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Supporting Information

Self-assembly and Structures of Nanoscale Double Emulsion Droplets by Coarse-grained Molecular Dynamics Simulations

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1 Coarse-grained Model

1.1 Bonded interactions of *n*-heptane and C12E4

***n*-heptane.** In the CG *n*-heptane molecule, there is only one bond type (i.e., C2E-C3) and one angle type (i.e., C2E-C3-C2E). For the bond interaction, three Gaussians are applied. For the angle interaction, four Gaussians are applied. The parameters are given in Table S1.

Table S1. Parameters of multi-centred Gaussians for the potentials of bond stretching and angle bending in the CG *n*-heptane model. Both $r_{c,i}^{CG}$ and $\omega_{r,i}^{CG}$ have the unit of nm. Both $\theta_{c,i}^{CG}$ and $\omega_{\theta,i}^{CG}$ have the unit of degree.

Bond	$\boldsymbol{G_1}$			$\boldsymbol{G_2}$			$\boldsymbol{G_3}$		
	$r_{c,1}^{CG}$	$\omega_{r,1}^{CG}$	$A_{r,1}^{CG}$	$r_{c,2}^{CG}$	$\omega_{r,2}^{CG}$	$A_{r,2}^{CG}$	$r_{c,3}^{CG}$	$\omega_{r,3}^{CG}$	$A_{r,3}^{CG}$
C2E-C3	0.2682	0.0181	0.0620	0.3001	0.0130	0.4797	0.3264	0.0105	0.5189

Angle	$\boldsymbol{G_1}$			$\boldsymbol{G_2}$			$\boldsymbol{G_3}$			$\boldsymbol{G_4}$		
	$\theta_{c,1}^{CG}$	$\omega_{\theta,1}^{CG}$	$A_{\theta,1}^{CG}$	$\theta_{c,2}^{CG}$	$\omega_{\theta,2}^{CG}$	$A_{\theta,2}^{CG}$	$\theta_{c,3}^{CG}$	$\omega_{\theta,3}^{CG}$	$A_{\theta,3}^{CG}$	$\theta_{c,4}^{CG}$	$\omega_{\theta,4}^{CG}$	$A_{\theta,4}^{CG}$
C2E-C3-C2E	139.13	32.06	0.4230	139.13	8.57	0.1356	155.88	11.75	0.2786	173.51	8.95	0.5621

C12E4. In the CG C12E4 molecule, there are five bond types (i.e., C3E-C3, C3-C3, C3-EO, EO-EO, and EO-EG) and six angle types (i.e., C3E-C3-C3, C3-C3-C3, C3-C3-EO, C3-EO-EO, EO-EO-EO, and EO-EO-EG). Similarly, three Gaussians and four Gaussians are applied to represent the bond and angle potentials, respectively. The parameters of CG bonds and angles for C12E4 are given in Table S2 and Table S3.

Table S2. Parameters of multi-centred Gaussians for the bond stretching potentials in the CG C12E4 model. Both $r_{c,i}^{CG}$ and $\omega_{r,i}^{CG}$ have the unit of nm.

Bond	$\boldsymbol{G_1}$			$\boldsymbol{G_2}$			$\boldsymbol{G_3}$		
	$r_{c,1}^{CG}$	$\omega_{r,1}^{CG}$	$A_{r,1}^{CG}$	$r_{c,2}^{CG}$	$\omega_{r,2}^{CG}$	$A_{r,2}^{CG}$	$r_{c,3}^{CG}$	$\omega_{r,3}^{CG}$	$A_{r,3}^{CG}$
C3E-C3	0.3322	0.0249	0.0732	0.3563	0.0135	0.4028	0.3846	0.0104	0.6676
C3-C3	0.3291	0.0242	0.0687	0.3527	0.0135	0.3877	0.3805	0.0106	0.6880
C3-EO	0.2870	0.0198	0.0201	0.3323	0.0353	0.6570	0.3607	0.0202	0.6136
EO-EO	0.3179	0.0317	0.1754	0.3491	0.0256	0.7903	0.3653	0.0105	0.2178
EO-EG	0.3877	0.0505	0.3314	0.4060	0.0214	0.5072	0.4307	0.0127	0.4192

Table S3. Parameters of multi-centred Gaussians for the angle bending potentials in the CG C12E4 model. Both $\theta_{c,i}^{CG}$ and $\omega_{\theta,i}^{CG}$ have the unit of degree.

Angle	G_1			G_2			G_3			G_4		
	$\theta_{c,1}^{CG}$	$\omega_{\theta,1}^{CG}$	$A_{\theta,1}^{CG}$	$\theta_{c,2}^{CG}$	$\omega_{\theta,2}^{CG}$	$A_{\theta,2}^{CG}$	$\theta_{c,3}^{CG}$	$\omega_{\theta,3}^{CG}$	$A_{\theta,3}^{CG}$	$\theta_{c,4}^{CG}$	$\omega_{\theta,4}^{CG}$	$A_{\theta,4}^{CG}$
C3E-C3-C3	127.60	28.60	0.1224	140.11	18.25	0.3312	151.09	9.01	0.1218	172.43	16.15	0.8489
C3-C3-C3	126.84	29.65	0.1276	139.82	18.05	0.3252	151.00	9.02	0.1211	172.61	16.61	0.8057
C3-C3-EO	97.73	22.17	0.0895	125.92	21.54	0.4036	152.23	25.49	0.5336	250.82	45.46	98.04
C3-EO-EO	97.66	20.86	0.1311	127.82	30.57	0.2577	166.18	41.84	0.9839	176.10	7.03	0.0189
EO-EO-EO	101.10	22.18	0.1446	131.90	39.48	0.3754	158.71	36.50	0.6402	175.12	7.05	0.0318
EO-EO-EG	93.54	23.62	0.1453	119.19	21.53	0.1035	156.31	43.86	0.9957	174.69	7.22	0.0305

1.2 Non-bonded interactions

The CG beads in present models are principally classified as hydrophilic or hydrophobic beads. The hydrophilic beads include W3, EO, and EG, and the hydrophobic beads include C3, C2E and C3E. Table S4 lists the parameters of pairwise non-bonded interactions described by 12-6 LJ potential form.

Table S4. Parameters of CG non-bonded interaction potentials.

Bead *i*	Bead *j*	σ_{LJ} (nm)	ε_{LJ} (kJ/mol)
W3	W3	0.4305	4.47
W3	EO	0.4380	4.75
W3	EG	0.4360	5.80
EO	EO	0.4120	2.86
EO	EG	0.4160	3.85
EG	EG	0.4400	6.60
C3 or C3E	C3 or C3E	0.4660	2.67
C3 or C3E	C2E	0.4490	2.18
C2E	C2E	0.4320	1.78
W3	C3 or C3E	0.4487	2.15
W3	C2E	0.4315	1.43
EO	C3 or C3E	0.4710	2.14
EO	C2E	0.4520	1.71
EG	C3 or C3E	0.4600	4.30
EG	C2E	0.4385	3.65

1.3 Validations

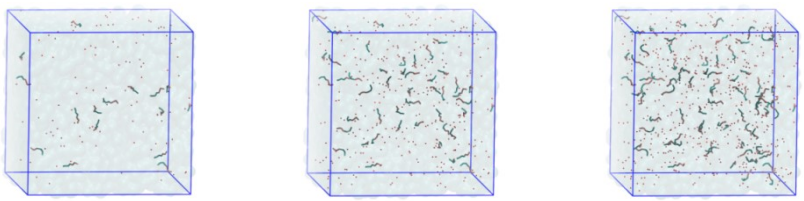
As part of the validations for our coarse-grained models, Table S5 lists the density and viscosity of various systems from MD simulations and experiment. Note that the temperature is 298.15 K, and the pressure is 1 bar.

Table S5. Density and viscosity from CG MD simulation and experiment.

System	Density (kg/m^3)		Viscosity (cP)	
	CG MD	Expt.	CG MD	Expt.
water	997.08	997.05	0.890	0.892
n-hexane	654.9	654.8	0.30	0.296
n-heptane	679.5	679.6	0.39	0.388
n-nonane	713.9	714.1	0.65	0.654
n-dodecane	745.5	745.7	1.33	1.359
n-pentadecane	768.8	769.0	2.62	2.576
1-ethoxyethane	707.9	708	0.22	0.222
1-ethoxypropane	724.3	724	0.31	0.306
2-ethoxyethanol	908.1	907	2.69	2.7
2-propoxyethanol	883.5	883	1.84	1.867
PEG-4	1121.6	1122	41.2	41.1
PEG-2/water = 0.2			1.82	1.9
PEG-4/water = 0.2			2.12	2.1

2 Snapshots

Figure S1 shows the snapshots of the initial simulation box with $^{v}{}_{w/s}$ = 1.0/1.0.



(a) (b) (c)

Figure S1. Initial conformation of the ternary mixtures with $^{v}{}_{w/s}$ = 1.0/1.0 and (a) 1% water; (b) 3% water; (c) 5% water. The temporary box size is 20 nm, and the compositions is determined by the pre-set volume of (10 nm)^3.

Figure S2 shows the snapshots of three emulsion systems in batch 1 and batch 2 before continuing the simulations for long-time equilibration. In batch 1, many small or big droplets can be observed. With the increase of water volume fraction, these droplet intermediates are bigger. In batch 2, the simulation box is a product of 3×3×3 of the $(10\ \text{nm})^3$ boxes, in each of which there is only one small droplet.

However, at this stage, all the droplets take the configuration of simple water-in-oil type. It means that, double emulsion droplets do not immediately form after the mixing of three components. When the mixtures were in the process of being equilibrated, simple emulsion droplets firstly formed. Double emulsion droplets are the further product of self-reorganization of small simple emulsion droplets which were merely the intermediates.

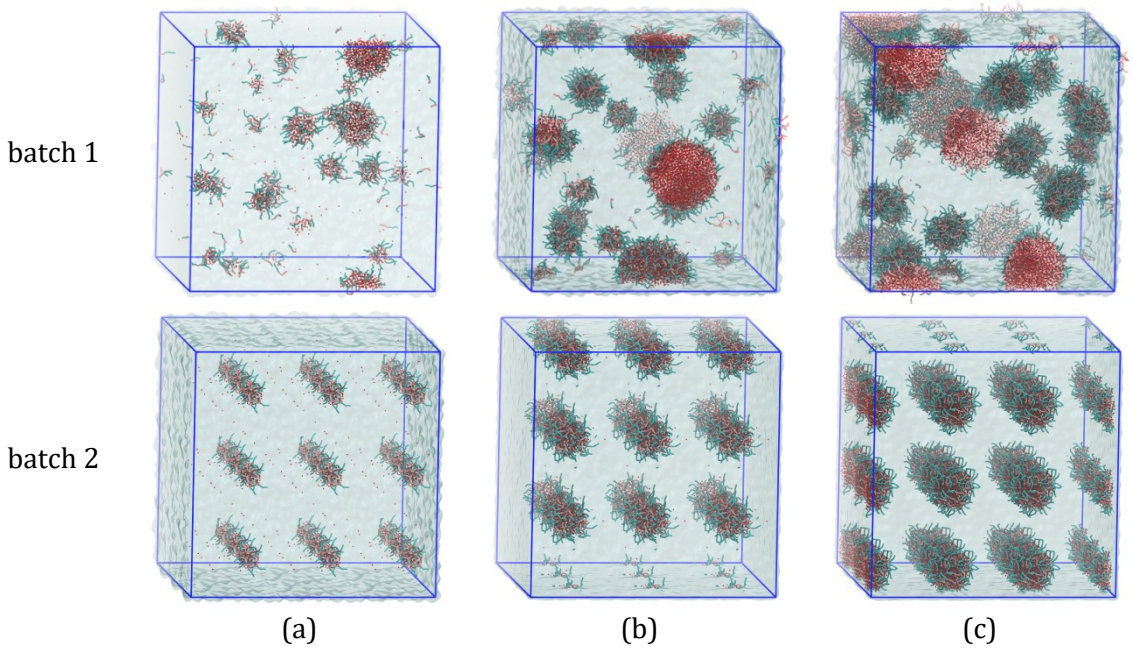
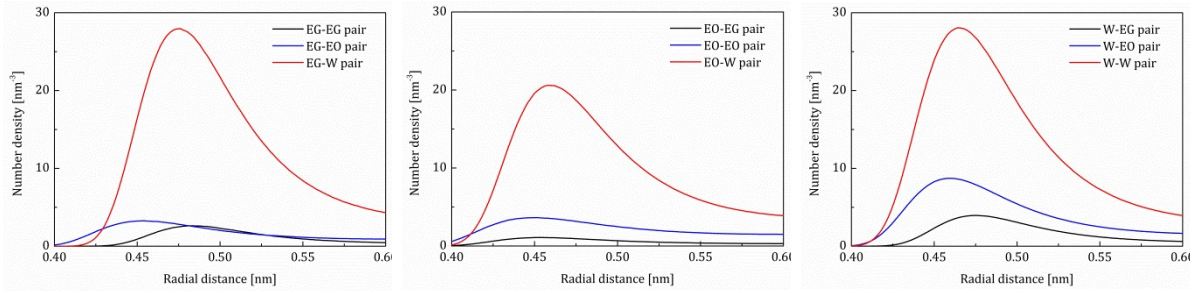


Figure S2. Conformation of the ternary mixtures at the beginning of the long-time equilibration (time = 0 μs) in batch 1 (top) and batch 2 (bottom) with $^{v}_{w/s}$ = 1.0/1.0 and (a) 1% water; (b) 3% water; (c) 5% water. The box size in the figures is ~ 30 nm.

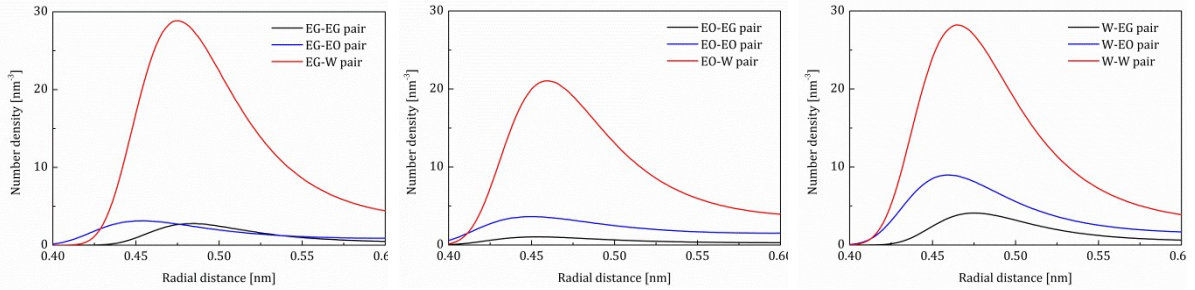
3 Radial Distribution Function

Figure S3 and Figure S4 plot the profiles of the radial distribution function (RDF) among the hydrophilic beads and waters for the emulsion systems in batch 1 with 3% and 5% water, respectively.



(a) (b) (c)

Figure S3. Radial distribution functions of the hydrophilic bead pairs in the emulsion system with 3% water in batch 1: (a) around EG; (b) around EO; (c) around W.



(a) (b) (c)

Figure S4. Radial distribution functions of the hydrophilic bead pairs in the emulsion system with 5% water in batch 1: (a) around EG; (b) around EO; (c) around W.