Supplementary Information for: Impact of nonionic surfactants on the water activity of binary and ternary aqueous solutions

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Bulk-to-surface partitioning

Surfactants partition to interfaces, and in high surface-area-to-volume ratio systems, this can lead to a depleted surfactant concentration in the system bulk as the surface concentration becomes non-negligible. 8 mL samples for water activity measurements are placed in a cylindrical dish with a 1.5-inch (3.81 cm) diameter. If we assume the surfactant partitions only to the air-water interface, the surface-area-to-volume ratio of the sample is 1.425 cm^{-1}, and if we assume the surfactant can partition to the container interface as well, the surface-area-to-volume ratio of the sample is 3.9 cm^{-1}. These surface-area-to-volume ratios correspond to spherical droplets of radii 2.1 and 0.77 cm, respectively.

We use a simple kinetic partitioning scheme[1,2] to predict the depletion ratio in the sample bulk as a function of total surfactant concentration (c_{tot}).

$$\frac{c_{bulk}}{c_{tot}} = \frac{1}{2}\left(1-\zeta-\frac{\zeta}{f}\right)+\frac{1}{2}\sqrt{\left((1-\zeta-\frac{\zeta}{f}\right)^2+4\frac{\zeta}{f}} \tag{S1}$$

$$f = \frac{\Gamma_{max} A K_{eq}}{V} \tag{S2}$$

$$\zeta = \frac{\Gamma_{max} A}{c_{tot} V} \tag{S3}$$

Here, c_{bulk} is the depleted bulk concentration, Γ_{max} and K_{eq} are the surfactant-dependent maximum surface excess and equilibrium partitioning constant determined from the Langmuir isotherm (taken from refs[2,3]), A is the surface area, and V is the volume.

Fig. S5 shows the predicted depletion ratio for Tween20, Triton X-100, and OTG in a 1 cm radius droplet. Changing the droplet size to 0.77 or 2.1 cm slightly changes the shape of the

curves in the low surfactant concentration region, but does not impact the total concentration where the depletion ratio reaches unity.

For Tween20 and Triton X-100, the stronger two surfactants, bulk-to-surface partitioning is expected to reduce the surfactant dissolved in the solution bulk by up to 4% at the lowest surfactant concentrations. When the surfactant critical micelle concentration (CMC) is reached, the loss of surfactant to the interface is expected to reduce the bulk concentration by less than 1%. For OTG, the weakest surfactant, bulk-to-surface partitioning is expected to reduce the bulk concentration by less than 0.5% over the full surfactant concentration range. At surfactant concentrations of 3 mM (corresponding to water mass fractions of 0.996, 0.998, and 0.999 for Tween20, Triton X-100, and OTG, respectively), the depletion ratio is approximately unity for every surfactant. Therefore, at water mass fractions lower than 0.996, bulk-to-surface partitioning is not expected to significantly impact the total surfactant concentration in the sample bulk during water activity measurements, for any surfactant system investigated here.

Surfactant hygroscopicity

The hygroscopicity of each surfactant was determined by calculating the radial hygroscopic growth factor. Dry particles with a 50 nm radius were used in all calculations. The dry surfactant mass was then determined using the pure surfactant density (1100, 1070, and 999.8 kg/m^3 for Tween20, Triton X-100, and OTG, respectively).[4] We assume that the change in droplet volume can be used to determine the volume, and thus mass of water added to the droplet, allowing the calculation of the surfactant mass fraction at each step. The radial growth factor is then calculated as the ratio of the wet particle diameter and the dry diameter. The equilibrium water activity predicted by AIOMFAC for each surfactant mass fraction was then

calculated. For Tween20 and Triton X-100, the oxyethylene subgroup description was used as it more closely agrees with the experimentally determined water activities.

The hygroscopicity κ was then determined at 95% RH for each surfactant.[5] V_{dry} is the dry particle volume and V_{water} is the volume of water added to the particle.

$$\frac{1}{a_w} = 1 + \kappa \frac{V_{dry}}{V_{water}} \tag{S4}$$

Table S1: Organic subgroups from Fig. S2 used to define surfactant molecules for AIOMFAC calculations. Tween20 and Triton X-100 (1) use ether and alkyl groups to describe the hydrophilic tail, while Tween20 and Triton X-100 (2) use oxyethylene groups.

Subgroup	Tween20 (1)	Tween20 (2)	Triton X-100 (1)	Triton X-100 (2)	OTG
CH_3	1	1	5	5	1
CH_2	28	11	9	1	6
CH	4	4	–	–	1
C	–	–	2	2	–
ACH	–	–	4	4	–
AC	–	–	2	2	–
OH	3	3	1	1	4
CH_2[OH]	3	3	1	1	1
CH[OH]	–	–	–	–	3
CH_2O	21	5	9	1	1
CHO[ether]	–	–	–	–	1
CH_2COO	1	1	–	–	–
CH_2OCH_2[oxyethylene]	–	16	–	8	–

Table S2: κ values for strong nonionic surfactants at 85, 90 and 95% RH.

Surfactant	80%	90%	95%
Tween20	0.10	0.08	0.06
Triton X-100	0.05	0.05	0.03
OTG	0.04	0.03	0.02

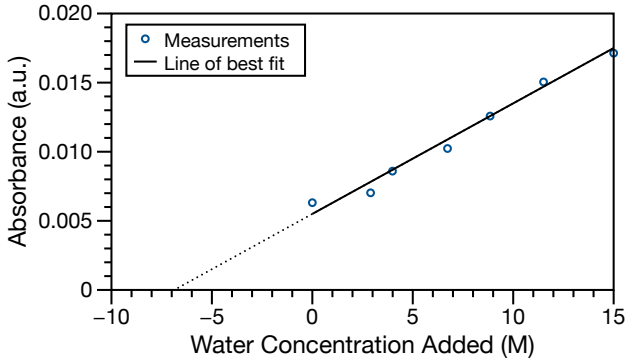

Figure S1: Standard addition calibration curve to determine the amount of water in 'pure' Tween20. Line of best fit: $y = 0.0008x + 0.0055$, $R^2 = 0.9818$, and x-intercept: 6.88 ± 0.90 M.

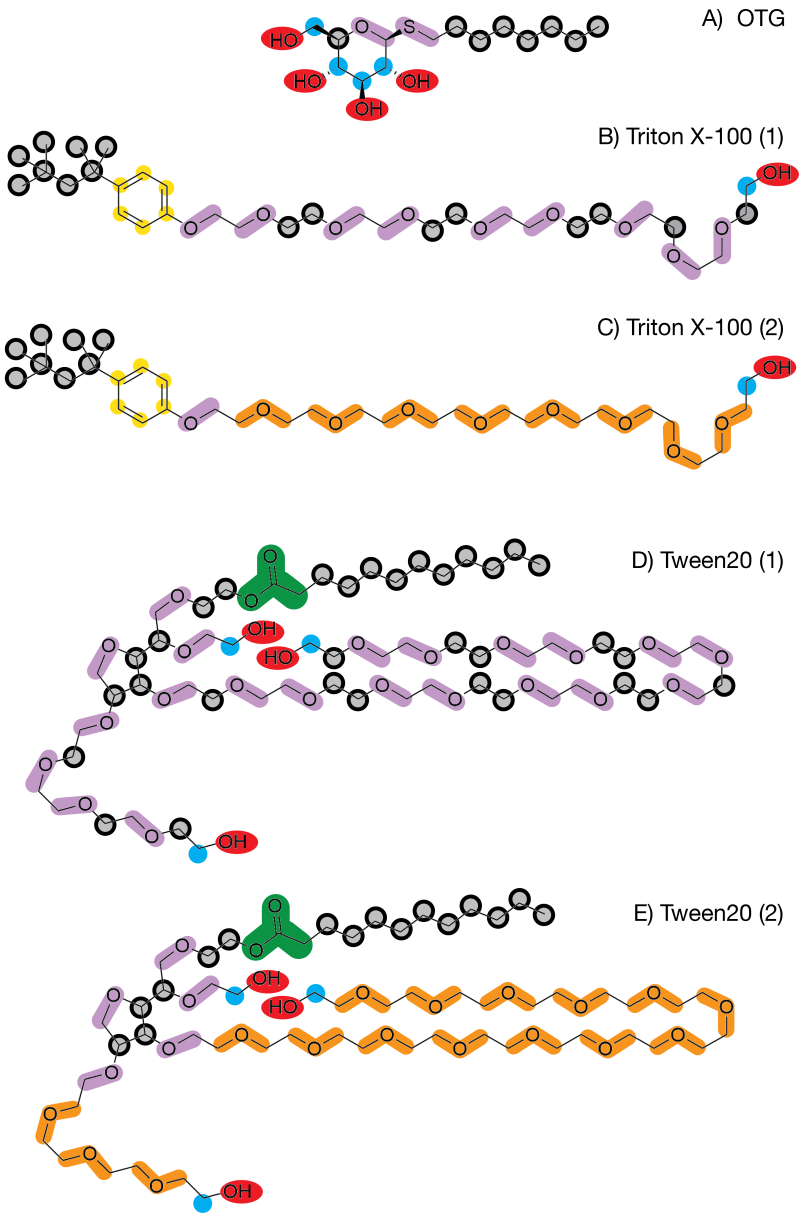

Figure S2: Nonionic surfactant structure of A) OTG, B/C) Triton X-100, and D/E) Tween20 used to determine functional subgroups for AIOMFAC calculations. OTG contains a sulfur atom, which is not currently included in any AIOMFAC organic subgroups. We have used oxygen to replace sulfur in OTG due to their shared number of valence electrons and similarity in electronegativity. Triton X-100 contains a mixture of OCH_2CH_2 tail lengths with an average of 9.5 repeat units. Here we have used 9 repeat units. We find no significant difference in AIOMFAC outputs if 10 repeat units are used instead. Tween20 is a mixture of molecules with different OCH_2CH_2 chain lengths at different positions. The depicted structure is one possible configuration. The length of each chain does not impact the definition of functional subgroups.

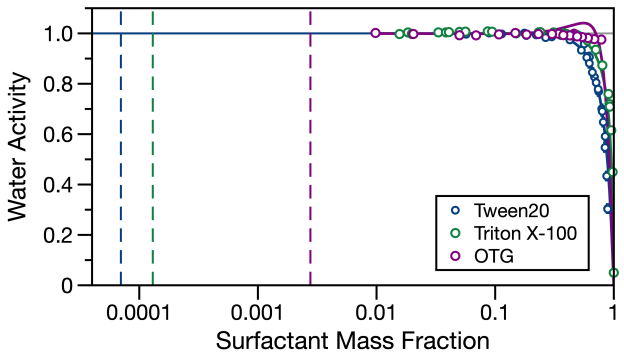

Figure S3: Water activity as a function of surfactant mass fraction plotted on a log scale, for binary surfactant solutions shown in Fig. 1 of the main text. The CMC of each surfactant is shown by the vertical dashed line in the same color as the points. The AIOMFAC model lines for each surfactant are also shown as solid lines in the same color.

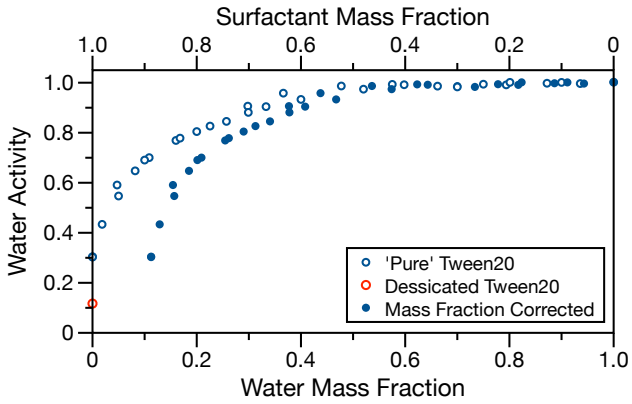

Figure S4: Water activity measurements for 'pure' Tween20 before and after mass fraction of water correction. The open red point shows the water activity of 'pure' Tween20 after a sample was left in the desiccator for a week.

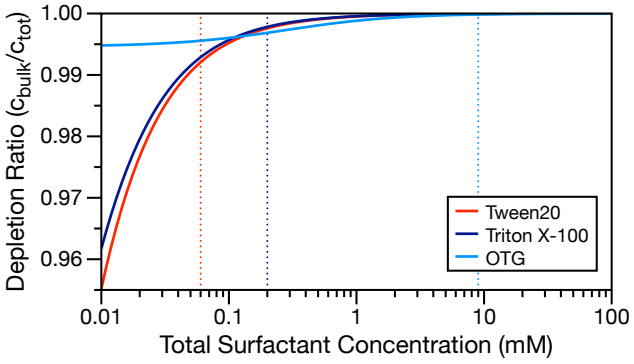

Figure S5: Predicted depletion ratios due to bulk-to-surface partitioning in an 8 mL sample using a simple kinetic partitioning model based on the Langmuir isotherm.[1] Vertical dotted lines in the same color indicate the CMC of each surfactant.

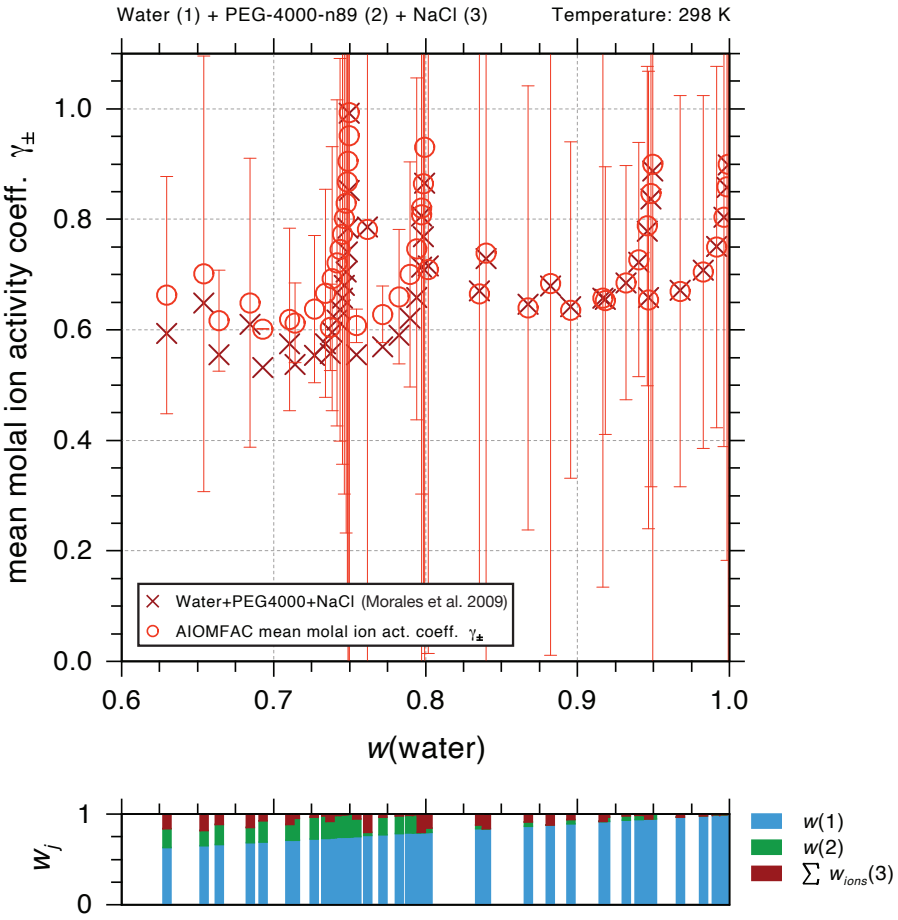

Figure S6: Mean molal ion activity coefficients for water–PEG4000–NaCl solutions predicted using an analogy to the CH_nO ether group approach in AIOMFAC to provide interaction parameters between the oxyethylene group, and Na^+ and Cl^- ions, compared to those determined experimentally by Morales et al.[6]

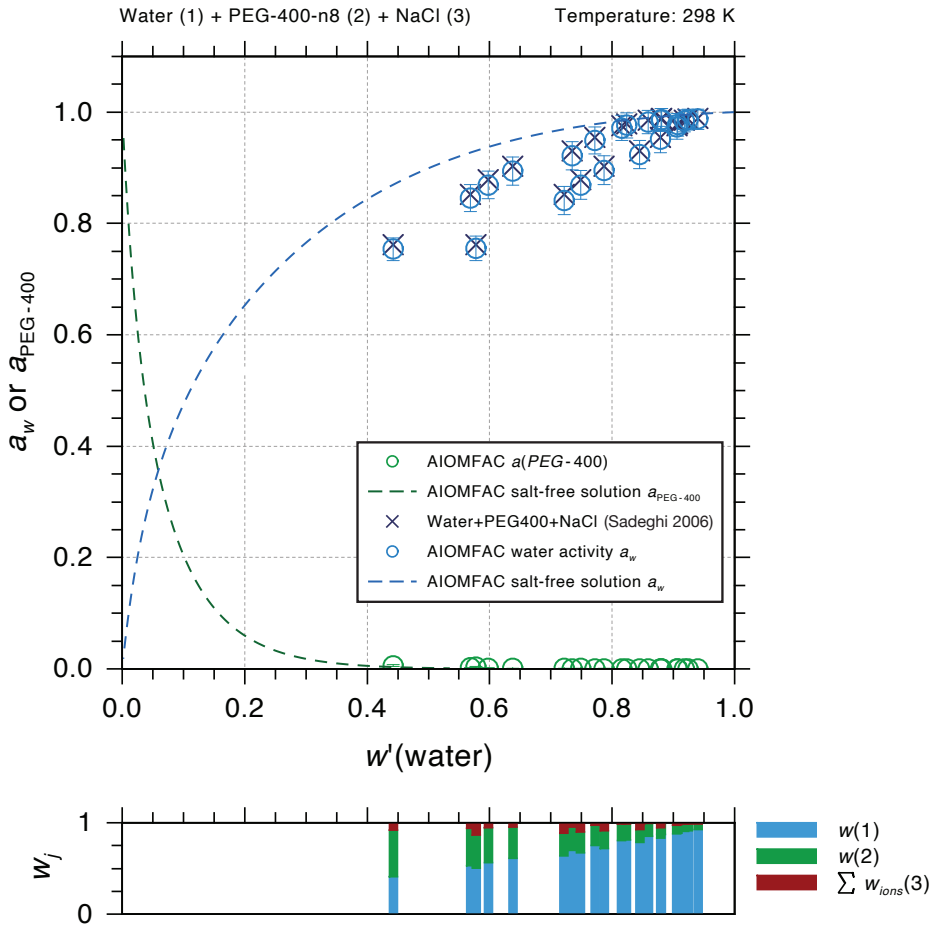

Figure S7: Water activities for water–PEG400–NaCl solutions predicted using an analogy to the CH_nO ether group approach in AIOMFAC to provide interaction parameters between the oxyethylene group, and Na^+ and Cl^- ions, compared to those determined experimentally by Sadeghi and Ziamajidi.[7] The x-axis refers to the mass fraction of water, w'(water), of the salt-free solvent mixture, while the lower panel indicates the ternary mixture composition of each data point in mass fractions of water, PEG-400 and NaCl.

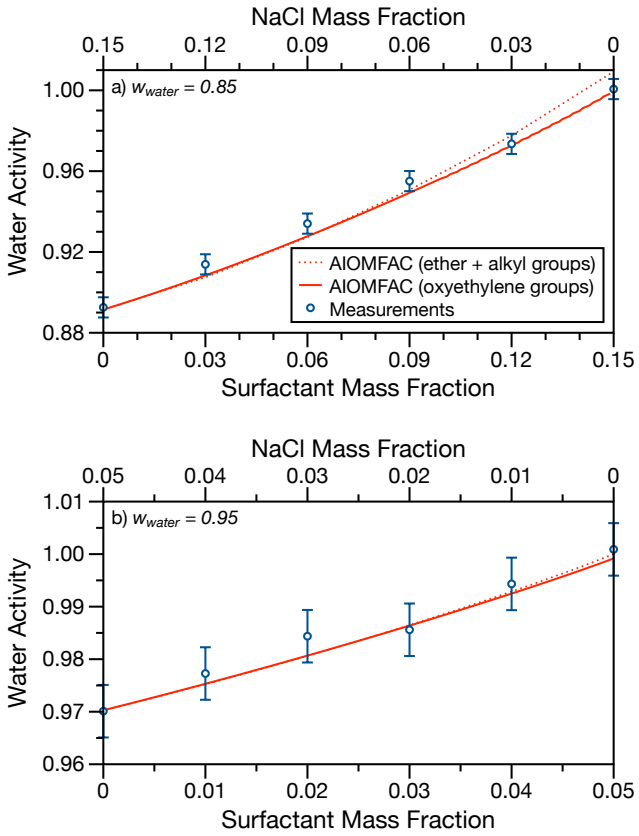

Figure S8: Water activity of aqueous solutions containing NaCl and Triton X-100, a) w_{water} = 0.85 and b) w_{water} = 0.95. The mass fraction of water is held constant while the mass ratio of surfactant to NaCl is varied. The solid line shows the predictions from the online version of AIOMFAC using the oxyethylene subgroup, the dotted red line shows predictions using the ether/alkyl subgroups, and the data markers show the average of three experimental measurements. Error bars indicate the instrument precision (±0.005 water activity units), which is always larger than the standard deviation between measurements.

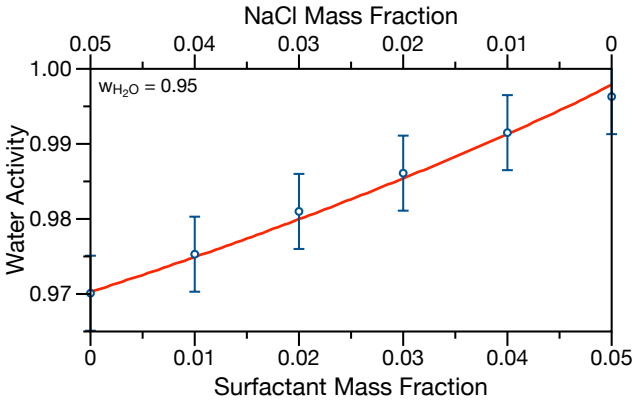

Figure S9: Water activity of aqueous solutions containing NaCl and OTG ($w_{water} = 0.95$). The mass fraction of water is held constant while the mass ratio of surfactant to NaCl is varied. The solid line shows the predictions from the online version of AIOMFAC, and the data markers show the average of three experimental measurements. Error bars indicate the instrument precision (± 0.005 water activity units), which is always larger than the standard deviation between measurements.

References

1. Alvarez, N. J.; Walker, M.; Anna, S. L. A criterion to assess the impact of confined volumes on surfactant transport to liquid–fluid interfaces. *Soft Matter* **2012**, *8*, 8917–8925.

2. Bain, A.; Prisle, N. L.; Bzdek, B. R. Model-measurement comparisons for surfactant-containing aerosol droplets. *ACS Earth Space Chem.* **2024**, *8*, 2244–2255.

3. Zdziennicka, A.; Szymczyk, K.; Krawczyk, J.; Jańczuk, B. Activity and thermodynamic parameters of some surfactants adsorption at the water-air interface. *Fluid Ph. Equilibria* **2012**, *318*, 25–33.

4. Bain, A.; Ghosh, K.; Prisle, N. L.; Bzdek, B. R. Surface-area-to-volume ratio determines surface tensions in microscopic, surfactant-containing droplets. *ACS Cent. Sci.* **2023**, *9*, 2076–2083.

5. Petters, M. D.; Kreidenweis, S. M. A single parameter representation of hygroscopic growth and cloud condensation nucleus activity. *Atmospheric Chemistry and Physics* **2007**, *7*, 1961–1971.

6. Morales, J. W.; Galleguillos, H. R.; Taboada, M. E.; Hernández-Luis, F. Activity coefficients of NaCl in PEG 4000+water mixtures at 288.15, 298.15 and 308.15K. *Fluid Ph. Equilibria* **2009**, *281*, 120–126.

7. Sadeghi, R.; Ziamajidi, F. Water activities of ternary mixtures of poly(ethylene glycol), NaCl and water over the temperature range of 293.15K to 313.15K. *J. Chem. Thermo.* **2006**, *38*, 1335–1343.