Supporting Information

Self-assembled Inverted Micelles Stabilize Ionic Liquid Domains in Supercritical CO_2

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Table S1: Force field parameters used. For atom notations, please refer to Fig. S1.

Bond Parameters

Bond	K_r (kJ mol^{-1}Å^{-2})	r_0 (Å)	Bond	K_r (kJ mol^{-1}Å^{-2})	r_0 (Å)
		[N-EtFOSA][24]			
CT-HC[a]	1422.56	1.090	N-S	1815.86	1.670
CT-CT[a]	1297.04	1.526	S-O	2928.80	1.441
CT-H1[a]	1422.56	1.090	S-CF[c]	985.00	1.818
CT-N[a]	1410.00	1.480	CF-F	1535.53	1.350
N-H[a]	1716.28	1.018	CF-CF	1121.30	1.550
		[TMG]$^+$ [23]			
CT-H1	1464.40	1.085	CA-N	1464.40	1.332
N1-CT	1255.20	1.467	N-H	2050.16	0.995
CA-N1	1464.40	1.330			
		[BMIM]$^+$ [22]			
C T-H1	2845.00	1.080	CW-H4	2845.00	1.080
CT-NA	2820.00	1.467	CR-H5	2845.00	1.080
CW-NA	3574.00	1.381	CT-CT	2242.00	1.528
CR-NA	3992.00	1.315	CT-HC	2845.00	1.090
CW-CW	4352.00	1.340			

$[Ac]^-$ [23], $[PF_6]^-$ [22], $[NO_3]^-$ [22], $[BF_4]^-$ [22] and CO_2 [26]

C-O2	1553.69	1.264	N-O	5307.00	1.227
C-CT	727.56	1.535	B-F	1213.36	1.392
C-HC	882.99	1.094	C_c-O_c	-	1.149
P-F	3100.00	1.605			

Angle Parameters

Angle	K_θ (kJ mol^{-1}rad^{-2})	θ_0 (deg)	Angle	K_θ (kJ mol^{-1}rad^{-2})	θ_0 (deg)
		[NEtFOSA] [24]			
H-CT-H[a]	146.44	109.5	N-S-CF[c]	408.00	100.2
CT-CT-H[a]	209.20	109.5	O-S-O	435.14	119.0
CT-CT-N[b]	334.72	109.7	O-S-CF[c]	435.00	102.6
H1-CT-N[b]	209.20	109.5	S-CF-CF[b]	261.08	111.9
CT-N-H[b]	209.20	118.0	S-CF-F[c]	347.00	111.8
CT-N-S	209.20	120.0	CF-CF-F	209.20	109.5
H-N-S	230.12	111.0	F-CF-F	322.17	109.1
N-S-O	502.08	107.0	CF-CF-CF	244.14	112.7
		$[TMG]^+$ [23]			
H1-CT-H1	154.81	108.9	N1-CA-N1	292.88	121.9
N1-CT-H1	217.57	110.0	N-CA-N1	309.62	119.0
CT-N1-CT	292.88	115.0	CA-N-H	209.20	121.5
CA-N1-CT	209.20	121.9	H-N-H	108.78	117.0
		$[BMIM]^+$ [22]			
H1-CT-H1	276.10	107.8	CR-NA-CW	585.80	108.5
H1-CT-NA	313.80	110.7	CW-CW-H4	292.90	130.9
CT-NA-CR	585.80	126.4	CT-CT-NA	488.30	112.7
CT-NA-CW	585.80	125.6	CT-CT-H1	313.80	110.7
NA-CW-H4	292.90	122.0	CT-CT-CT	488.30	112.7
NA-CW-CW	585.80	107.1	CT-CT-HC	313.80	110.7
NA-CR-H5	292.90	125.1	HC-CT-HC	276.10	107.8
NA-CR-NA	585.80	109.8			
		$[Ac]^-$ [23], $[PF_6]^-$ [22], $[NO_3]^-$ [22] and $[BF_4]^-$ [22]			
O2-C-O2	561.91	124.9	F-P-F	1165.0	90.0
O2-C-CT	592.04	117.6	O-N-O	1011.0	120.0
C-CT-HC	450.23	109.5	F-B-F	669.5	109.5
HC-CT-HC	139.33	106.8			

Dihedral Parameters

Dihedral	V_0(kJ mol^{-1})	V_1(kJ mol^{-1})	V_2(kJ mol^{-1})	V_3(kJ mol^{-1})	V_4(kJ mol^{-1})
		[NEtFOSA][24]			
HC-CT-CT-H1[a]	0.000	0.000	0.000	1.255	0.000
HC-CT-CT-N[b]	0.000	0.000	0.000	1.941	0.000
CT-CT-N-H	0.000	0.000	0.000	0.000	0.000
CT-CT-N-S	-0.368	12.255	-10.598	2.079	0.000
H1-CT-N-H	0.000	0.000	0.000	0.000	0.000
H1-CT-N-S	0.502	5.669	-6.096	0.623	0.000
CT-N-S-O	0.000	0.000	0.000	0.000	0.000
CT-N-S-CF[d]	0.000	-19.682	-32.267	8.819	16.954
H-N-S-O	0.000	0.000	0.000	0.000	0.000
H-N-S-CF[a]	0.000	0.000	9.205	0.000	0.000
N-S-CF-F[c]	0.000	0.000	0.000	1.322	0.000
N-S-CF-CF[d]	0.000	-12.016	0.000	5.113	3.539
O-S-CF-F[c]	0.000	0.000	0.000	1.451	0.000
O-S-CF-CF	0.000	0.000	0.000	0.000	0.000
S-CF-CF-F[b]	0.000	0.000	0.000	1.464	0.000
S-CF-CF-CF[d]	0.000	-27.367	-4.527	8.192	0.000
F -CF -CF –F	0.000	-10.460	0.000	1.046	0.000
CF-CF-CF-F	0.000	1.255	0.000	1.674	0.000
CF-CF-CF-CF	0.000	27.706	3.966	-5.807	-8.862
		[TMG]$^+$ [23]			
CT-N1-CT-H1	0.000	0.000	0.000	1.372	0.000
CA-N1-CT-H1	0.000	0.000	0.000	0.000	0.000
N1-CA-N1-CT	0.000	0.000	23.430	0.000	0.000
N-CA-N1-CT	0.000	0.000	23.430	0.000	0.000
N1-CA-N-H	0.000	0.000	14.364	0.000	0.000
		[BMIM]$^+$ [22]			
H1-CT-NA-CR	0.000	0.000	0.000	0.000	0.000
H1-CT-NA-CW	0.000	0.000	0.000	0.519	0.000
X-CR-NA-X	0.000	0.000	19.460	0.000	0.000
X-CW-NA-X	0.000	0.000	12.550	0.000	0.000
X-CW-CW-X	0.000	0.000	44.980	0.000	0.000
CW-NA-CT-CT	0.000	-7.154	6.106	0.759	0.000
CR-NA-CT-CT	0.000	-5.269	0.000	0.000	0.000
NA-CT-CT-CT	0.000	-7.480	3.164	-1.203	0.000
NA-CT-CT-HC	0.000	0.000	0.000	0.367	0.000
CT-CT-CT-CT	0.000	7.280	-0.657	1.167	0.000
CT-CT-CT-HC	0.000	0.000	0.000	1.531	0.000
HC-CT-CT-HC	0.000	0.000	0.000	1.331	0.000

		$[Ac]^-$ [23]			
HC–CT–C-O2	0.000	6.694	0.000	0.669	0.000

Nonbonded Parameters

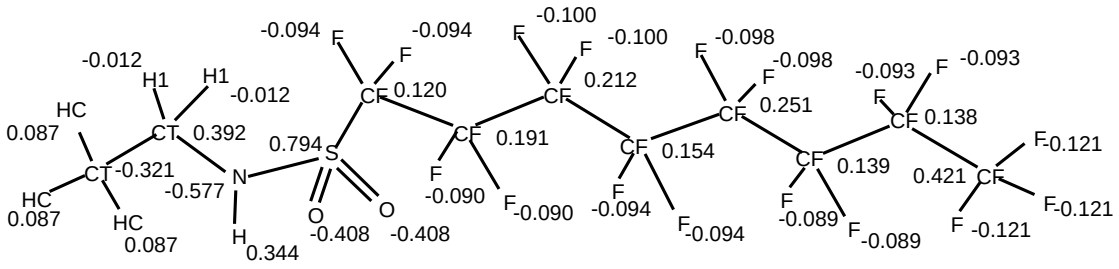
atom ID	ε_{ii} (kJ mol^{-1})	σ_{ii} (Å)	atom ID	ε_{ii} (kJ mol^{-1})	σ_{ii} (Å)
			$[NEtFOSA]$ [24]		
CT	0.4577	3.399	S	1.0460	3.550
HC	0.0657	2.650	O	0.7113	2.960
H1	0.0657	2.471	CF	0.2761	3.500
N	0.7113	3.250	F	0.2218	2.950
H	0.0660	1.069			
			$[TMG]^+$ [23]		
CA	0.3598	3.399	CT	0.4577	3.399
N	0.7113	3.250	H1	0.0657	2.471
N1	0.7113	3.250	H	0.0657	1.069
			$[BMIM]^+$ [22]		
HC	0.1255	2.500	CT	0.2761	3.500
H1	0.1255	2.500	CR	0.2929	3.550
H4	0.1255	2.420	CW	0.2929	3.550
H5	0.1255	2.420	NA	0.7113	3.250
			$[Ac]^-$ [23], $[PF_6]^-$ [22], $[NO_3]^-$ [22], $[BF_4]^-$ [22], $[Cl]^-$ [22] and CO_2 [26]		
O2	0.8786	2.960	O_N	0.6100	2.770
C	0.3598	3.399	B	0.3975	3.581
CT	0.4577	3.399	F_B	0.2552	3.118
HC	0.0657	2.650	Cl	0.8300	3.650
P	0.8368	3.740	C_c	0.2340	2.757
F_P	0.2552	3.118	O_c	0.6690	3.033
N	0.3380	3.060			

F_P: Fluorine in $[PF_6]^-$; O_N: Oxygen in $[NO_3]^-$; F_B: Fluorine in $[BF_4]^-$; and c stands for CO_2. Atomic charge on chloride is set to -1.

[a]From AMBER parameter set: a) W. D. Cornell, P. Cieplak, C. I. Bayly, I. R. Gould, K. M. Merz, D. M. Ferguson, D. C. Spellmeyer, T. Fox, J. W. Caldwell, P. A. Kollman, *J. Am. Chem. Soc.* **1995**, *117*, 5179-5197. b) J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman, D. A. Case, *J. Comput. Chem*. **2004**, *25*, 1157-1174.
[b]From OPLS parameter set: W. L. Jorgensen, D. S. Maxwell, J. Tirado-Rives, *J. Am. Chem. Soc.* **1996,** *118,* 11225-11236.
[c]From Ref. 22.
[d]Developed in this work.

Table S2: Comparison of simulated crystal structure of N-EtFOSA with experimental data from the Cambridge structural database (Lehmler, H. J.; Rama Rao, V.V.V.N.S.; Nauduri, D.; Vargo, J. D.; Parkin, S.; *J. Fluorine Chem.* **2007**, 128, 595–607). The objective of the simulations was to test the performance of the force field in predicting both the crystal density and its structural properties, such as the dimensions and director angles of the crystalline unit cell. A similar simulation protocol, as prescribed by Padua and coworkers, was followed.[22] The liquid-state properties could not be compared due to the unavailability of experimental data.

Formula	$C_2H_5NHSO_2C_8F_{17}$
Molecular mass	527.22
Crystal system	Triclinic
Space group	P -1
Molecules/box	48
Stacked cells	4x3x1
T/*K*	90
Cut off/Å	12.0
Molecules/cell	4
a_{exp}/ Å	6.341
a_{sim}/ Å	6.265
b_{exp}/ Å	9.567
b_{sim}/ Å	9.180
c_{exp}/ Å	28.230
c_{sim}/ Å	28.476
α_{exp}/deg	88.579
α_{sim}/deg	90.0
β_{exp}/deg	85.758
β_{sim}/deg	90.0
γ_{exp}/deg	87.348
γ_{sim}/deg	90.0
V_{exp}/ Å^3	1705.69
V_{sim}/ Å^3	1636.54
ρ_{exp}/g cm^{-3}	2.053
ρ_{sim}/g cm^{-3}	2.139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F
F
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F
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F
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-0.012
H1
H1
-0.012
CF
0.120
CF
0.212
CF
0.251
F
CF
0.138
HC
0.087
CT
0.392
0.794
S
CF
0.191
CF
0.154
CF
0.139
F
-0.121
CT
-0.321
N
-0.577
F
-0.090
F
-0.090
F
-0.094
F
-0.094
F
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F
-0.089
0.421
CF
F
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HC
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HC
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O
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H
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F
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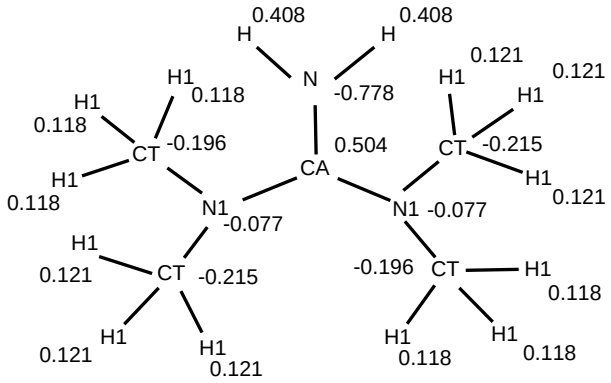
(a)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H1
0.118
H1
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0.121
H1
CT
-0.196
0.504
CA
CT
-0.215
H1
0.118
H1
0.121
N1
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N1
-0.077
H1
0.121
CT
-0.215
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H1
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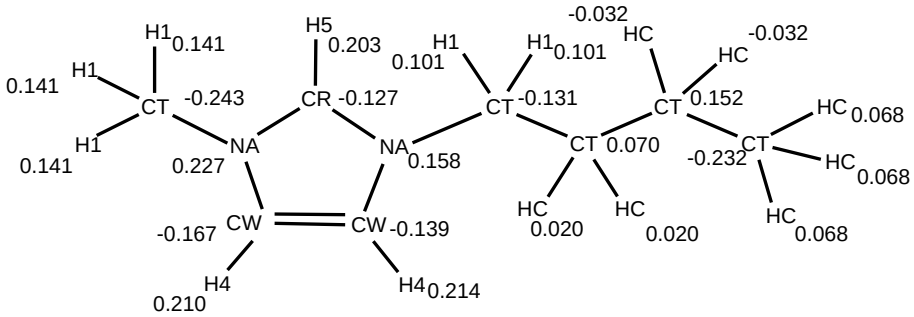
0.118

(b)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H5
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0.101
H1
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HC
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HC
H1
0.141
CT
-0.243
CR
-0.127
CT
-0.131
CT
0.152
HC
0.068
H1
0.141
NA
0.227
NA
0.158
CT
0.070
CT
-0.232
HC
0.068
HC
0.068
CW
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CW
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HC
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HC
0.020
H4
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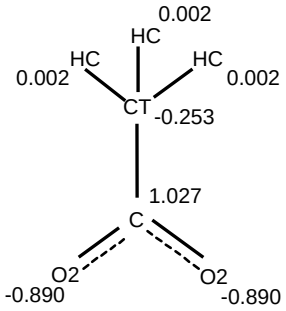
H4
0.214

(c)



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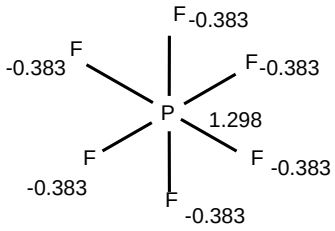

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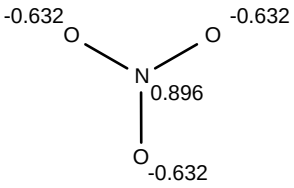

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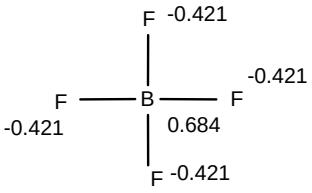

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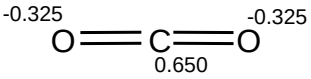

(h)

Figure S1: Atom-centered point charges on surfactant and IL ions. (a) N-EtFOSA (b) $[TMG]^+$ (c) $[BMIM]^+$ (d) Ac^- (e) PF_6^- (f) NO_3^- (g) BF_4^- (h) CO_2.

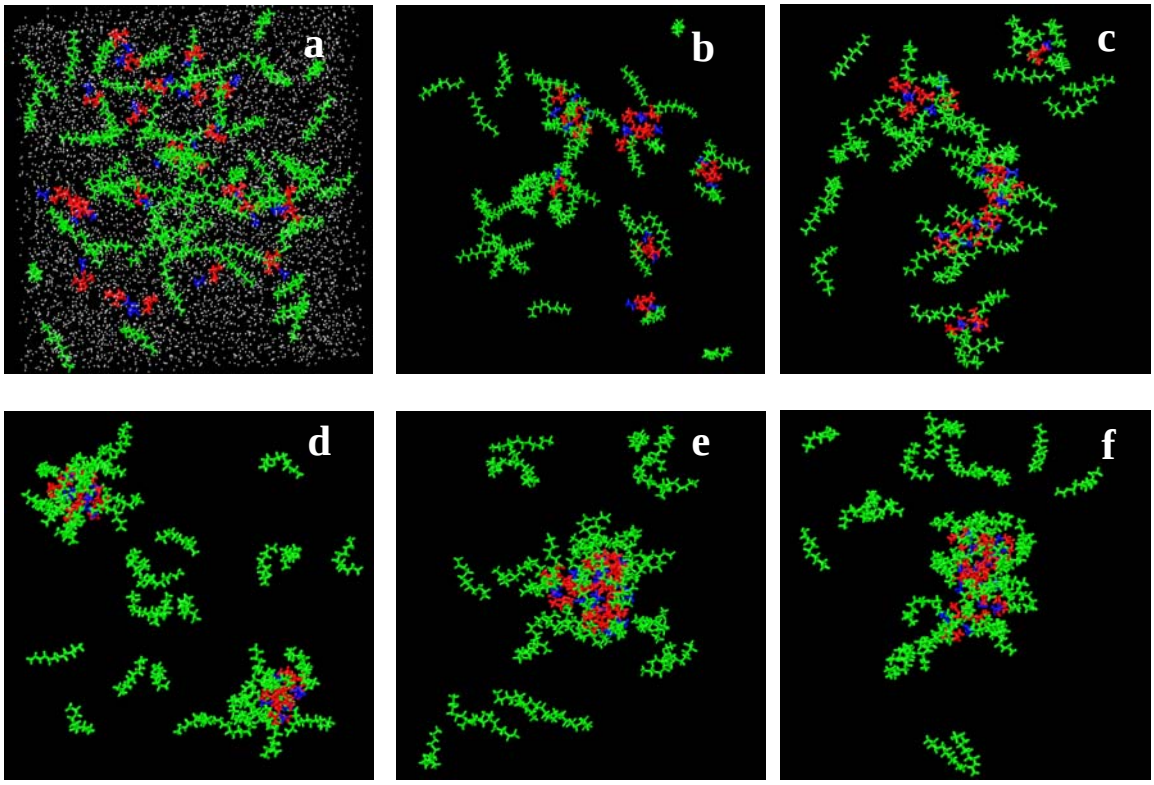

Figure S2. Time evolution of the ternary mixture of [TMG][Ac]/N-EtFOSA/CO_2 at W_o = 0.4. Snapshots are taken at (a) 0 ns (b) 0.5 ns (c) 30 ns (d) 70 ns (e) 120 ns and (f) 200 ns. Color scheme: red, cations; blue, anions; green, surfactants; white dots, C of CO_2. In (b) - (f), CO_2 is omitted for clarity.

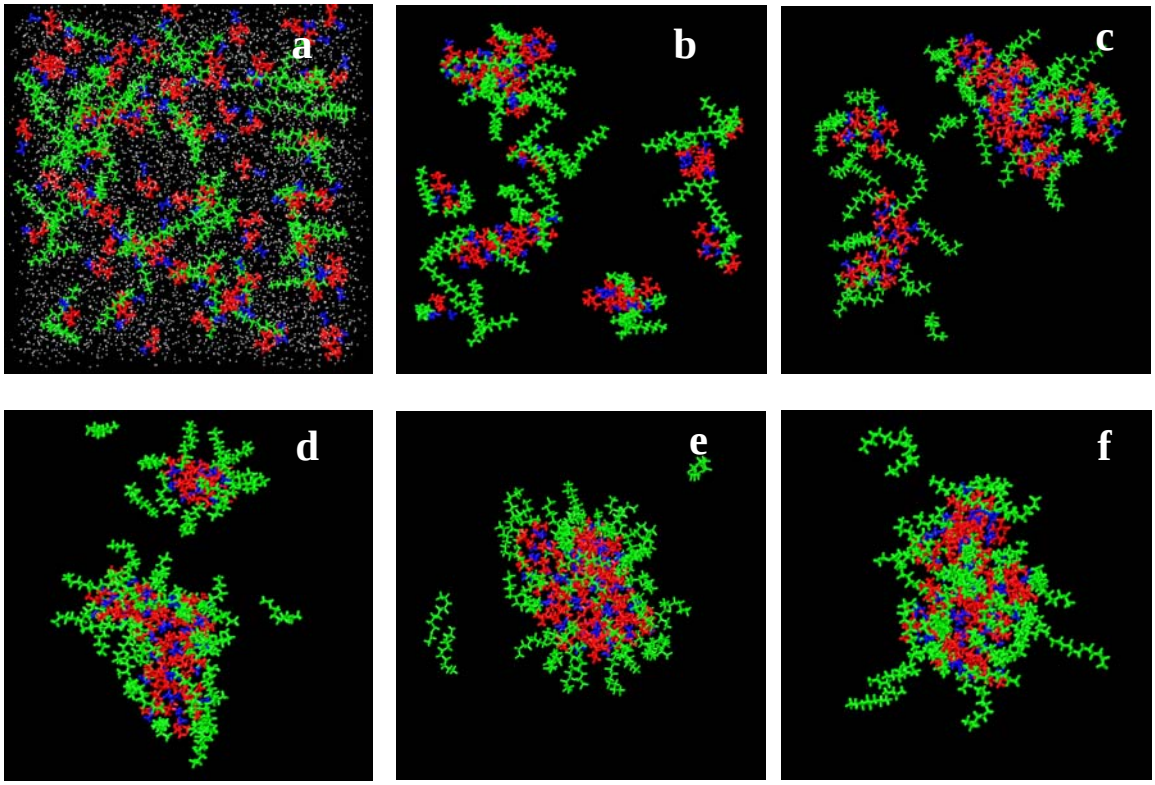

Figure S3. Time evolution of the ternary mixture of [TMG][Ac]/N-EtFOSA/CO_2 at W_o = 1.2. Snapshots are taken at (a) 0 ns (b) 0.3 ns (c) 20 ns (d) 70 ns (e) 100 ns and (f) 200 ns. Color scheme: red, cations; blue, anions; green, surfactants; white dots, C of CO_2. In (b) - (f), CO_2 is omitted for clarity.

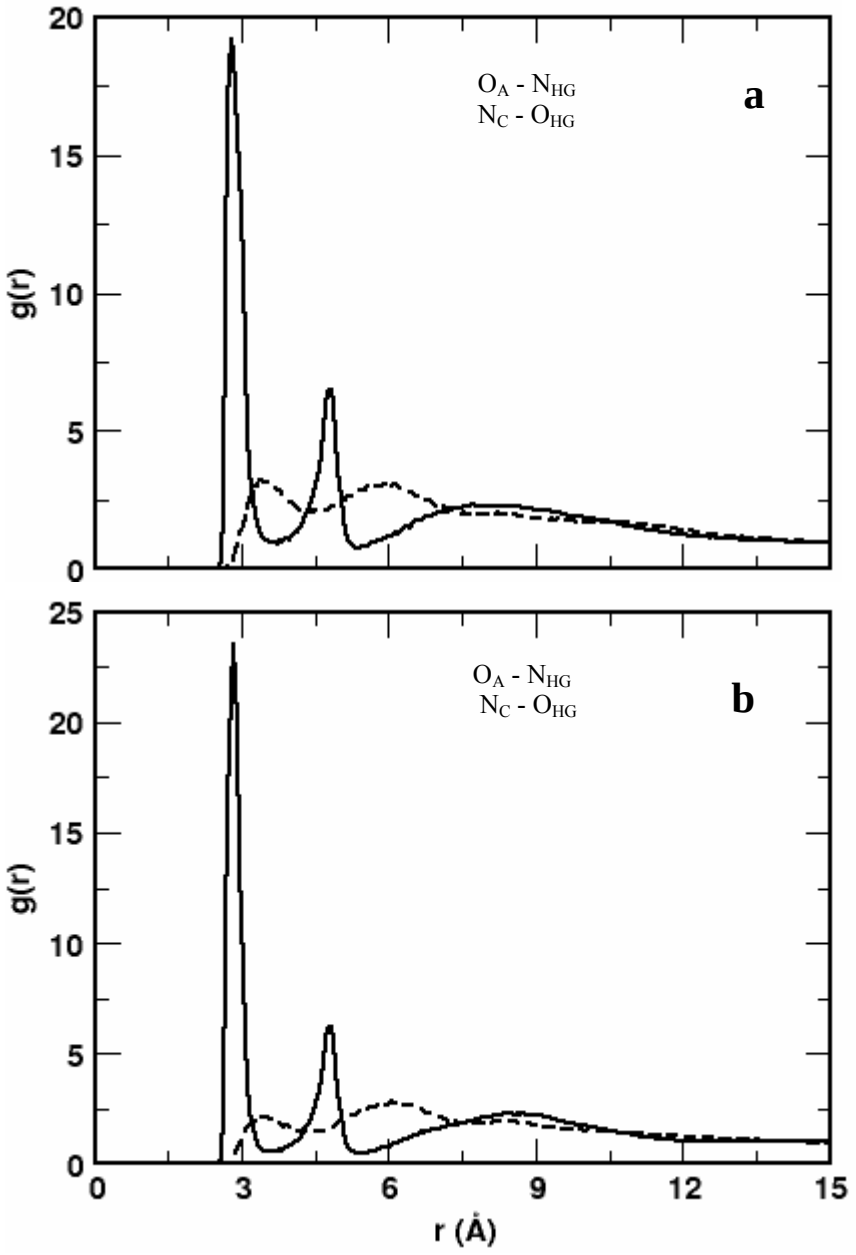

Figure S4. Radial distribution functions for the [TMG][Ac] – surfactant pairs in [TMG][Ac]/N-EtFOSA/CO2 systems with (a) Wo = 0.4 and (b) Wo = 1.2. Solid line: anion – headgroups, dashed line: cation - headgroups. The site-site distribution functions with maximum intensity in each category are compared.

Multi-author Complete References:

(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V. B., A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; Gaussian 03, Revision C.02; Gaussian, Inc. Wallingford CT, **2004**.

(26) Case, D.A.; Darden, T.A.; Cheatham, III, T.E.; Simmerling, C.L.; Wang, J.; Duke, R.E.; Luo, R.; Merz, K.M.; Pearlman, D.A.; Crowley, M.; Walker, R.C.; Zhang, W.; Wang, B.; Hayik, S.; Roitberg, A.; Seabra, G.; Wong, K.F.; Paesani, F.; Wu, X.; Brozell, S.; Tsui, V.; Gohlke, H.; Yang, L.; Tan, C.; Mongan, J.; Hornak, V.; Cui, G.; Beroza, P.; Mathews, D.H.; Schafmeister, C.; Ross, W.S.; Kollman, P.A. *Amber 9.0*; : University of California, San Francisco, CA., **2006**.