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

Supporting Information for: Molecular-Scale Origins of Solution Nanostructure and Excess Thermodynamic Properties in a Water/Amphiphile Mixture

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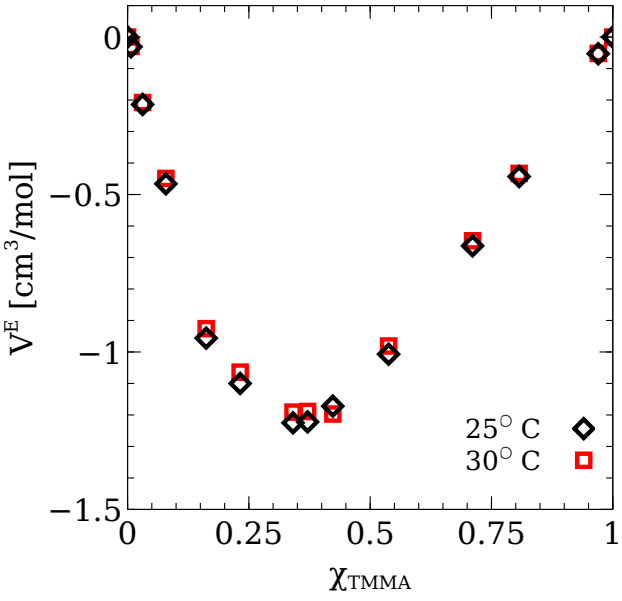

Figure S1: Comparison of experimental percent excess volume for 25° and 30° C.

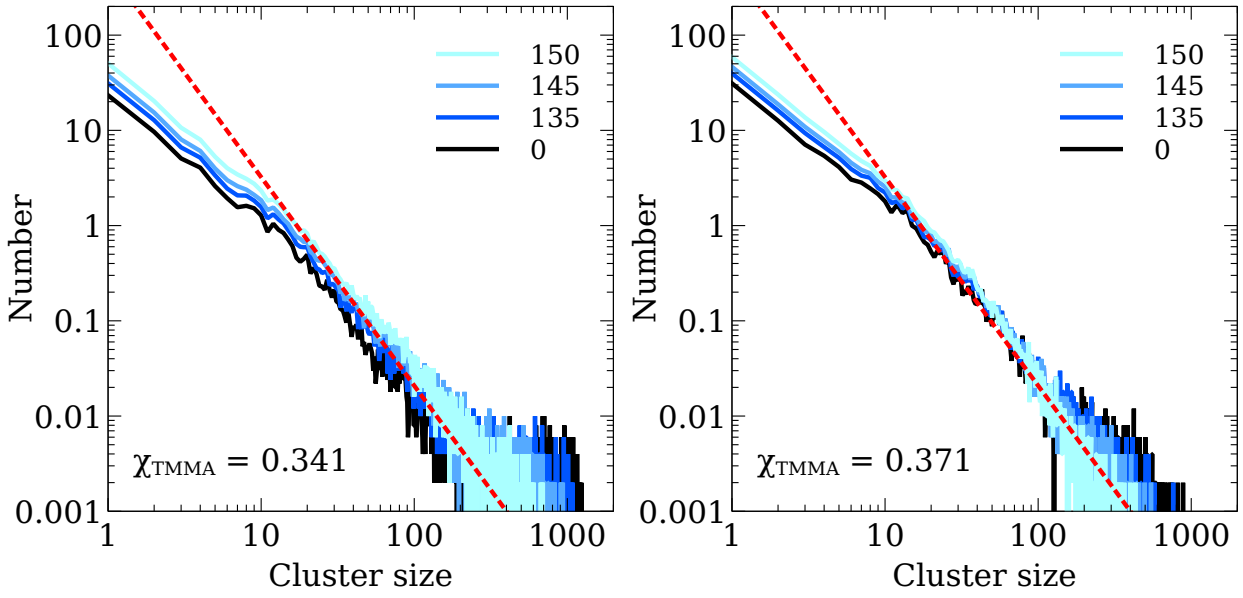

Figure S2: Water hydrogen bonded cluster distributions for $\chi_{\mathrm{TMMA}} = 0.341$ (left) and $\chi_{\mathrm{TMMA}} = 0.371$ (right) for different O-H...O angle cutoffs.

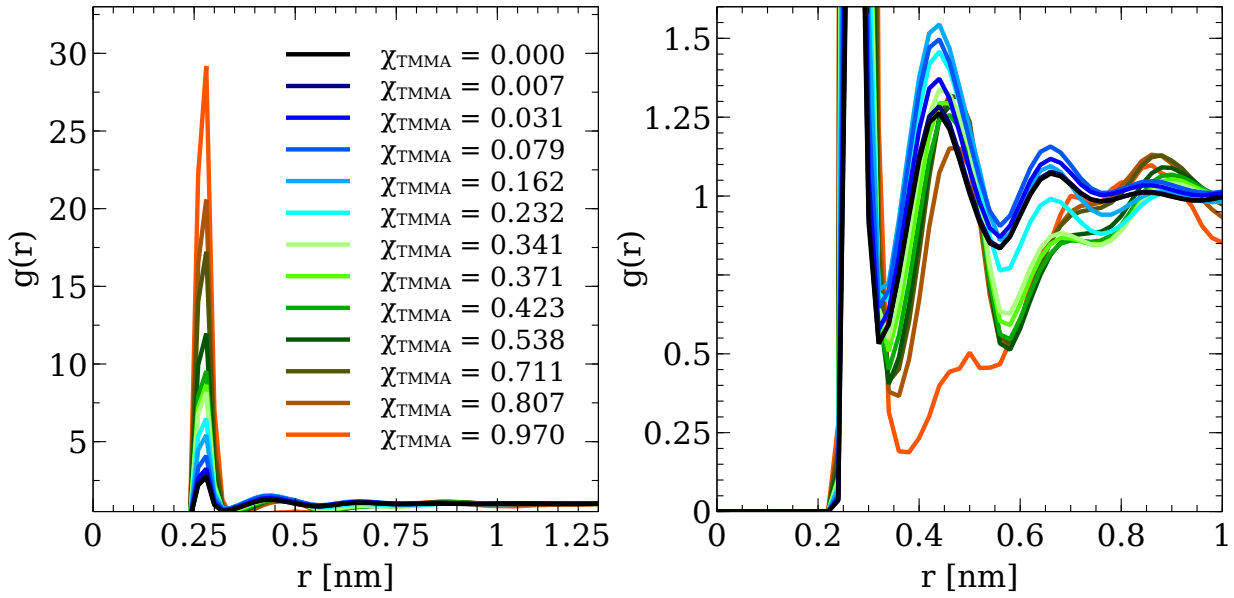

Figure S3: Water oxygen-oxygen RDFs for each simulation. Data for compositions with $\chi_{\mathrm{TMMA}} \geq 0.423$ are extended by 100 ns for improved statistical accuracy.

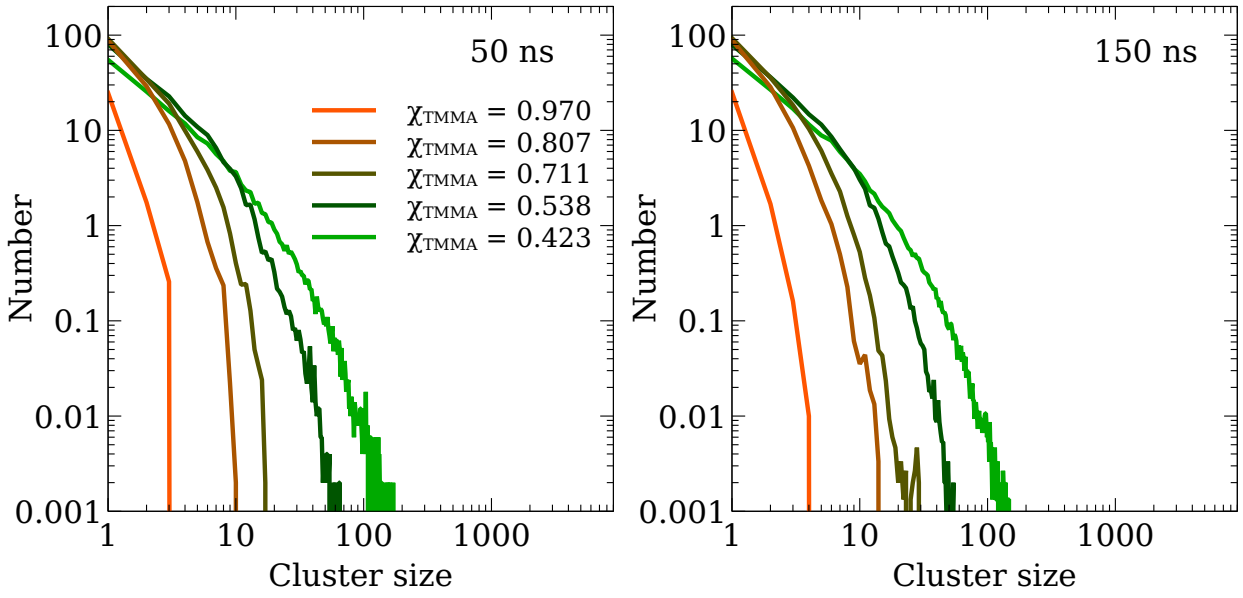

Figure S4: The water cluster size distributions for the TMMA-rich compositions are plotted for the 50 ns production trajectory (left panel) and for extended trajectories with an additional 100 ns (right panel).

The high-energy incident photons provide an adequate q range both for normalizing intensities and sufficient peak resolution in *g(r)* after Fourier transform. The total scattering function, $S(q)$, was obtained from the experimental data using weighting factors determined based on relative atomic concentrations and appropriate form factors, as described in detail elsewhere.[1–3] The total experimental pair correlation functions, $g(r)$, was obtained from $S(q)$ by Fourier transform,

$$g(r) = 1 + \frac{1}{2\pi^2 \rho_0 r} \int q(S(q) - 1) \sin(qr) dq, \tag{1}$$

where ρ_0 is the average atomic density, and plotted in Figure S2.

Scattering intensities, $I(q)$, are computed as described by Walter et al.[4] for the periodic simulation box with

$$I(q) = \sum_{i}^{N} \sum_{i \neq j}^{N} f_i(q) f_j(q) e^{-iqr_{ij}}, \tag{2}$$

where r_{ij} is the distance between atoms i and j and $f_i(q)$ is the atomic form factor for atom

i determined by Cromer-Mann expansions.[5] Intensities were normalized by a scalar factor for comparison to experimental data.

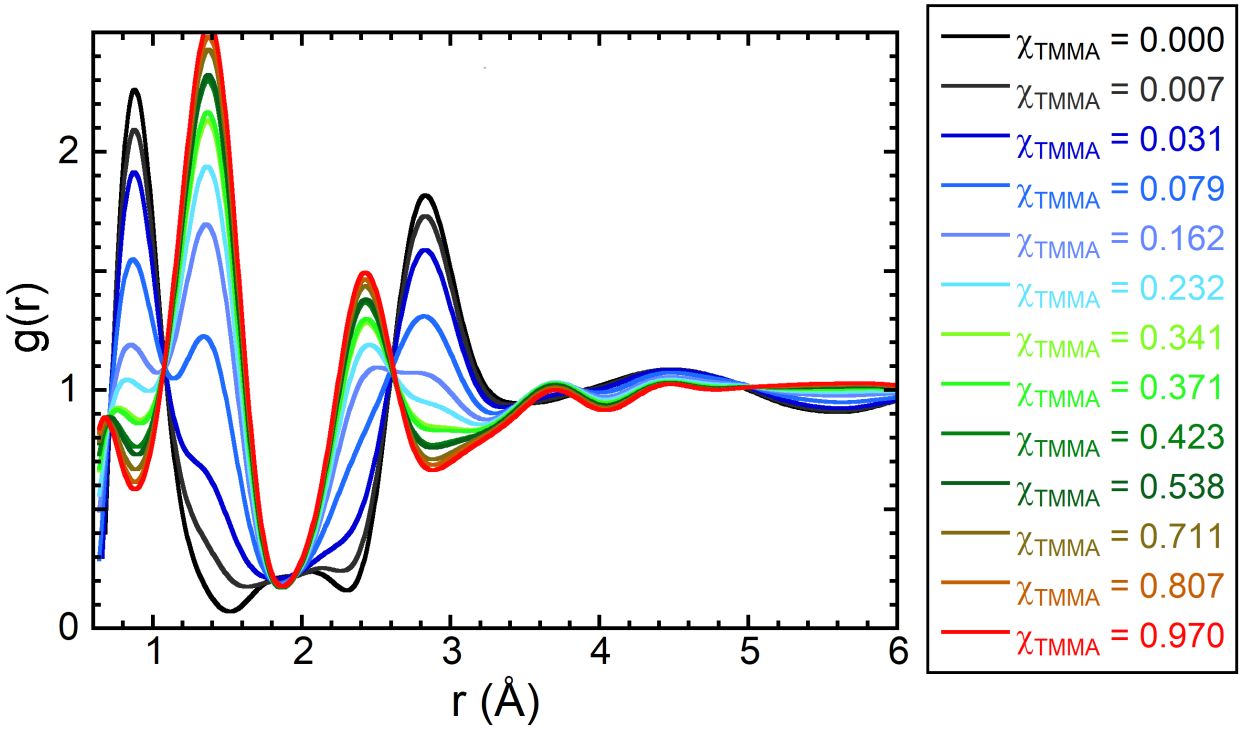

Figure S5: Pair distribution function generated by the Fourier transform of the experimental X-ray scattering data.

Simulation Lennard-Jones parameters for TMMA are provided in Table S1, with mixed terms derived using Lorentz-Berthelot mixing rules. The bonded potential parameters for TMMA are given in the GROMACS .itp topology file at the end of this document.

Table 1: Lennard-Jones parameters for TMMA atoms.

Atom name	σ_{ii} [nm]	ϵ_{ii} [kJ/mol]
H1	0.2422	0.0870
HC	0.2600	0.0870
CT	0.3398	0.4510
C	0.3315	0.4134
N	0.3181	0.6845
O	0.3048	0.6121

References

(1) Soderholm, L.; Skanthakumar, S.; Gorman-Lewis, D.; Jensen, M.; Nagy, K. Characterizing solution and solid-phase amorphous uranyl silicates. *Geochimica et Cosmochimica Acta* **2008**, *72*, 140–150.

(2) Egami, T.; Billinge, S. *Underneath the Bragg Peaks: Structural Analysis of Complex Materials*; Pergamon Materials Series; Elsevier Science, 2003.

(3) Als-Nielsen, J.; McMorrow, D. *Elements of Modern X-ray Physics*; Wiley, 2011.

(4) Walter, N. P.; Jaiswal, A.; Cai, Z.; Zhang, Y. LiquidLib: A comprehensive toolbox for analyzing classical and ab initio molecular dynamics simulations of liquids and liquid-like matter with applications to neutron scattering experiments. *Computer Physics Communications* **2018**, *228*, 209–218.

(5) Cromer, D. T.; Mann, J. B. X-ray scattering factors computed from numerical Hartree–Fock wave functions. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography* **1968**, *24*, 321–324.


```
; gaff2 TMMA

[ moleculetype ]
; Name                nrexcl
TMMAL                   3

[ atoms ]
;AT.NUM   TYPE   RESID   RESNAME PDB-NAME  IGRP    CHRGE    MASS
     1     CT       1      TMMAL     C1       1     0.0185    12.0100
     2     H1       1      TMMAL     H1       1     0.0481     1.0080
```

```
     3     H1       1      TMMAL     H2       1     0.0481     1.0080
     4     H1       1      TMMAL     H3       1     0.0481     1.0080
     5     CT       1      TMMAL     C2       2     0.0061    12.0100
     6     H1       1      TMMAL     H4       2     0.0519     1.0080
     7     H1       1      TMMAL     H5       2     0.0519     1.0080
     8     H1       1      TMMAL     H6       2     0.0519     1.0080
     9     CT       1      TMMAL     C3       3    -0.2247    12.0100
    10     HC       1      TMMAL     H7       3     0.0942     1.0080
    11     HC       1      TMMAL     H8       3     0.0942     1.0080
    12     CT       1      TMMAL     C4       4     0.0178    12.0100
    13     H1       1      TMMAL     H9       4     0.0482     1.0080
    14     H1       1      TMMAL     H10      4     0.0482     1.0080
    15     H1       1      TMMAL     H11      4     0.0482     1.0080
    16     CT       1      TMMAL     C5       5     0.0061    12.0100
    17     H1       1      TMMAL     H12      5     0.0518     1.0080
    18     H1       1      TMMAL     H13      5     0.0518     1.0080
    19     H1       1      TMMAL     H14      5     0.0518     1.0080
    20     N        1      TMMAL     N1       6    -0.2418    14.0100
    21     C        1      TMMAL     C6       6     0.5072    12.0100
    22     O        1      TMMAL     O1       6    -0.5715    16.0000
    23     C        1      TMMAL     C7       7     0.5072    12.0100
    24     O        1      TMMAL     O2       7    -0.5715    16.0000
    25     N        1      TMMAL     N2       7    -0.2418    14.0100

[ bonds ]
;   I1    I2  TYPE      r0(nm)   K(kJ/nm^2/mol)
     1     2     1      0.1097     157284.929
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```
     1      3      1       0.1097     157284.929
     1     20      1       0.1462     110361.368
     1      4      1       0.1097     157284.929
     5      6      1       0.1097     157284.929
     5      7      1       0.1097     157284.929
     5      8      1       0.1097     157284.929
     5     20      1       0.1462     110361.368
     9     10      1       0.1097     157284.929
     9     21      1       0.1524     101763.248
     9     23      1       0.1524     101763.248
     9     11      1       0.1097     157284.929
    12     13      1       0.1097     157284.929
    12     14      1       0.1097     157284.929
    12     25      1       0.1462     110361.368
    12     15      1       0.1097     157284.929
    16     17      1       0.1097     157284.929
    16     18      1       0.1097     157284.929
    16     19      1       0.1097     157284.929
    16     25      1       0.1462     110361.368
    20     21      1       0.1379     149038.265
    21     22      1       0.1218     273035.289
    23     24      1       0.1218     273035.289
    23     25      1       0.1379     149038.265

[ angles ]
;   I1    I2    I3  TYPE    theta(deg)  K(kJ/rad^2/mol)
     1    20     5     1      115.64      271.45792
```

1	20	21	1	120.69	273.01437
2	1	3	1	108.46	162.34757
2	1	20	1	108.88	257.50010
2	1	4	1	108.46	162.34757
3	1	20	1	108.88	257.50010
3	1	4	1	108.46	162.34757
4	1	20	1	108.88	257.50010
5	20	21	1	120.69	273.01437
6	5	7	1	108.46	162.34757
6	5	8	1	108.46	162.34757
6	5	20	1	108.88	257.50010
7	5	8	1	108.46	162.34757
7	5	20	1	108.88	257.50010
8	5	20	1	108.88	257.50010
9	21	20	1	115.18	352.56895
9	21	22	1	123.20	353.76557
9	23	24	1	123.20	353.76557
9	23	25	1	115.18	352.56895
10	9	21	1	108.77	198.36762
10	9	23	1	108.77	198.36762
10	9	11	1	107.58	163.00864
11	9	21	1	108.77	198.36762
11	9	23	1	108.77	198.36762
12	25	16	1	115.64	271.45792
12	25	23	1	120.69	273.01437
13	12	14	1	108.46	162.34757
13	12	25	1	108.88	257.50010

```
    13     12     15      1       108.46      162.34757
    14     12     25      1       108.88      257.50010
    14     12     15      1       108.46      162.34757
    15     12     25      1       108.88      257.50010
    16     25     23      1       120.69      273.01437
    17     16     18      1       108.46      162.34757
    17     16     19      1       108.46      162.34757
    17     16     25      1       108.88      257.50010
    18     16     19      1       108.46      162.34757
    18     16     25      1       108.88      257.50010
    19     16     25      1       108.88      257.50010
    20     21     22      1       123.05      476.18523
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    24     23     25      1       123.05      476.18523

[ pairs ]
;   I1   I4
    1    6
    1    7
    1    8
    1    9
    1   22
    2    5
    2   21
    3    5
    3   21
    4    5
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4	21
5	9
5	22
6	21
7	21
8	21
9	12
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10	24
10	25
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11	22
11	24
11	25
12	17
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12	24
13	16
13	23
14	16
14	23
15	16
15	23
16	24

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   17    23
   18    23
   19    23
   20    23
   21    24
   21    25
   22    23

[ dihedrals ]
;   I1    I2    I3    I4   TYPE   theta(deg) K(kJ/rad^2/mol)     N
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     1    20     5     8     9      0.0000      0.0000          2
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     1    20    21     9     9      0.0000      2.0920          1
     1    20    21    22     9    180.0000     10.4600          2
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     2     1    20    21     9      0.0000      0.0000          2
     3     1    20     5     9      0.0000      0.0000          2
     3     1    20    21     9      0.0000      0.0000          2
     4     1    20     5     9      0.0000      0.0000          2
     4     1    20    21     9      0.0000      0.0000          2
     5    20    21     9     9    180.0000      1.0878          2
     5    20    21     9     9      0.0000      2.0920          1
     5    20    21    22     9    180.0000     10.4600          2
     6     5    20    21     9      0.0000      0.0000          2
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8	5	20	21	9	0.0000	0.0000	2
9	23	25	12	9	180.0000	1.0878	2
9	23	25	12	9	0.0000	2.0920	1
9	23	25	16	9	180.0000	1.0878	2
9	23	25	16	9	0.0000	2.0920	1
10	9	21	20	9	0.0000	0.0000	2
10	9	21	22	9	0.0000	3.4727	1
10	9	21	22	9	180.0000	0.1674	3
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10	9	23	24	9	180.0000	0.1674	3
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11	9	21	20	9	0.0000	0.0000	2
11	9	21	22	9	0.0000	3.4727	1
11	9	21	22	9	180.0000	0.1674	3
11	9	23	24	9	0.0000	3.4727	1
11	9	23	24	9	180.0000	0.1674	3
11	9	23	25	9	0.0000	0.0000	2
12	25	16	17	9	0.0000	0.0000	2
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12	25	16	19	9	0.0000	0.0000	2
12	25	23	24	9	180.0000	10.4600	2
13	12	25	16	9	0.0000	0.0000	2
13	12	25	23	9	0.0000	0.0000	2
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15	12	25	16	9	0.0000	0.0000	2
15	12	25	23	9	0.0000	0.0000	2

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    17    16    25    23     9      0.0000      0.0000          2
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    23    24     9    25     4    180.0000     43.9320          2
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[ system ]
TMMAL

[ molecules ]
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