Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information: Predicting liquid-liquid phase separation in ternary organic–organic–water mixtures

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S1 Comparing COSMO*therm* calculations with experiments

Song et al.[S1] studied the occurrence of LLPS in particles containing a single organic compound at varying relative humidities. They detected LLPS in diethyl sebacate (DES) particles at relative humidities higher than 97.7 ± 3.1 % at 290 K. The measured solubility of DES in water is 5.6×10^{-6} mole fraction at 293 K.[S2] COSMO*therm* predicts a solubility of 3.0×10^{-6} mole fraction at 296 K, when conformers of DES are selected based on their chemical potentials in water and pure compound. If only conformers with lowest chemical potentials in water are used for DES, COSMO*therm* predicts 2.1×10^{-4} mole fraction solubility in water, which is much higher than the experimental value. In the latter case, the mixing of water and DES is more favorable than in the former case. At LLPS, the COSMO*therm*-derived water activity is very close to unity. This indicates that the relative humidity needed for phase separation is close to 100 %, which is in agreement with the experimental result of Song et al.[S1]

Kołodziejczyk et al.[S3,S4] measured the aqueous solubilities of cis-pinonic acid, diaterpenylic acid acetate (DTAA) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) at various temperatures, as well as their melting temperatures and enthalpies of fusion. At the lowest temperatures, 319.39 K for cis-pinonic acid, 303.69 K for DTAA and 308.15 K for MBTCA, the aqueous solubilities were 0.002, 0.00314 and 0.04 in mole fraction, respectively. COSMO*therm*-derived solubilities at the corresponding temperatures are 0.0035, 0.0032 and 0.00034 mole fraction for cis-pinonic acid, DTAA and MBTCA, respectively. For DTAA, Kołodziejczyk et al.[S4] found a solid-solid phase transition close to the melting temperature. The solid-solid phase transition enthalpy was therefore added to the enthalpy of fusion of DTAA in the COSMO*therm* solubility calculation to account for the enthalpy change from crystalline solid to liquid phase. Additionally, Kołodziejczyk et al.[S4] noted that the heat of fusion of MBTCA was higher than of other α-pinene SOA constituents. This explains the

discrepancy between the measured and computed aqueous solubilities of MBTCA. Using a lower heat of fusion for MBTCA in COSMO*therm* solubility calculation leads to a better agreement with the experimental aqueous solubility. The heat of fusion of MBTCA would have to be around 46 kJ/mol lower than what was measured by Kołodziejczyk et al.[S4] to obtain the same aqueous solubility from calculations and measurements.

Table S1: Liquid-liquid phase separation behaviors of ternary solutions at 296 K. Color coding: Blue - LLPS at RH > 99%, Magenta - LLPS at RH < 99% RH, Red - LLPS at all RH. The numbers indicate the maximum number of liquid phases in the mixture. The molecules are ordered by molecular weight (MW in g/mol).

SMILES	MW	octanol	WIOM	DES	DOP
OCC(O)CO glycerol	92.09	2	2	2	2
OC(=O)C=CC(O)=O maleic acid	116.07	2	2	2	2
CC1(CO)OC1CO *cis/trans*-β-IEPOX	118.13	2	2	2	2
CC(O)(CO)C1CO1 δ_1-IEPOX	118.13	2	2	2	2
CC1(CO1)C(O)CO δ_4-IEPOX	118.13	2	2	2	2
CC1(C)C(C1C(O)=O)C(O)=O caronic acid	158.15	2	2	2	2
OC(CC(O)C(O)=O)C(O)=O	164.11	2	2	2	2
OOC(CCC(O)=O)C(O)=O	164.11	2	2	2	2
CC(=O)C1CC(CC(O)=O)C1(C)C *cis*-pinonic acid	184.23	2	2	2	3
CC1(C)C(CC(O)=O)C1CC(O)=O	186.20	2	2	2	3
CC1(C)C(CC1C(O)=O)CC(O)=O	186.20	2	2	2	3
CC(C)(CCC(O)C(O)=O)C(O)=O	188.18	2	1	2	2
CC(=O)C(O)C(O)CC(=O)C(O)=O	190.15	2	2	2	2
CC(C)(C(O)=O)C(=O)CC(=O)OO	190.15	2	2	2	2
OCC(=O)CC(=O)C(O)C(=O)CO	190.15	2	2	2	2
CC(C=O)C(O)COS(O)(=O)=O	198.19	2	2	2	3
CC1(C)C(CC(O)=O)C1CC(=O)CO	200.23	2	2	2	2
OOC(=O)C1CC(C1)C(=O)CC(O)=O	202.16	2	2	2	2
CC(=O)C(C(O)=O)C(C)(C)C(=O)OO	204.18	2	2	2	2
CC(C)(C(CC(O)=O)C(O)=O)C(O)=O	204.18	2	2	2	2
CC1(C)C(O)C(O)C(O)C(=O)OC1=O	204.18	2	2	2	2
CC(C)(C(=O)CC(=O)OO)C(=O)OO	206.15	2	2	2	2
CC(C)(C(O)=O)C(=O)C(OO)C(O)=O	206.15	2	2	2	2
CC(C)(C(O)C(OO)C(O)=O)C(O)=O	206.15	2	2	2	2
OC(C1CC(C1)C(=O)CC(O)=O)C(O)=O	216.19	2	2	2	2
OOC(=O)CC1CC(C1)C(=O)CC(O)=O	216.19	2	2	2	3
CC(C)(C(CC(=O)OO)C(O)=O)C(O)=O	220.18	2	2	2	2
CC(C)(C(O)C(O)C(O)C(O)=O)C(O)=O	220.18	2	2	2	2
CC(C)=C(CC(O)=O)C(OO)C(=O)OO	220.18	2	2	2	2
CC1(C)C(O)C(OO)C1C(=O)C(=O)OO	220.18	2	2	2	2
CC1(C)OC(=O)CC1C(OO)C(=O)OO	220.18	2	2	2	2
CC(=O)C1CC(OOC1(C)C)C(=O)C(O)=O	230.21	2	2	2	3
CC1(C)C(CC1C(=O)C(O)=O)C(O)C(O)=O	230.21	2	2	2	2
CC(=O)C(=O)CC(CC(=O)OO)C(C)(C)O	232.23	2	2	2	3
CC(=O)C1CC(OOC1(C)C)C(O)C(O)=O	232.23	2	2	2	2

Table S1 – continued from previous page

SMILES	*MW*	octanol	WIOM	DES	DOP
CC(=O)OC(C)(C)C(CC(O)=O)CC(O)=O	232.23	2	2	2	3
CC1(C)C(CC1C(=O)CO)C(OO)C(O)=O	232.23	2	2	2	2
OC(CC(=O)C(O)=O)C(O)C(=O)CC(O)=O	234.16	2	2	2	2
CC(=O)C(=O)C(O)C(C(O)=O)C(C)(C)OO	234.20	2	2	2	3
CC(=O)C1(CC(OOC1(C)C)C(O)=O)OO	234.20	2	2	2	2
CC(=O)C1(O)CC(OOC1(C)C)C(=O)OO	234.20	2	2	2	3
CC1(C)C(CC1C(=O)OO)C(OO)C(O)=O	234.20	2	2	2	2
CC(=O)C(CC(=O)C(=O)C(=O)OO)C(C)(C)O	246.21	2	2	2	3
CC(=O)C(CC(=O)C(=O)C(O)=O)C(C)(C)OO	246.21	2	2	2	3
CC(=O)C1(O)CC(OOC1(C)C)C(=O)C(O)=O	246.21	2	2	2	2
CC(=O)C1CC(OOC1(C)C)C(=O)C(=O)OO	246.21	3	2	2	3
CC1(C)C(CC1C(=O)C(=O)OO)C(O)C(O)=O	246.21	2	2	2	2
CC(C)(C(C(O)=O)C(=O)CC(O)=O)C(=O)OO	248.19	2	2	2	2
CC(=O)C(C(O)C(=O)C(=O)C(O)=O)C(C)(C)OO	262.21	2	2	2	2
CC(=O)C(CC(=O)C(=O)C(=O)OO)C(C)(C)OO	262.21	2	2	2	2
CC(=O)C1C(=O)C(OOC1(C)C)C(OO)C(O)=O	262.21	2	2	2	2
CC1(C)C(CC1C(=O)C(=O)OO)C(O)C(=O)OO	262.21	2	2	2	2
CC1(C)C(CC1C(=O)C(O)=O)C(OO)C(=O)OO	262.21	2	2	2	2
CC(=O)C1(O)C(O)C(OOC1(C)C)C(O)C(O)=O	264.23	2	2	2	2
CC(=O)C1CC(OOC1(C)C)C(OO)C(=O)OO	264.23	2	2	2	3
CC(=O)OC(C)(C)C(CC(O)=O)C(OO)C(O)=O	264.23	2	2	2	2
CC1(C)C(CC1C(=O)COO)C(OO)C(=O)OO	264.23	2	2	2	2
CC(C)(OO)C(C(OO)C(O)COO)C(=O)COO	286.23	2	2	2	2
CC1(C)OOC(COO)C(OO)C1C(COO)OO	286.23	2	2	2	2
OOC(=O)CCCC(OOC(CCCC=O)C=O)C=O	290.27	3	2	2	3
OOC(CCCC(=O)OOC(CCCC=O)C=O)C=O	290.27	3	2	2	3
OC(CCCC(=O)OOC(O)C(O)CCCC=O)C=O	292.28	2	2	2	2
OC(CCCC(O)C=O)OOC(=O)CCCC(O)C=O	292.28	2	2	2	2
OOC(CCCC(O)OOC(CCCC=O)C=O)C=O	292.28	2	2	3	2
OOC(CCCC=O)C(O)OOC(CCCC=O)C=O	292.28	2	2	2	2
CC(=O)C(CC(=O)C(=O)C(=O)OO)(OO)C(C)(C)OO	294.21	2	2	2	2
CC(=O)C(O)(C(OO)C(=O)C(=O)C(=O)OO)C(C)(C)O	294.21	2	2	2	2
CC(=O)C1(OO)C(=O)C(OOC1(C)C)C(O)C(=O)OO	294.21	2	2	2	2
CC(=O)C1(OO)C(=O)C(OOC1(C)C)C(OO)C(O)=O	294.21	2	2	2	2
OOC(=O)C(O)CCCC(=O)OOC(=O)CCCC(O)C=O-R,S	322.26	3	2	2	3
OOC(=O)C(O)CCCC(=O)OOC(=O)CCCC(O)C=O-S,S	322.26	2	2	2	3
OOC(=O)CCCC(OOC(CCCC(=O)OO)C=O)C=O-R,S	322.26	3	2	2	3
OOC(=O)CCCC(OOC(CCCC(=O)OO)C=O)C=O-S,S	322.26	3	2	2	2

Table S1 – continued from previous page

SMILES	*MW*	octanol	WIOM	DES	DOP
OOC(=O)CCCC(OOC(CCCC=O)C=O)C(=O)OO-R,S	322.26	3	2	2	3
OOC(=O)CCCC(OOC(CCCC=O)C=O)C(=O)OO-S,S	322.26	3	2	2	2
OOC(CCC(OOC(CCCC=O)C=O)C(=O)OO)C=O	322.26	3	2	2	3
OOC(=O)C(O)CCCC(=O)OOC(O)C(O)CCCC=O	324.28	2	3	3	3
OOC(=O)C(O)CCCC(=O)OOC(O)CCCC(O)C=O	324.28	2	2	2	2
OOC(=O)CCCC(O)C(O)OC(CCCC(=O)OO)C=O	324.28	3	2	2	3
OOC(=O)CCCC(O)C(O)OOC(=O)CCCC(O)C=O	324.28	3	3	3	3
OOC(CCCC(=O)OO)C(O)OOC(CCCC=O)C=O	324.28	2	2	2	3
OOC(CCCC(O)OOC(=O)CCCC(OO)C=O)C=O	324.28	2	3	3	3
OOC(CCCC(O)OOC(CCCC(=O)OO)C=O)C=O	324.28	2	2	2	3
OOC(CCCC=O)C(O)OOC(CCCC(=O)OO)C=O	324.28	3	2	2	3
CC(=O)C1CC(CC(=O)OC(=O)C(O)CC(O)C(O)=O)C1(C)C	330.33	2	2	2	2
CC1(C)OC(=O)CC1C(O)C(O)OC(=O)C1CC(=O)OC1(C)C	330.33	2	2	2	2
CC1(C)C(CC=O)CC1C(=O)OC(=O)CC1CC(C(O)=O)C1(C)C $C_{18}H_{26}O_6$	338.40	2	2	2	2
CC1(C)C2CC1C(C)(O)C(=O)C2OC(=O)C1CC(C(O)=O)C1(C)C	338.40	2	2	2	3
CC1(C)C(CC(O)C(C=O)C2CC(C=O)C2(C)C)CC1CC(O)=O	338.44	2	2	2	3
OOC(=O)CCCC(OOC(CCCC(=O)OO)C(=O)OO)C=O	354.26	3	2	2	2
OOC(CCC(OOC(CCCC(=O)OO)C=O)C(=O)OO)C=O	354.26	3	2	3	3
OOC(CCCC(=O)OO)C(O)OOC(CCCC(=O)OO)C=O	356.28	2	2	2	3
OOC(CCCC(=O)OOC(O)C(CCCC(=O)OO)OO)C=O	356.28	3	2	2	3
CC1(C)C(CC1C(O)=O)C(OOC(=O)C1CC(=O)OC1(C)C)C(O)=O	358.34	2	2	2	3
OOC(CCC(OOC(CCCC(=O)OO)C(=O)OO)C(=O)OO)C=O	386.26	3	2	2	2
OOC(CCC(OO)C(=O)OOC(O)C(CCCC(=O)OO)OO)C=O	388.27	3	2	2	3
CC1(C)C(CC(O)=O)CC1C(=O)C(O)OCC(=O)C(O)C(=O)CC(=O)CO	388.37	2	2	2	2
CC1(C)C(CC1C(=O)CO)C(OOCC(=O)CC(=O)CC(=O)CO)C(O)=O	388.37	2	2	2	2
CC1(C)C(CC1C(=O)OO)C(OO)C(=O)OC(=O)CC1CC(=O)OC1(C)C	388.37	2	2	2	3
CC1(C)C(CC1C(O)=O)CC(=O)OC(OO)C(=O)C2CC(CC(O)=O)C2(C)C	400.42	2	2	2	2

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