvic acid	0.50	0.79	67.1± 2.8%	100±1.5%	63.0± 2.9%	100±1.5%
β-nocaryophyllonic acid / Pyruvic acid	0.56	0.44	86.1±1.7%	100±1.5%	86.0±2.8%	100±1.5%
suberic acid monomethyl ester / Pyruvic acid	0.67	0.56	87.2±2.8%	100±1.5%	86.5±1.9%	100±1.5%
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. Parameterization of relative humidity of liquid-liquid phase separation

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

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

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

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.