Electronic supplementary information (ESI)

Does liquid-liquid phase separation impact ice nucleation in mixed polyethylene glycol and ammonium sulfate droplets?

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Supplemental Figures：

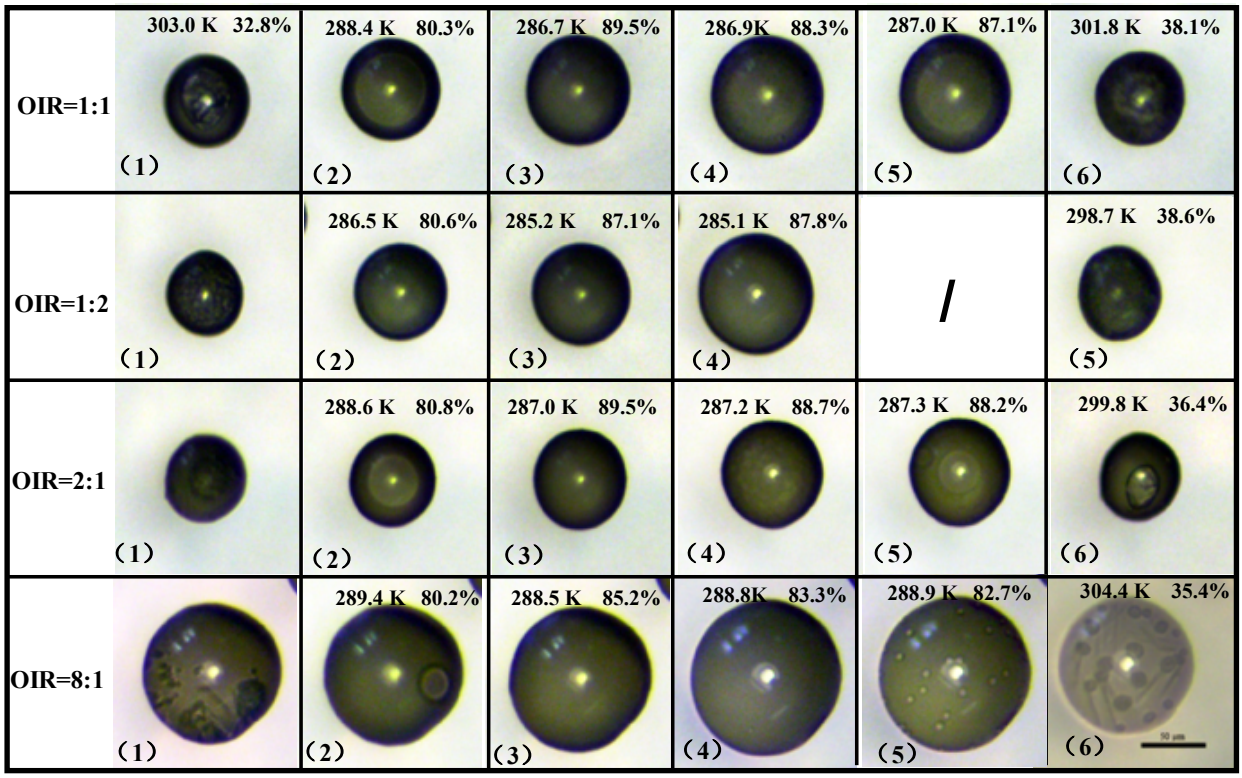

Figure S1. Typical observed morphologies of PEG400-AS (OIR=1:1, 1:2, 2:1, 8:1) particles at different RH. (1)-(3) indicate hydration process: (1) PEG400-AS particles at low RH; (2) PEG400-AS particles took up water after AS deliquescence; (3) PEG400-AS droplets in one-liquid phase. (4)-(6) indicate dehydration process: (4) Onset of LLPS within PEG400-AS droplets (first appearance of LLPS); (5) PEG400-AS droplets with LLPS except for OIR=1:2; (6) AS crystallized in the droplets. Scale bar is 50 μm.

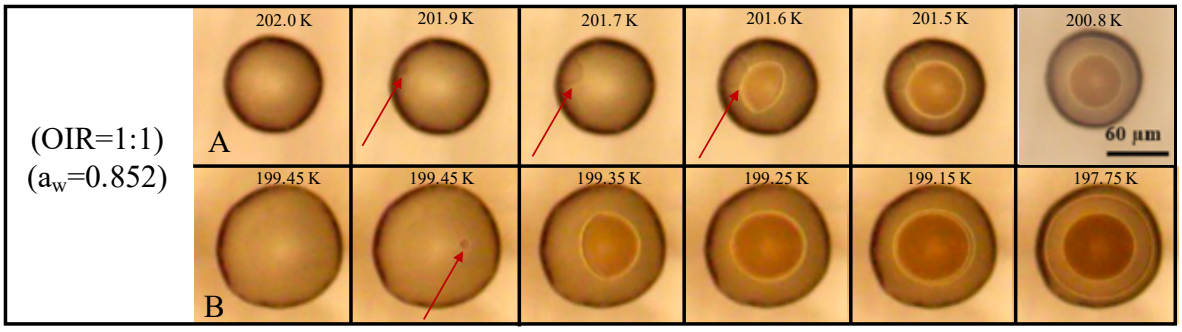

Figure S2. Ice nucleation occurred in the outside phase (A) and the inner phase (B) for PEG400-AS droplets (OIR=1:1) at a_w of 0.852. Red arrows indicate nucleation of ice. Scale bar is 60 μm.

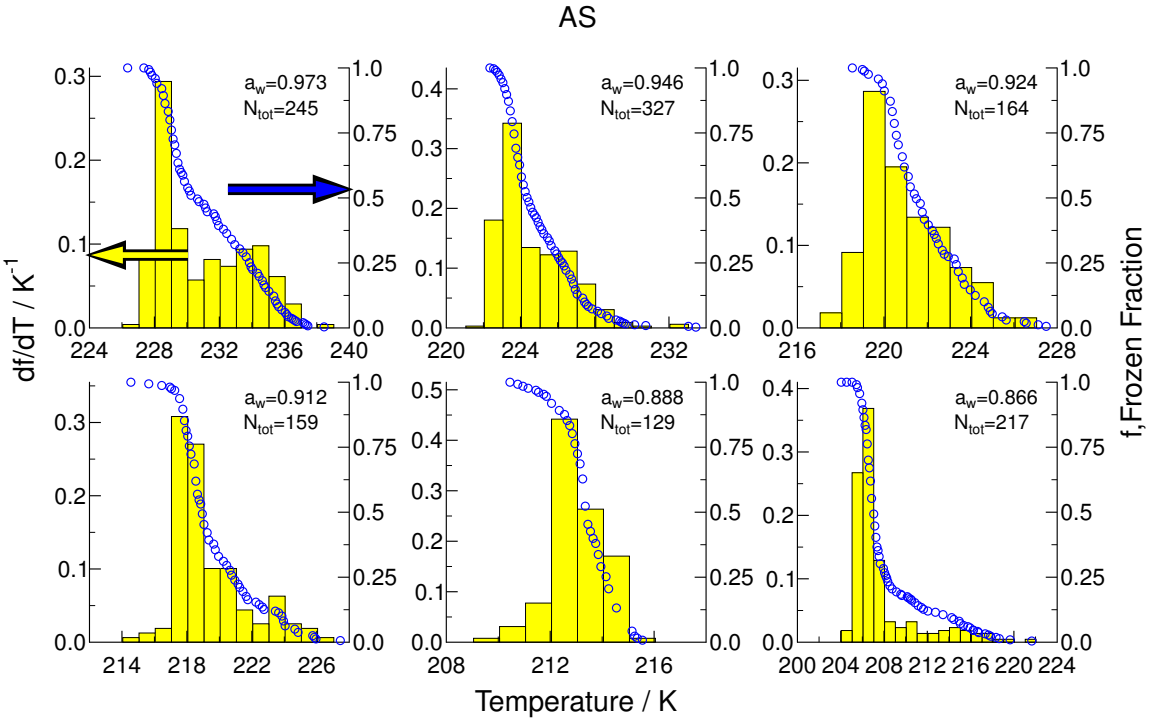

Figure S3. Summary of all observed ice nucleation events in AS droplets as a function of a_w and temperature (T). Frozen fraction (f) is represented by blue circles (right y-axis). Yellow bars show the probability density histogram (PDH) of nucleation events binned in 1.0 K increments (left y-axis). For each panel, a_w and the total number of analyzed droplets (N_{tot}) are given.

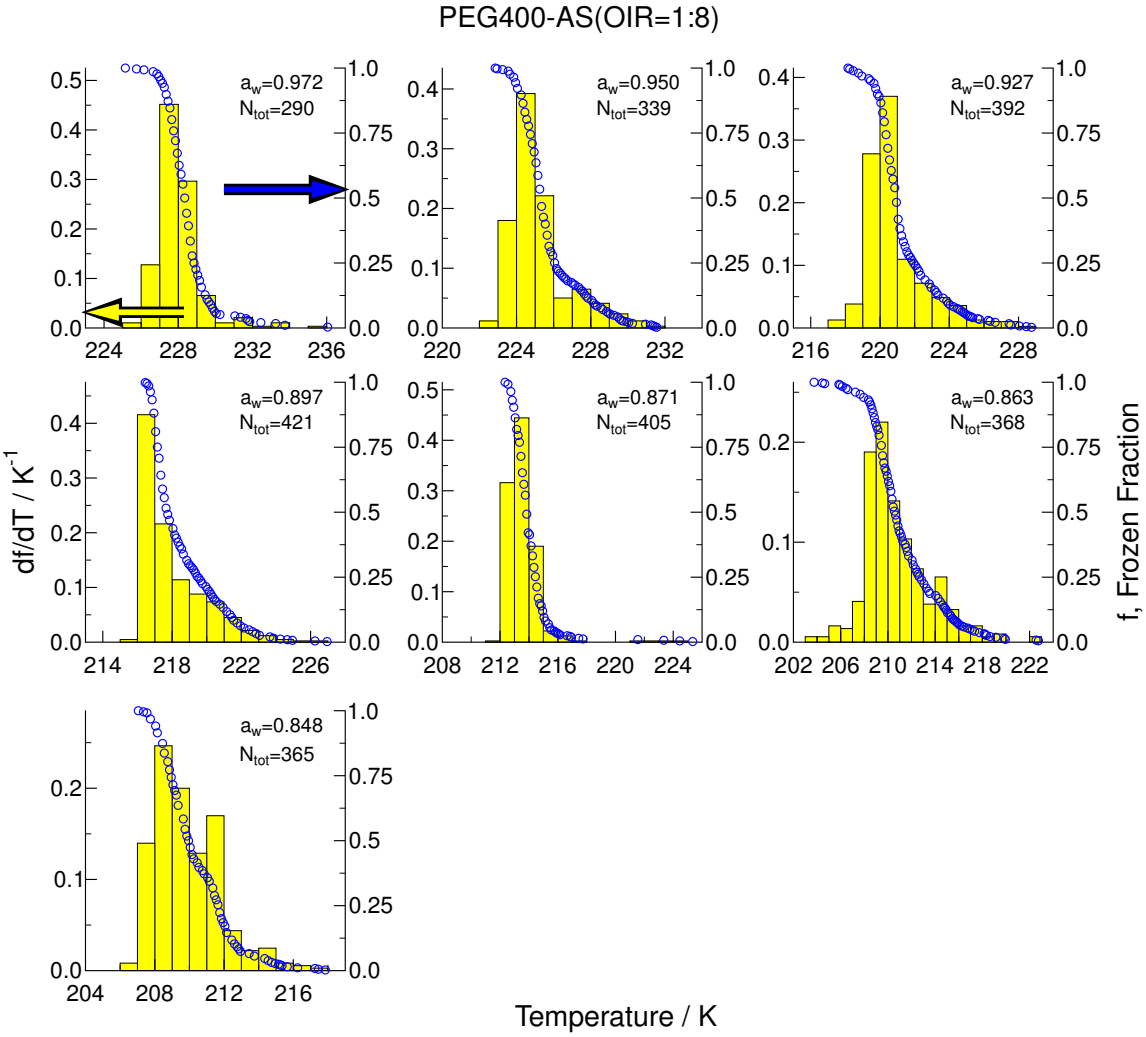

Figure S4. Summary of all observed homogeneous ice nucleation events in PEG400-AS droplets (OIR=1:8) as a function of a_w (see panel legend) and temperature. The lines and bars represent the same variables as indicated in the caption of Figure S3.

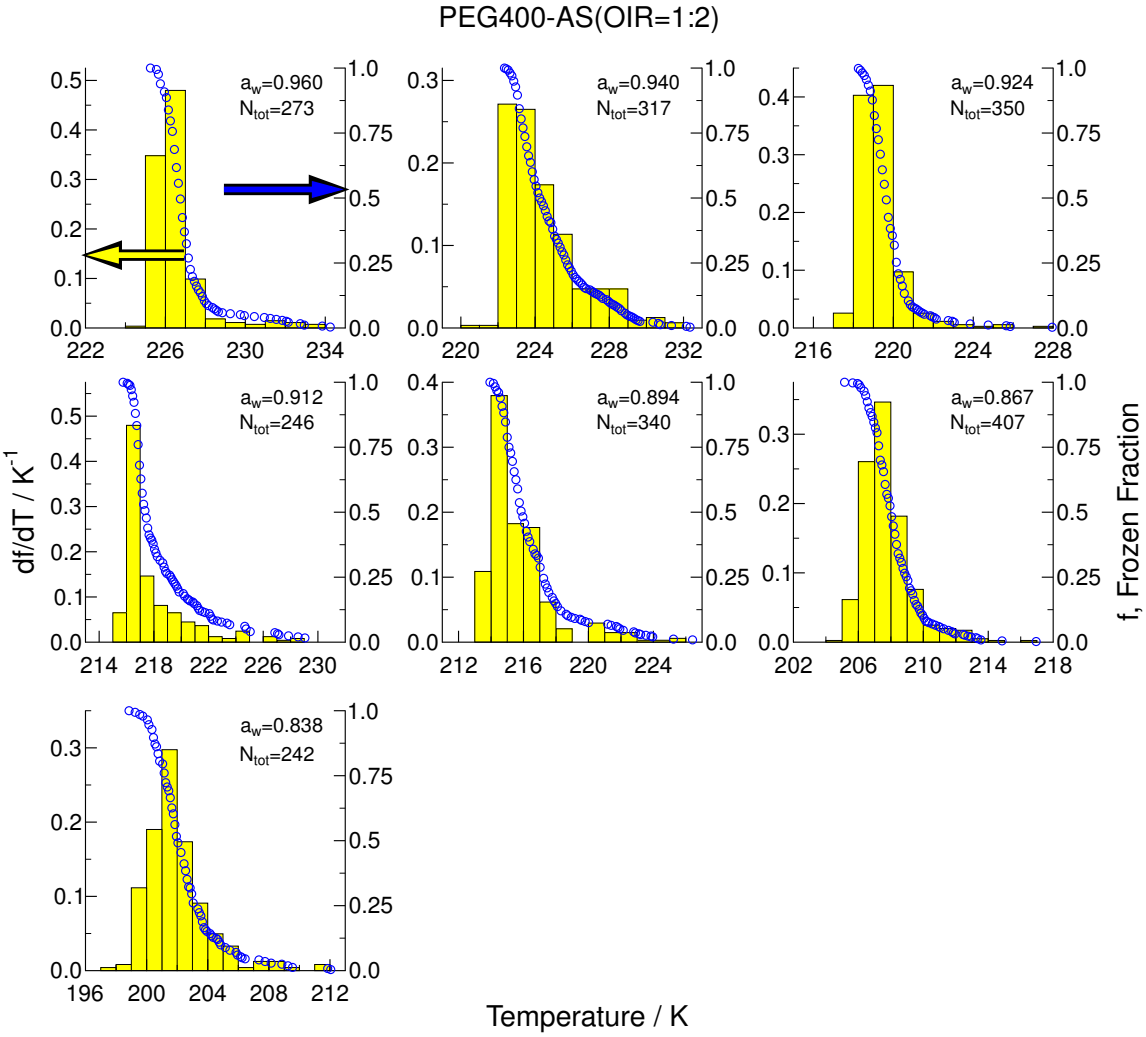

Figure S5. Summary of all observed homogeneous ice nucleation events in PEG400-AS droplets (OIR=1:2) as a function of a_w (see panel legend) and temperature. The lines and bars represent the same variables as indicated in the caption of Figure S3.

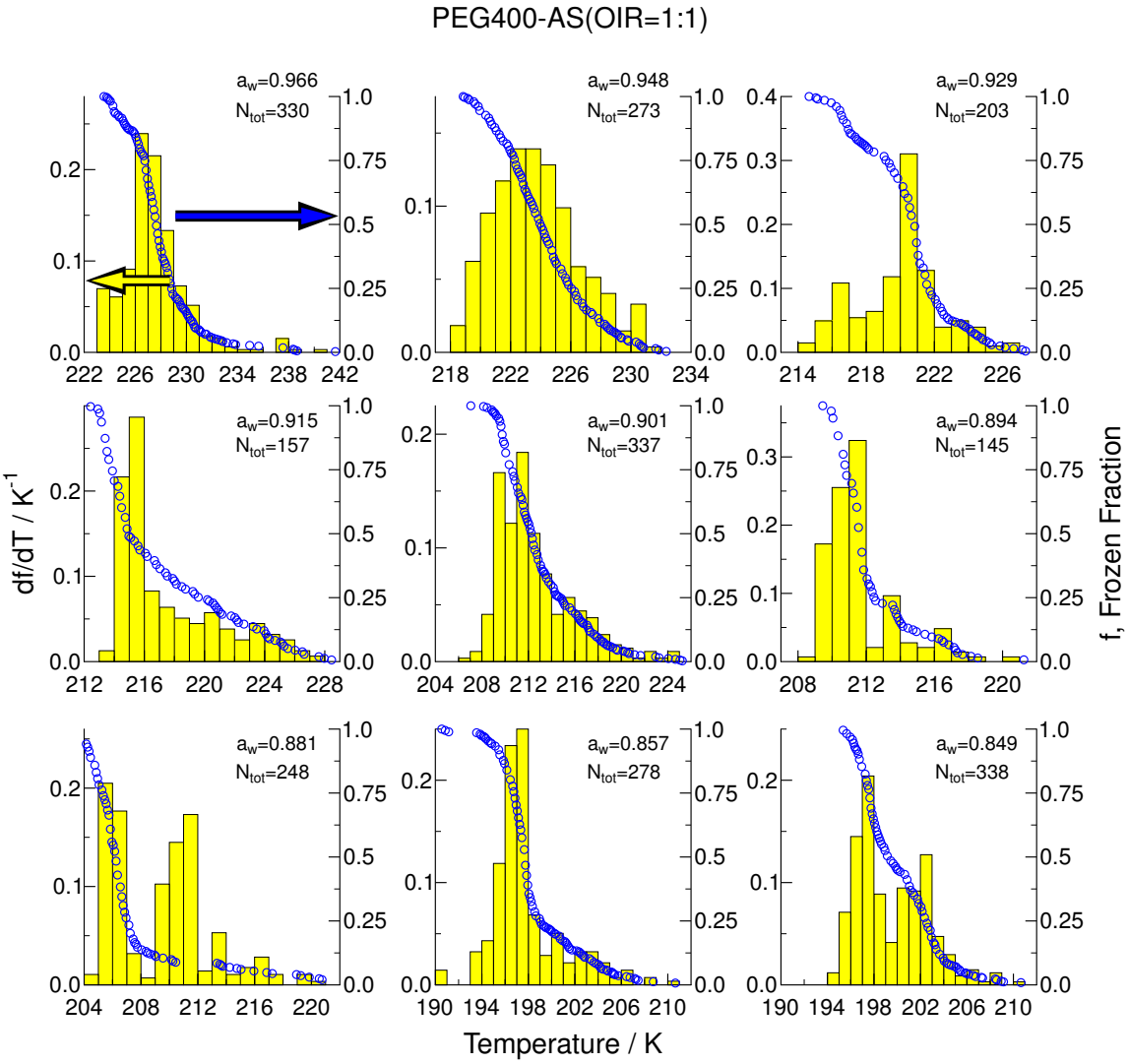

Figure S6. Summary of all observed homogeneous ice nucleation events in PEG400-AS droplets (OIR=1:1) as a function of a_w (see panel legend) and temperature. The lines and bars represent the same variables as indicated in the caption of Figure S3.

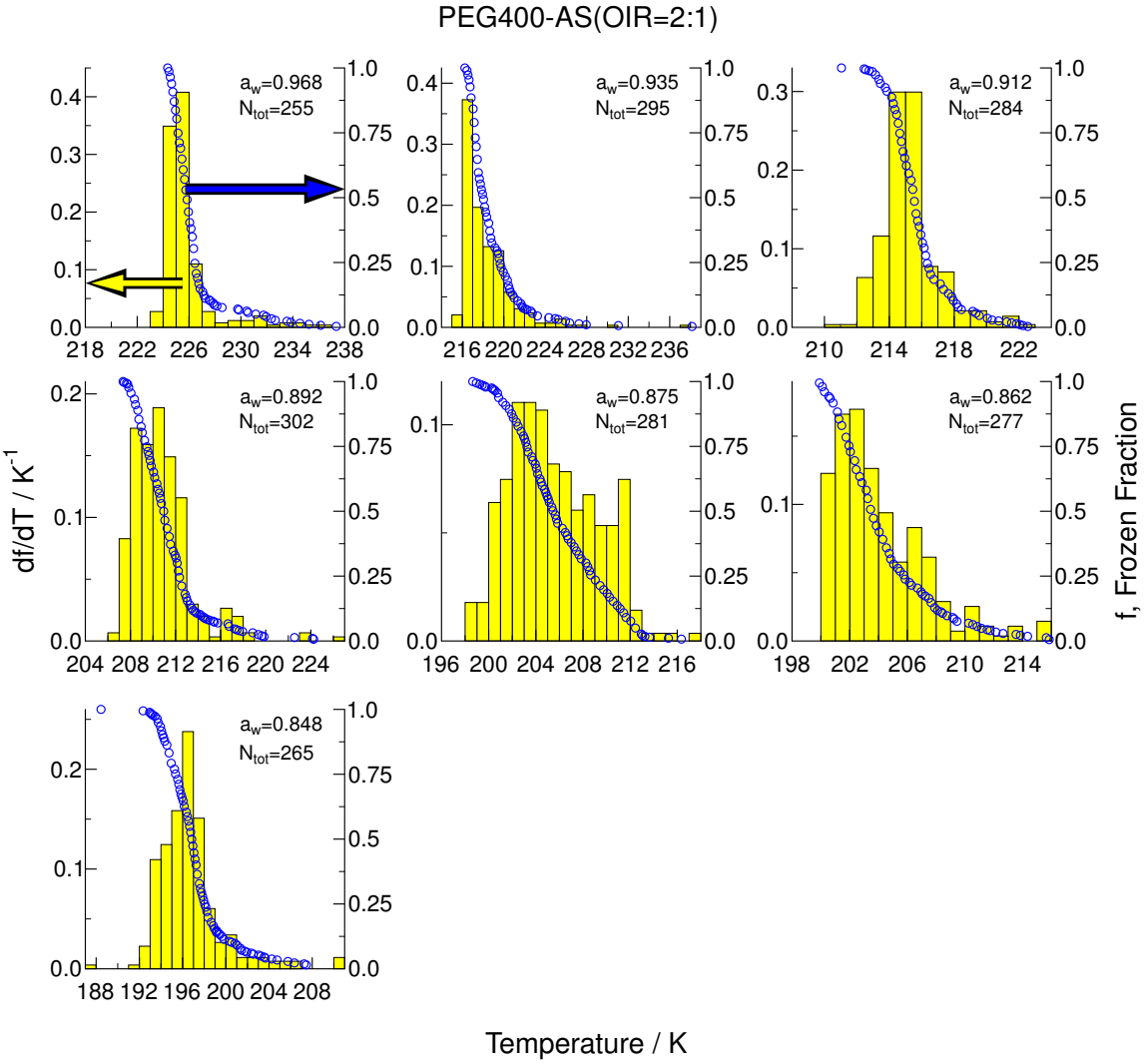

Figure S7. Summary of all observed homogeneous ice nucleation events in PEG400-AS droplets (OIR=2:1) as a function of a_w (see panel legend) and temperature. The lines and bars represent the same variables as indicated in the caption of Figure S3.

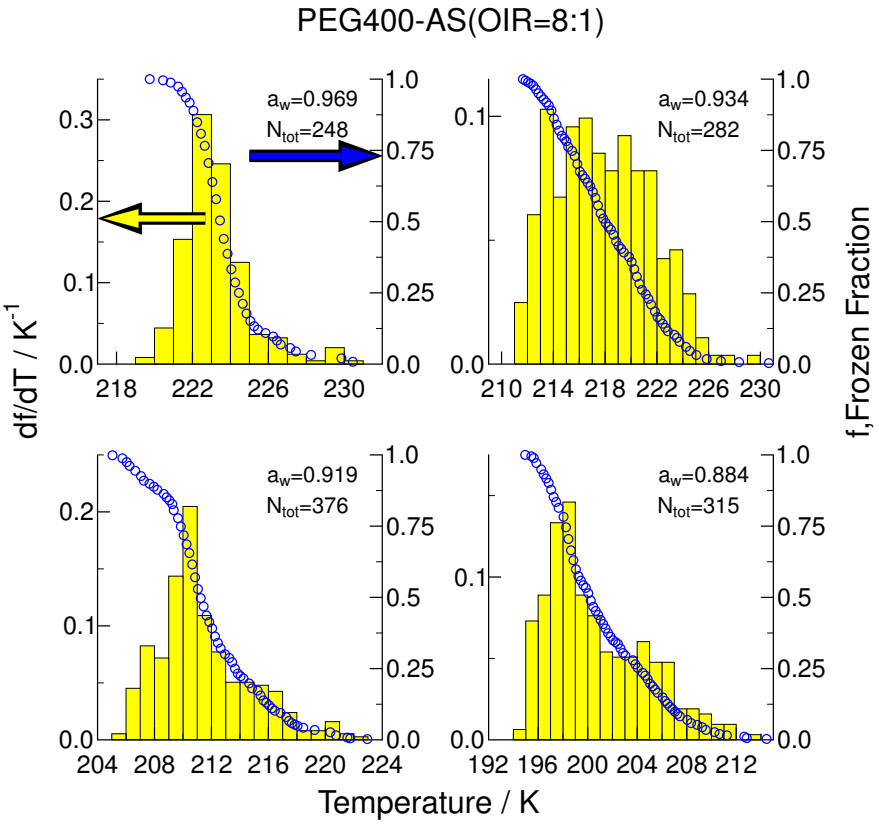

Figure S8. Summary of all observed homogeneous ice nucleation events in PEG400-AS droplets (OIR=8:1) as a function of a_w (see panel legend) and temperature. The lines and bars represent the same variables as indicated in the caption of Figure S3.

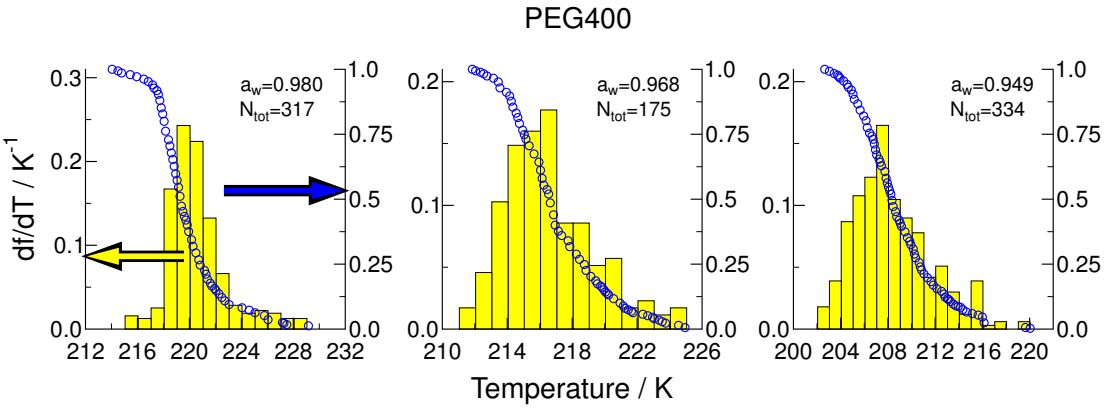

Figure S9. Summary of all observed homogeneous ice nucleation events in PEG400 droplets as a function of a_w (see panel legend) and temperature. The lines and bars represent the same variables as indicated in the caption of Figure S3.

Table S1. Summary of median freezing temperature (T_f) with the corresponding 10th percentile (T_{10}) and 90th percentile (T_{90}), mean melting temperature (T_m) with one standard deviation (T_m std.), the experimentally determined J_{hom} (J_{hom}^{exp}) and the predicted J_{hom} by the water-activity-based theory[2] (J_{hom}^{pre}) at median T_f for pure water, aqueous AS, PEG400, and PEG400-AS droplets at different OIRs and water activity (a_w) at the preparation conditions (~287 K) used in Figure 5 and Figure 8.

	a_w	T_f (K)	T_{90} - T_f (K)	$T_f - T_{10}$ (K)	T_m (K)	T_m std. (K)	J_{hom}^{exp} (cm^{-3} s^{-1})	J_{hom}^{pre} (cm^{-3} s^{-1})
Water	1.00	236.15	0.30	0.40	273.15	0.20	4.05E+06	1.01E+09
AS	0.973	230.45	1.50	3.92	269.46	0.22	3.55E+04	1.24E+09
	0.946	224.35	0.80	2.30	267.01	0.30	7.39E+05	2.72E+10
	0.924	220.90	1.05	2.23	265.09	0.53	4.63E+05	2.06E+09
	0.912	218.95	0.90	2.38	264.46	0.79	1.82E+05	4.36E+08
	0.888	213.35	0.50	0.90	261.08	0.87	1.49E+06	2.44E+08
	0.866	207.05	0.60	1.70	258.64	0.46	4.79E+06	1.94E+08
OIR=1:8	0.972	228.35	1.30	1.00	269.18	0.49	6.26E+05	3.45E+11
	0.950	225.25	2.82	1.00	267.54	0.33	2.64E+06	2.31E+10
	0.927	220.95	2.90	1.10	265.03	0.50	8.24E+05	7.65E+09
	0.897	217.65	3.70	0.70	262.80	0.64	8.33E+05	2.43E+06
	0.871	213.85	1.20	0.90	260.20	0.55	1.71E+06	3.46E+03
	0.863	210.55	4.80	1.90	257.22	0.79	4.26E+05	3.52E+04
	0.848	209.95	2.66	1.80	257.70	0.80	6.90E+05	8.46E+00
OIR=1:2	0.960	226.75	1.20	0.78	268.66	0.32	1.40E+06	7.73E+10
	0.940	224.25	3.70	1.20	267.31	0.36	6.34E+05	2.02E+09
	0.924	219.65	1.10	0.80	265.19	0.43	1.24E+06	3.06E+10
	0.912	217.35	4.80	0.70	263.34	0.29	3.85E+05	1.41E+10
	0.894	215.55	2.70	1.10	262.24	0.89	1.35E+06	4.15E+07
	0.867	207.95	2.04	1.30	258.14	0.77	1.26E+06	6.85E+07
	0.838	202.05	2.70	1.60	255.61	0.48	6.43E+05	2.72E+05
OIR=1:1	0.966	227.65	2.91	2.60	268.79	0.55	5.75E+05	9.01E+10
	0.948	223.95	4.38	3.30	266.12	0.27	1.92E+05	2.75E+11
	0.929	220.85	2.88	4.00	264.96	1.22	6.86E+05	2.42E+10
	0.915	216.35	7.60	1.20	263.41	0.64	2.04E+05	5.46E+11
	0.901	212.25	5.40	2.50	260.83	0.77	3.64E+05	1.37E+12
	0.894	211.55	3.90	1.20	261.77	0.61	8.00E+05	1.30E+11
	0.881	206.25	3.48	1.83	258.92	0.67	5.17E+05	2.27E+12
	0.857	197.65	5.60	2.10	255.66	0.57	1.21E+06	6.27E+12
	0.849	199.15	4.80	2.50	256.44	1.13	3.96E+04	8.94E+09
OIR=2:1	0.968	225.85	1.76	1.10	268.83	0.30	5.48E+05	5.37E+13

	0.935	218.05	3.30	1.20	265.45	0.28	4.18E+05	4.38E+14
	0.912	215.55	2.40	1.40	264.18	0.80	7.96E+05	6.83E+11
	0.892	210.95	3.17	2.30	261.72	1.00	3.57E+05	1.72E+11
	0.875	205.45	6.10	3.90	258.81	1.39	9.58E+04	2.64E+11
	0.862	203.45	5.08	2.44	258.80	0.57	6.11E+05	9.83E+09
	0.848	196.85	3.62	2.70	256.16	0.96	5.11E+05	3.14E+11
OIR=8:1	0.969	223.45	2.63	1.50	268.82	0.68	4.05E+05	7.70E+16
	0.934	217.85	5.46	4.10	265.27	0.39	7.08E+04	6.80E+14
	0.919	211.15	5.30	3.55	264.32	0.71	8.41E+04	5.03E+17
	0.884	200.25	6.66	3.36	260.14	0.73	2.85E+05	8.57E+17
PEG400	0.980	220.55	3.28	1.50	268.67	1.19	7.73E+05	4.00E+26
	0.968	216.65	4.14	2.56	266.83	0.46	1.06E+06	9.12E+28
	0.949	208.35	5.00	3.30	264.74	0.93	5.74E+05	4.86E+35

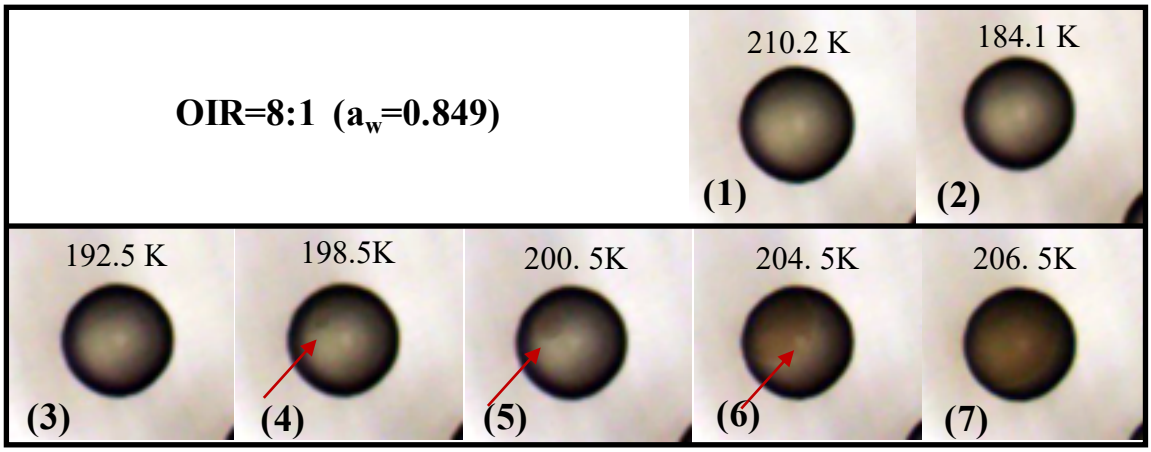

Figure S10. OM images of an example for freezing process of PEG400-AS (OIR=8:1) droplets at a_w of 0.849. Images (1,2) show no freezing during the cooling process. Images (3-7) show the freezing of the same droplet upon warming. Red arrows indicate the location of freezing (Image 4) and the slow ice growth within the droplet.

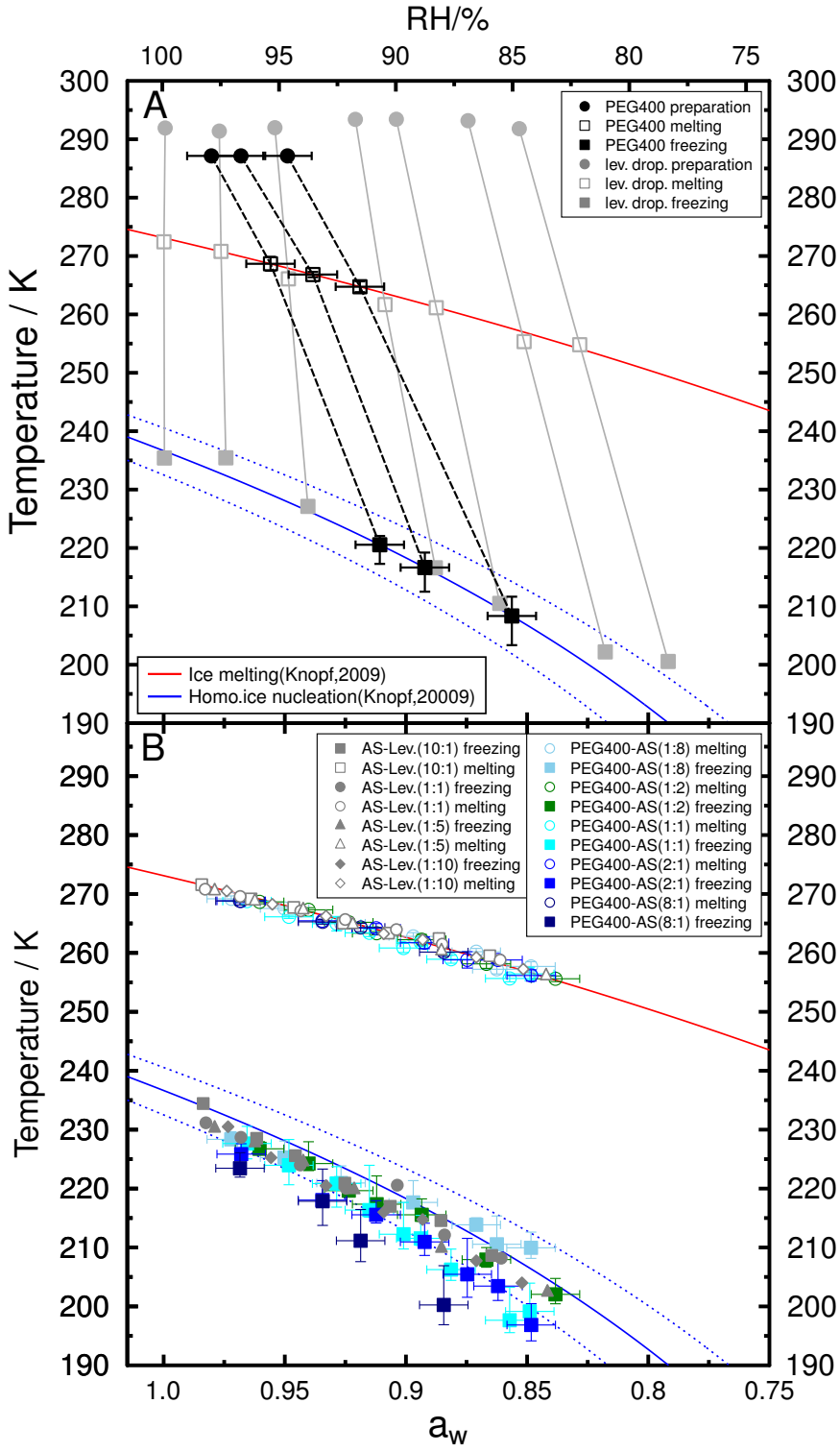

Figure S11. Water activities (a_w) of various aqueous solutions at different temperatures; see legend. (A) Aqueous solutions of levoglucosan data by Knopf and Lopez.[1] The experimental data for aqueous PEG400 droplets are from this study. (B) Aqueous AS-levoglucosan solutions with different mass ratios from Knopf and Rigg.[3] The experimental data for aqueous PEG400-AS droplets at different OIRs are from this study.

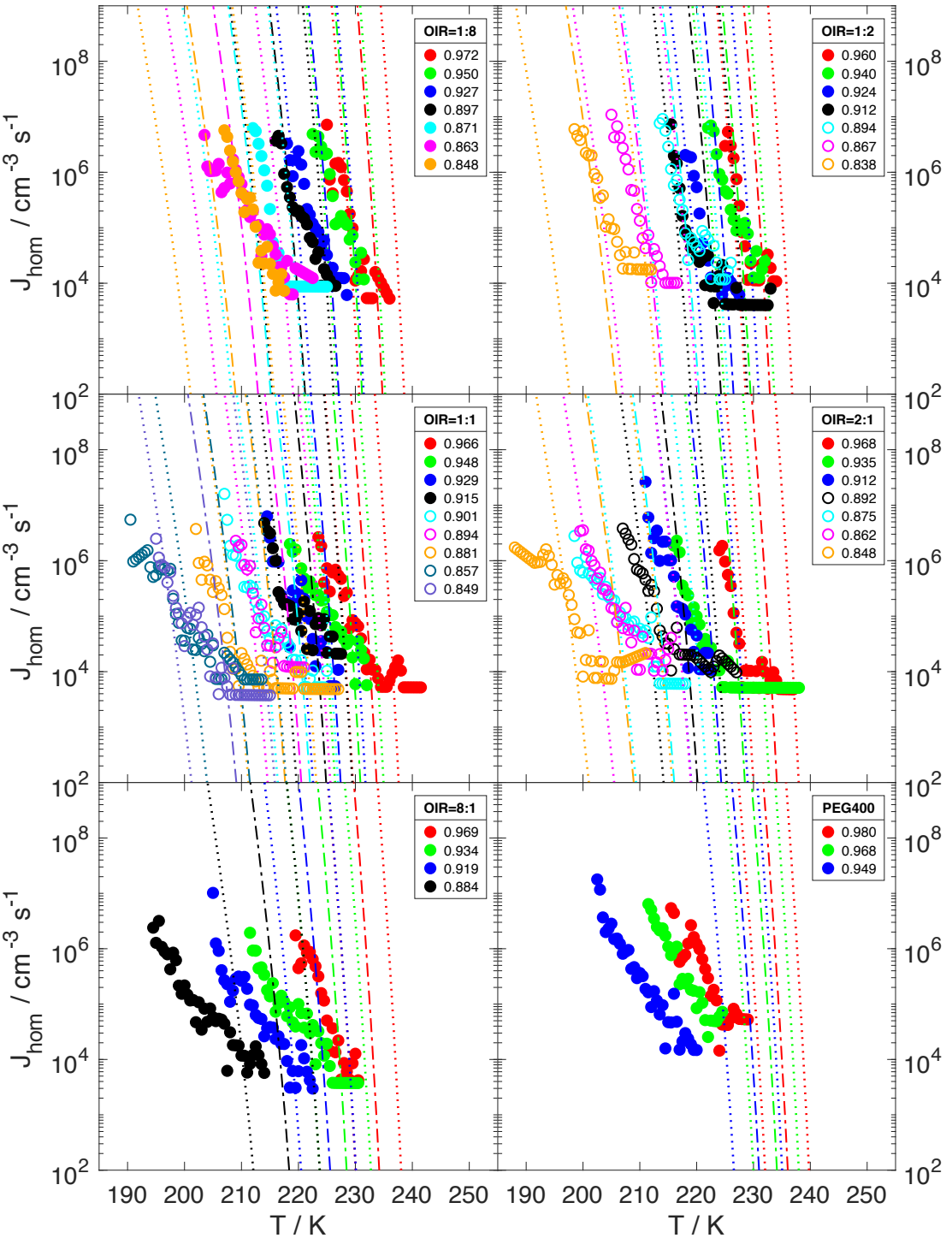

Figure S12. Similar to Fig.8 with additional dotted lines for each OIR and a_w representing the uncertainties in the predicted J_{hom} when an uncertainty of ±0.025 in a_w is employed using water-activity-based theory.

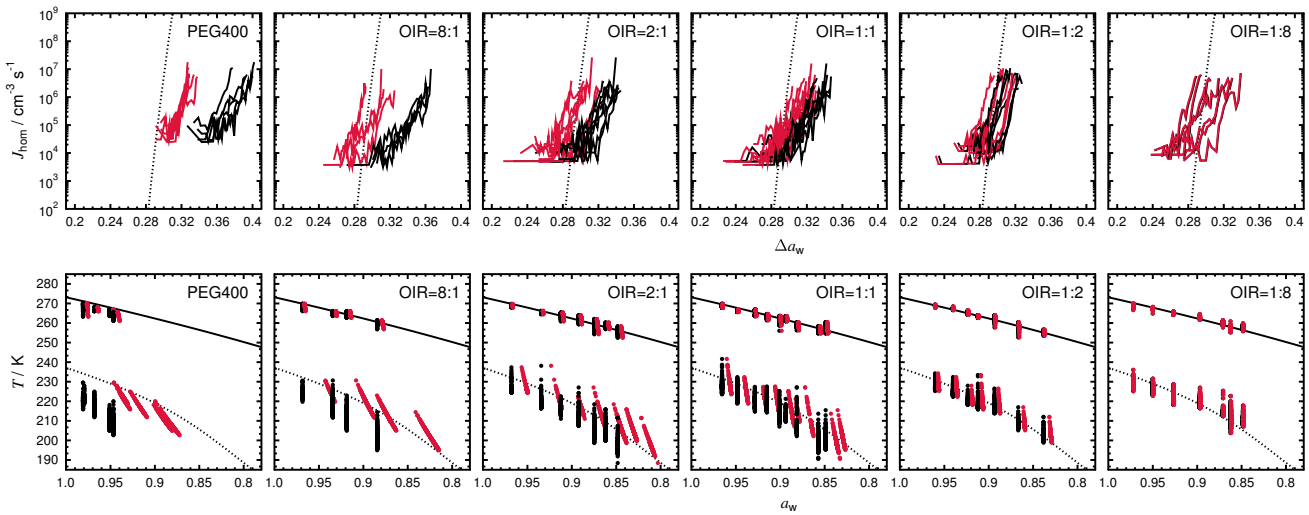

Figure S13. Upper panel: J_{hom} values as a function of Δa_w for aqueous PEG400-AS droplets at different OIRs. Each black line represents the unshifted data for each investigated a_w with assumption of constant a_w. The red lines are the shifted data considering the temperature dependence of a_w, i.e., the water activity offset (δa_w) according to Eq. (5)-(7). The dotted line indicates the predicted J_{hom} from the water-activity-based homogeneous ice nucleation theory.[2] Lower panel: Homogeneous freezing temperatures (T_f) and melting temperatures (T_m) as a function of a_w. The black dots represent the T_f and T_m assuming constant a_w. The red dots represent the T_f and T_m with consideration of the parameterized water activity offset. The black and dotted lines represent melting temperature and homogeneous ice nucleation temperature, respectively.[2]

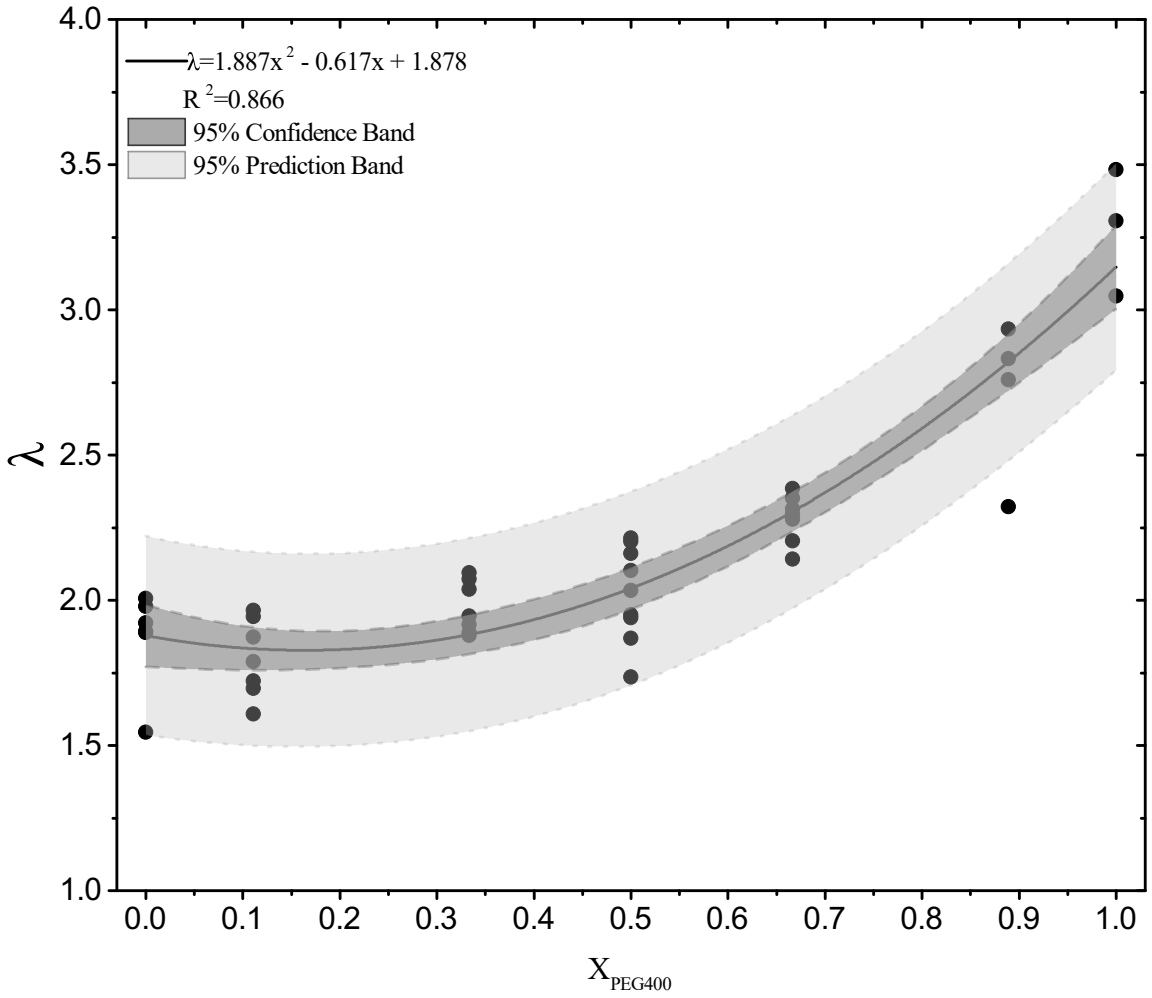

Figure S14. The λ values of aqueous PEG400-AS droplets (solid circles) are plotted as a function of mass fraction of PEG400 (X_{PEG400}) with respect to the total dry solute mass. Gray line is the fitting for the parameterization.

References

1. D. A. Knopf and M. D. Lopez, *Physical Chemistry Chemical Physics*, 2009, **11**, 8056-8068.
2. T. Koop, B. P. Luo, A. Tsias and T. Peter, *Nature*, 2000, **406**, 611-614.
3. D. A. Knopf and Y. J. Rigg, *Journal of Physical Chemistry A*, 2011, **115**, 762-773.