Electronic Supplementary Material (ESI) for Soft Matter.

SUPPORTING INFORMATION

Structure and dynamics of aqueous solution containing poly-(acrylic acid) and non-ionic surfactant octaethylene glycol n-decyl ether (C10E8) aggregates and their complexes investigated by molecular dynamics simulations

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Force-Field Details

The total intermolecular potential of the GROMOS 45a3force-field is given by the expression

$$U = \sum_{bonds} \frac{1}{4} k_i^b (b_i^2 - b_{i,0}^2)^2 + \sum_{angles} \frac{1}{2} k_i^\theta (\cos(\theta_i) - \cos(\theta_{i,0}))^2$$

$$+ \sum_{\substack{proper \\ torsion}} k_i^\varphi [1 + \cos(\delta_i)\cos(m_i \varphi_i)] + \sum_{\substack{improper \\ torsion}} \frac{1}{2} k_i^\varepsilon (\varepsilon_i - \varepsilon_{i,0})^2 + U_{nb} \qquad (1)$$

$$U_{nb} = \sum_{pairs-i,j} 4\,\varepsilon_{ij} \left(\left(\frac{\varepsilon_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\varepsilon_{ij}}{r_{ij}} \right)^{6} \right) + \sum_{pairs-i,j} \frac{1}{4\pi\varepsilon_o} \frac{q_i q_j}{r_{ij}^2}$$

In eq.(1) k_{ib}, $k_{i\theta}$, $k_{\varphi i}$ and $k_{\varepsilon i}$ represent force constants for bond lengths, bond angles, proper and improper torsion angles respectively, while b_i, θ_i, φ_i, and ε_i are i^{th} bond length, bending angle, proper and improper torsion angle respectively, whereas $b_{i,0}$, $\theta_{i,0}$, $\varphi_{i,0}$, and $\varepsilon_{i,0}$ are reference bond length, bending angle, proper and improper torsion angle respectively.

Equations used to calculate Aspect Ratio Φ and eccentricity e are as follows:

$$e = 1 - I_{min}/I_{avg} \qquad (2)$$

$$A = I_{max} / I_{min} \qquad (3)$$

$$I_{xx} = \frac{\sum_{i=1}^{N} (y_i - y_{com})^2 + (z_i - z_{com})^2}{2\sum_{i=1}^{N} m_i} \qquad (4)$$

$$I_{yy} = \frac{\sum_{i=1}^{N} (x_i - x_{com})^2 + (z_i - z_{com})^2}{2\sum_{i=1}^{N} m_i} \quad (5)$$

$$I_{zz} = \frac{\sum_{i=1}^{N} (x_i - x_{com})^2 + (y_i - y_{com})^2}{2\sum_{i=1}^{N} m_i} \quad (6)$$

Solvation enthalpy is calculated using the following relations:

$\Delta H_{sol(surf)} = H_{binarysystem} - (N*H_{surfactant\ in\ vacuum} + H_{pure\ water})$ (7)

$\Delta H_{sol(polymer)} = H_{ternary\ system} - (H_{binary\ system} + H_{polymerinvaccum})$ (8)

$\Delta H_{P\text{-}S\ bind} = H_{ternary\ system} - (H_{polymerin\ water} + H_{binary\ system})$ (9)

$\Delta H_{agg} = H_{binary\ system} - (N*H_{surfactantin\ water})$ (10)

$\Delta H_{form} = H_{ternarysystem} - (H_{purewater} + H_{polymer\ in\ vacuum} + N*H_{surfactant\ in\ vaccum})$ (11)

where H = U + PV, U is total internal energy (kJ/mol), P is the total system pressure (atm), δV is the volume change defined in the NPT ensemble, N is number of surfactant molecules in the system.

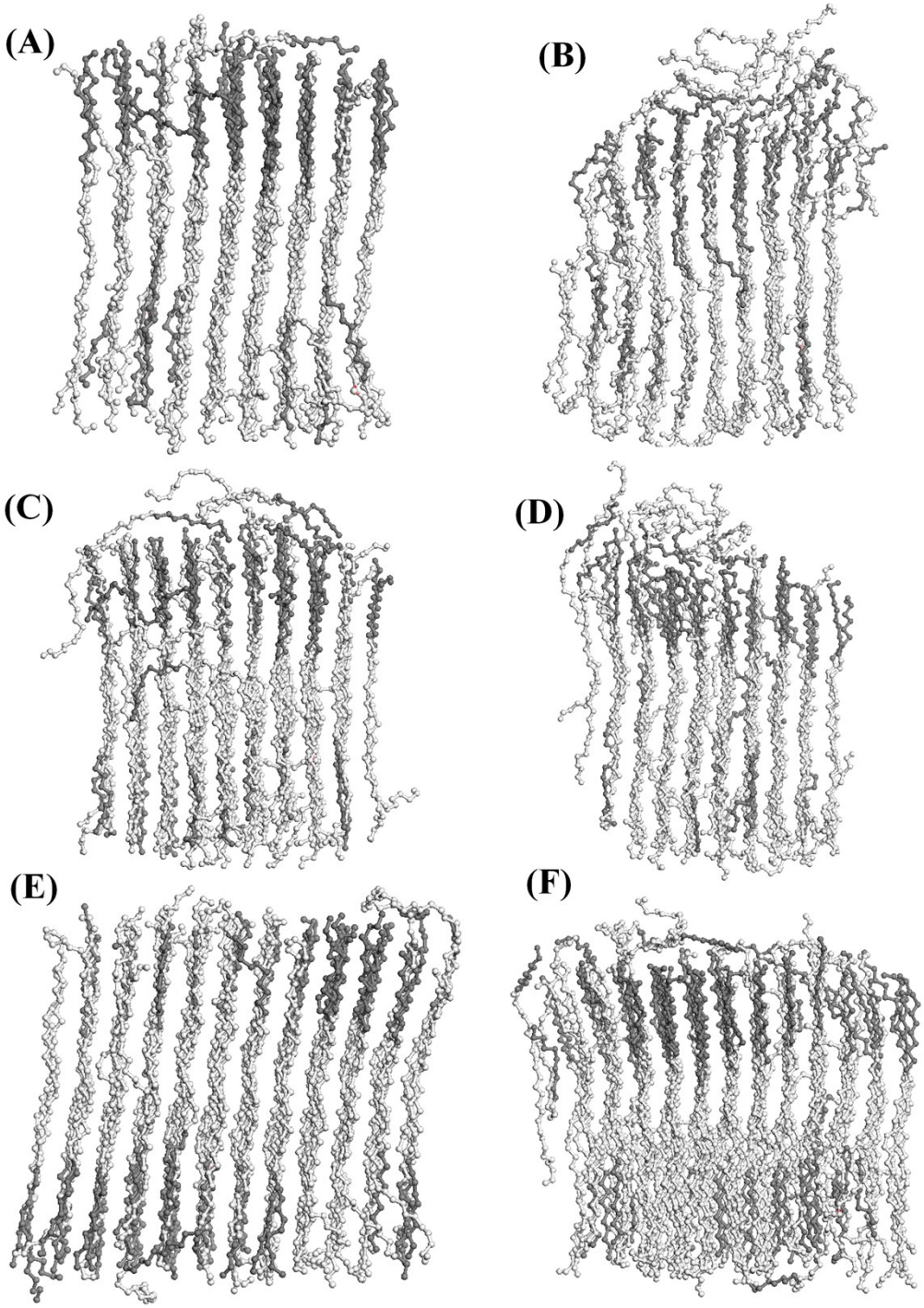

Figure1S. represents the snapshots in binary system at a concentration of (A) 53 molecules, (B) 61 molecules, (C) 69molecules , (D) 77molecules, (E) 85molecules, (F) 93 molecules respectively. White colour represents the polar part and black colour represents the non-polar part of the surfactant.

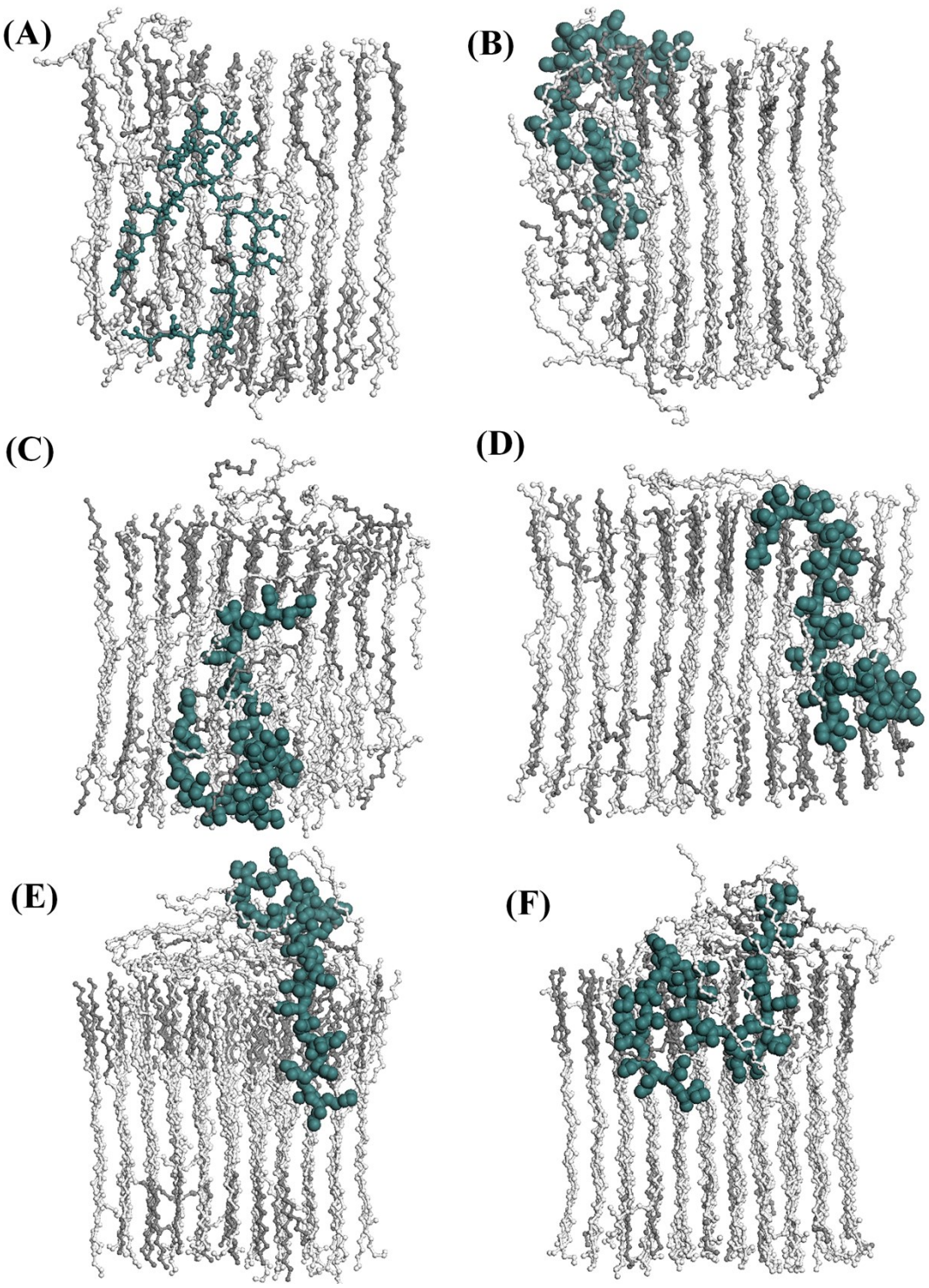

Figure 2S. represents the snapshots in ternary system at a concentration of (A) 53 molecules, (B) 61 molecules, (C) 69 molecules , (D) 77molecules, (E) 85molecules, (F) 93 molecules respectively. White colour represents the polar part and black colour represents the non-polar part of the surfactant.

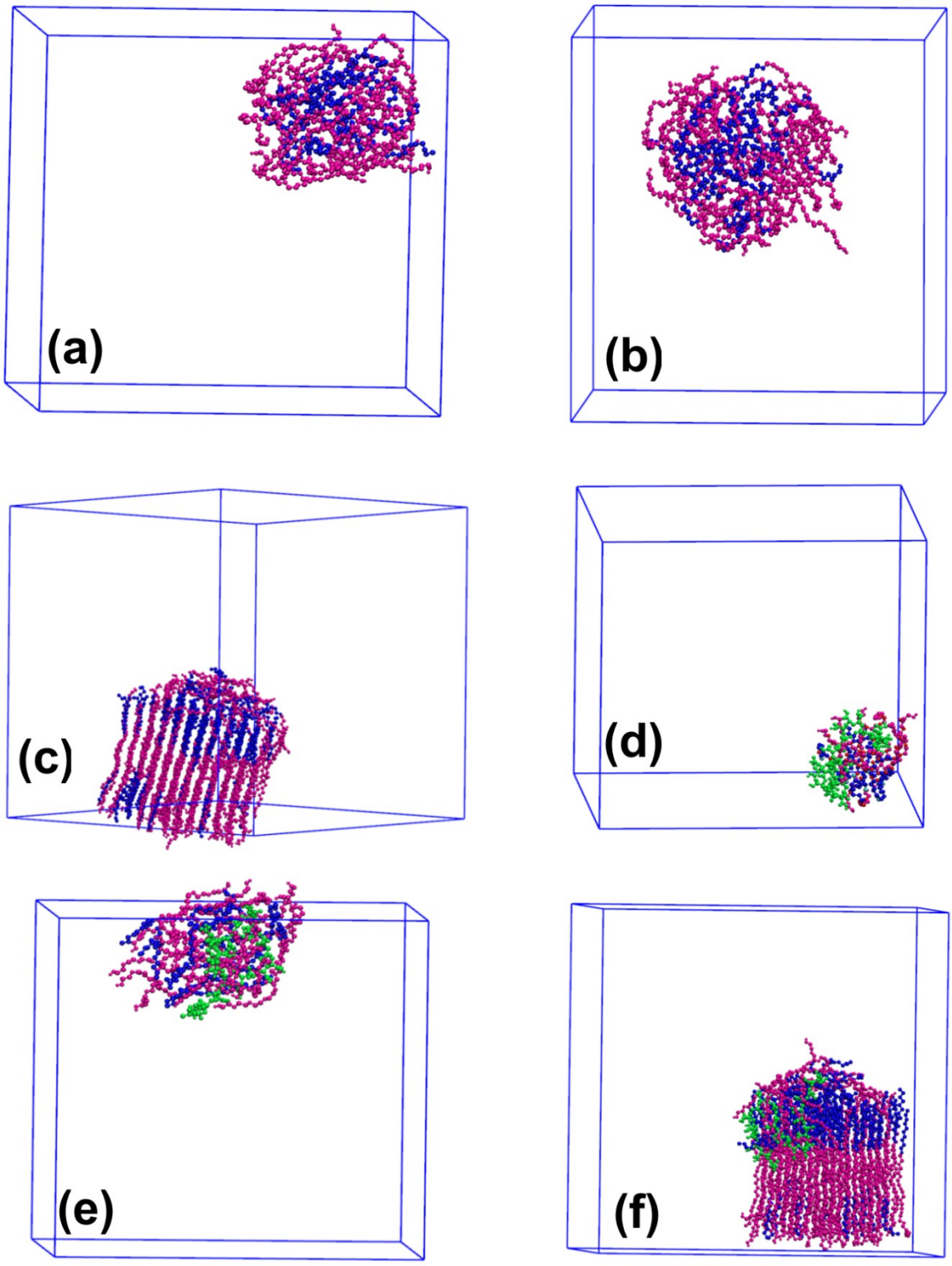

Figure 3S. Snapshots at different surfactant concentration.(a) 0.094 gmol/lit in binary solution. (b) 0.12 gmol/lit in binary solution, (c) 0.32 gmol/lit in binary solution. (d) 0.048 gmol/lit in ternary solution. (e) 0.062 gmol/lit in ternary solution. (f) 0.30 gmol/lit in ternary solution.

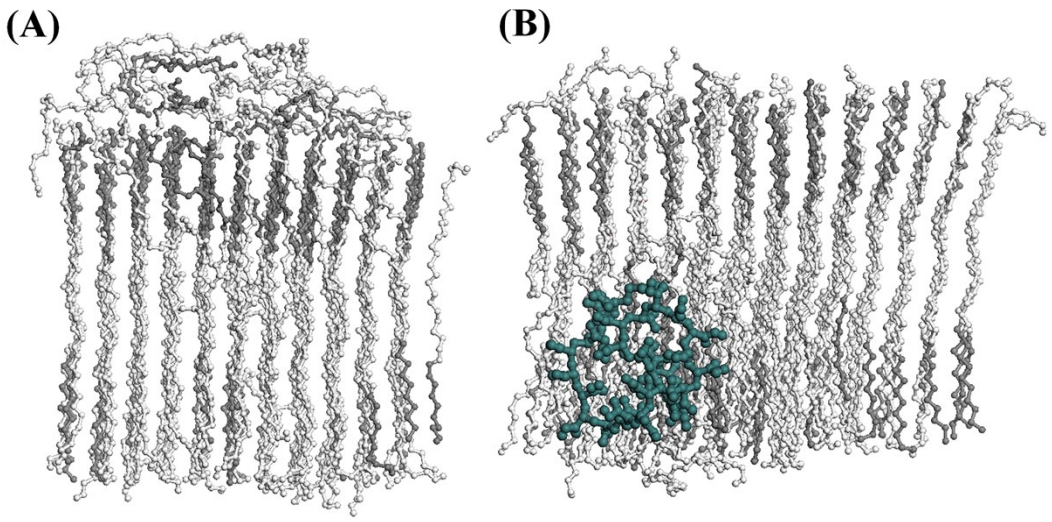

Figure 4S. represents the snapshots of (A) binary system at 101 molecules, (B) ternary system at 101molecules.

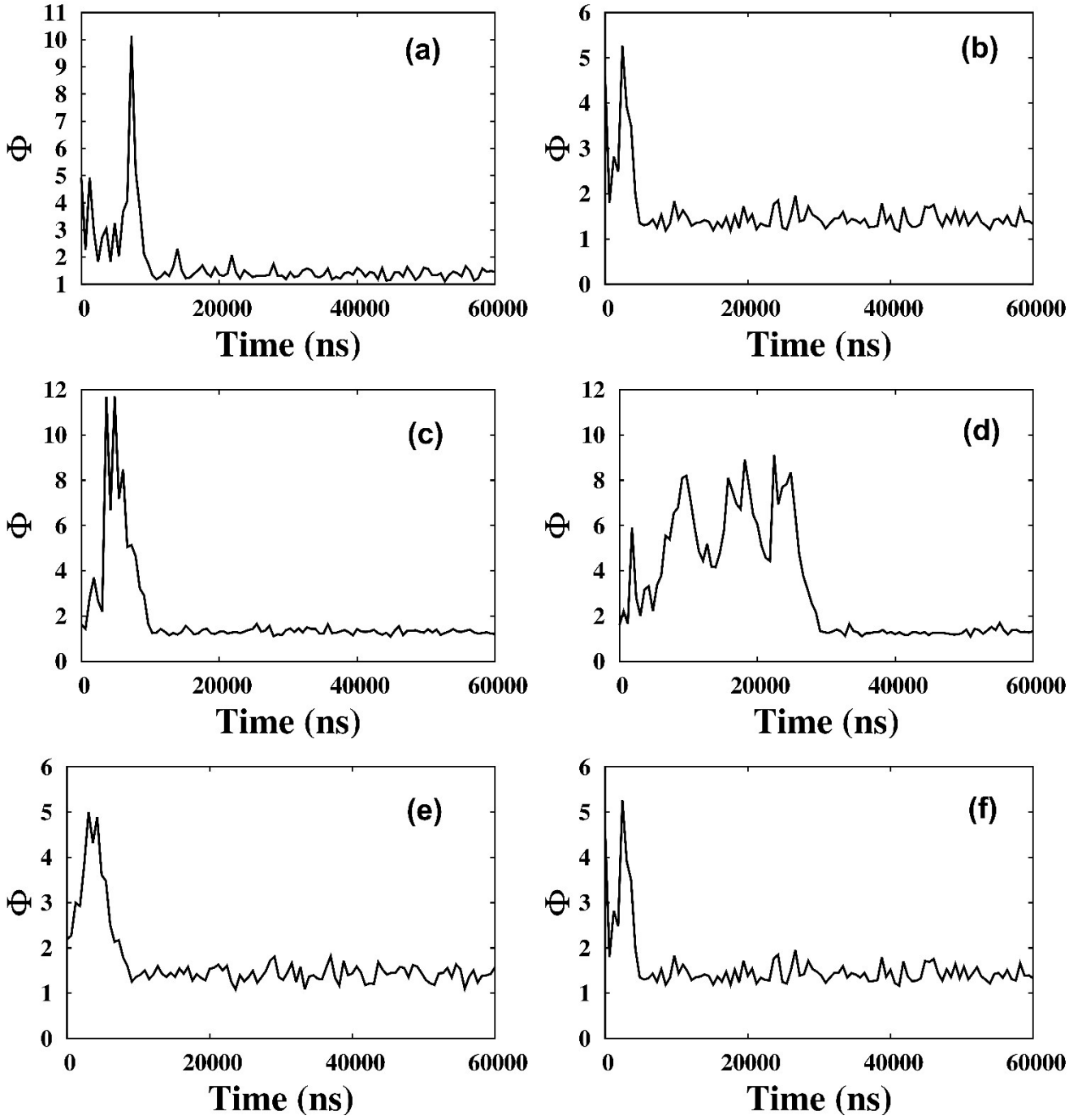

Figure 5S. Aspect ratio of micelles of different aggregation numbers corresponding to different surfactant concentration. (A) 0.042 gmol/lit in binary solution (B) 0.068 gmol/lit in binary solution (C) 0.094 gmol/lit in binary solution (D) 0.12 gmol/lit in binary solution (E) 0.042 gmol/lit in ternary solution (F) 0.068 gmol/lit in ternary solution.

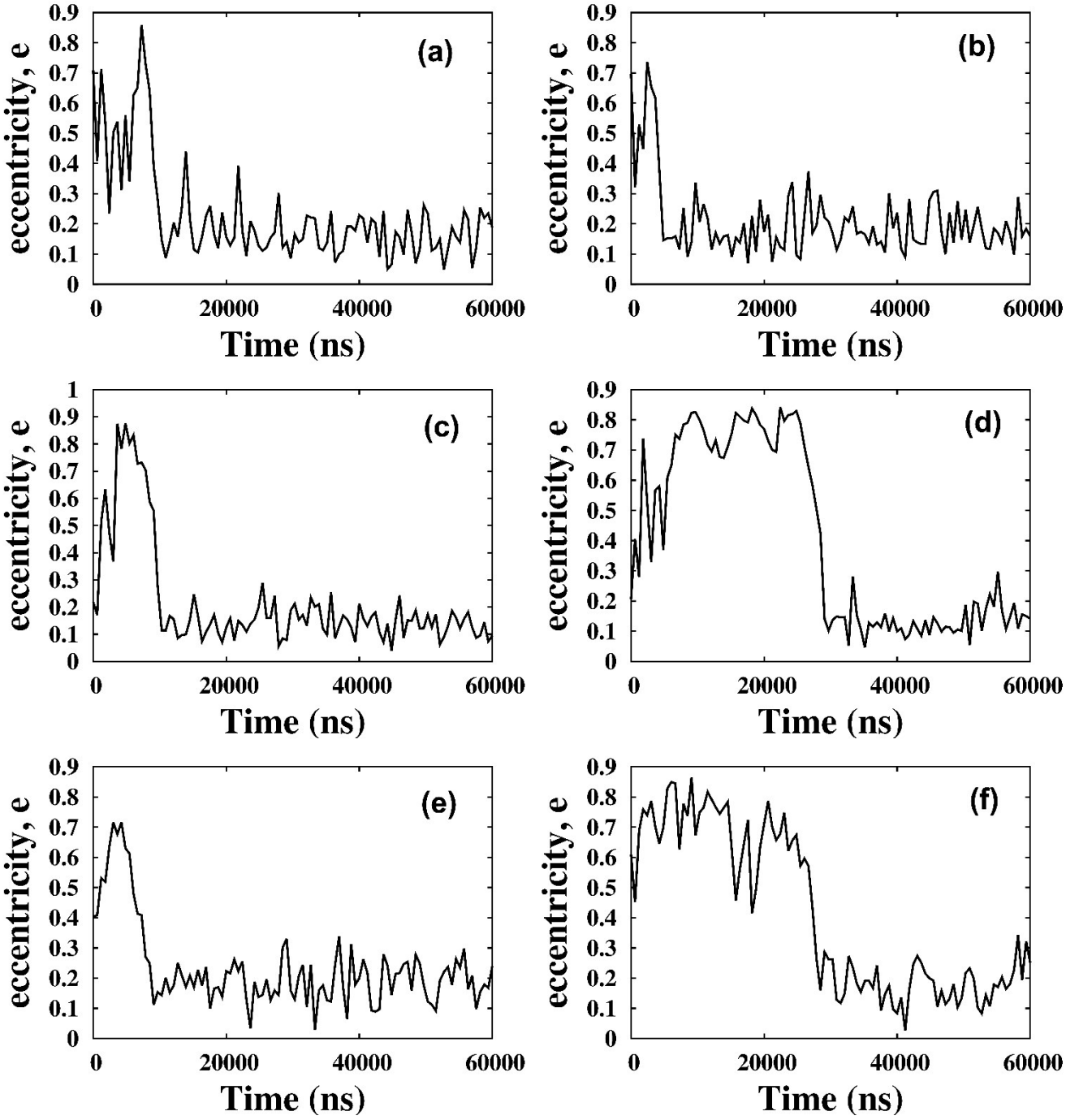

Figure 6S. Eccentricity of micelle of different aggregation numbers corresponding to different surfactant concentration. (A) 0.042 gmol/lit in binary solution (B) 0.068 gmol/lit in binary solution (C) 0.094 gmol/lit in binary solution (D) 0.12 gmol/lit in binary solution (E) 0.042 gmol/lit in ternary solution (F) 0.068 gmol/lit in ternary solution.

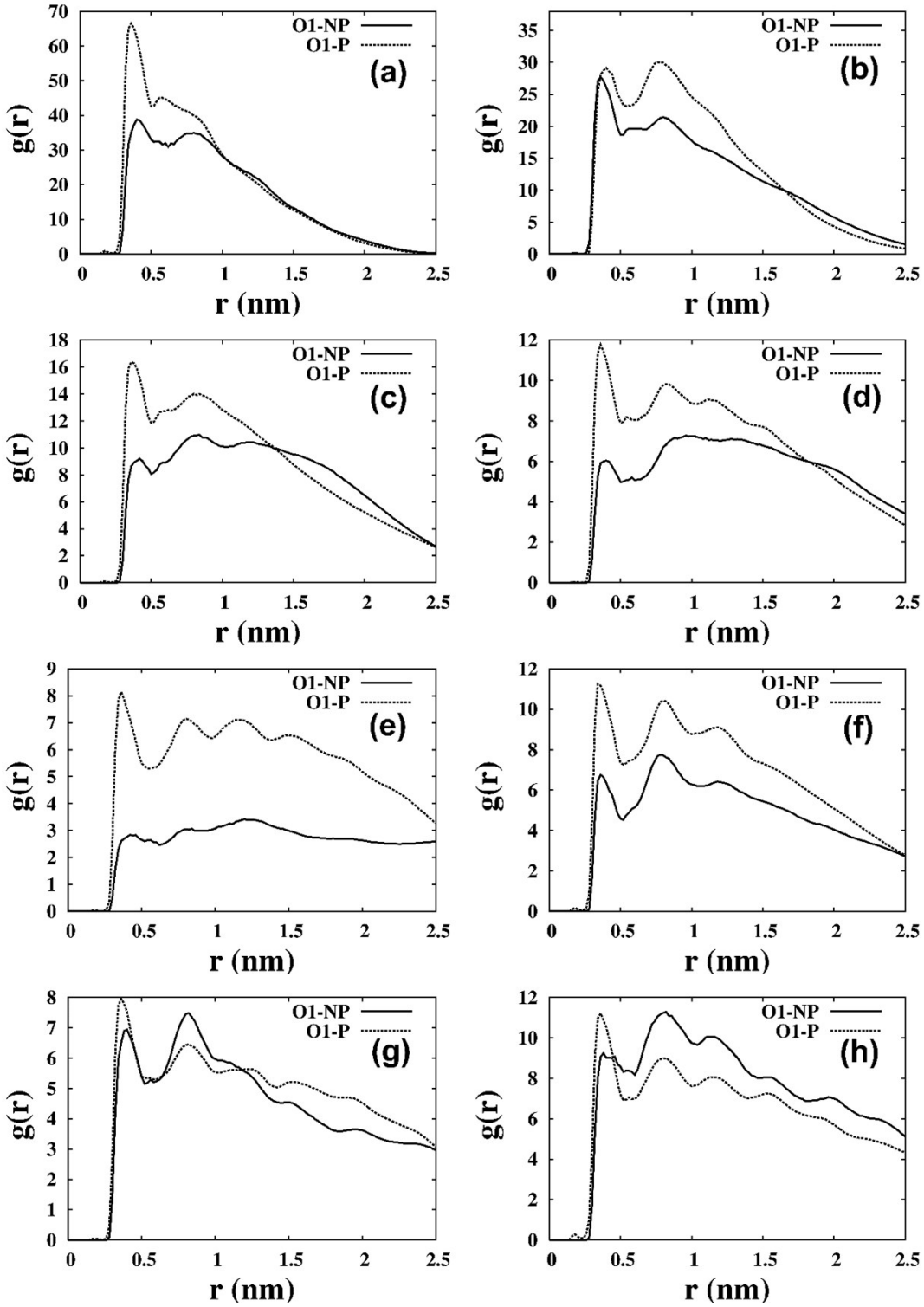

Figure 7S. Radial distribution functions (RDF's) for carbonyl oxygen (O1) of PAA with polar and non-polar parts of the surfactant in ternary solution at different values of $C_{10}E_8$ concentration. (a) 0.016 gmol/lit, (b) 0.042 gmol/lit, (c) 0.068 gmol/lit, (d) 0.094 gmol/lit, (e) 0.12 gmol/lit, (f) 0.14 gmol/lit (g) 0.17 gmol/lit, (h) 0.19 gmol/lit.

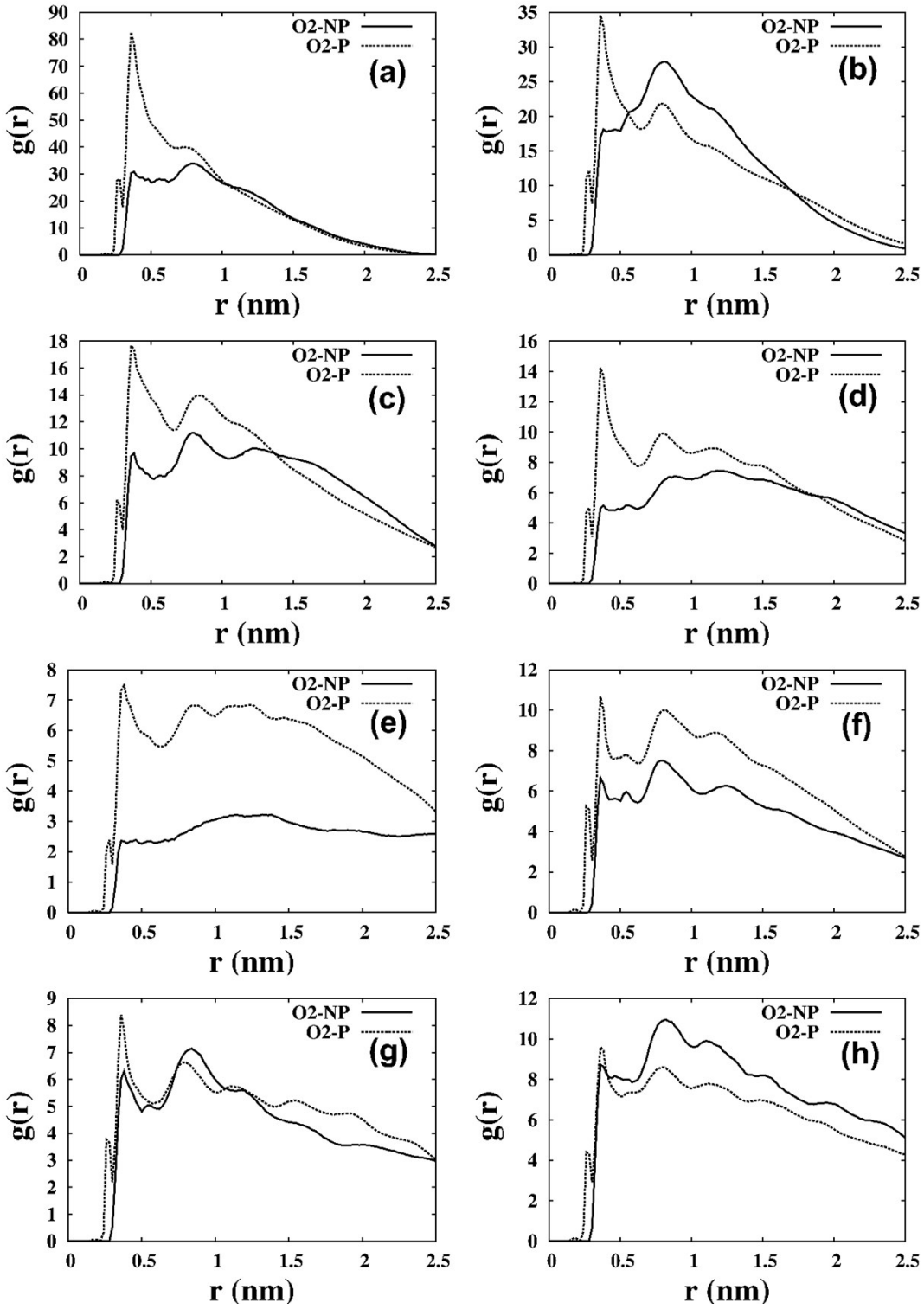

Figure 8S. Radial distribution functions (RDF's) between carbonyl oxygen (O1) and the polar and non-polar parts of surfactant in ternary solution at different concentration of $C_{10}E_8$ surfactant. (a) 0.016 gmol/lit (b) 0.042 gmol/lit, (c) 0.068 gmol/lit (d) 0.094 gmol/lit (e) 0.12 gmol/lit (f) 0.14 gmol/lit (g) 0.17 gmol/lit (h) 0.19 gmol/lit.

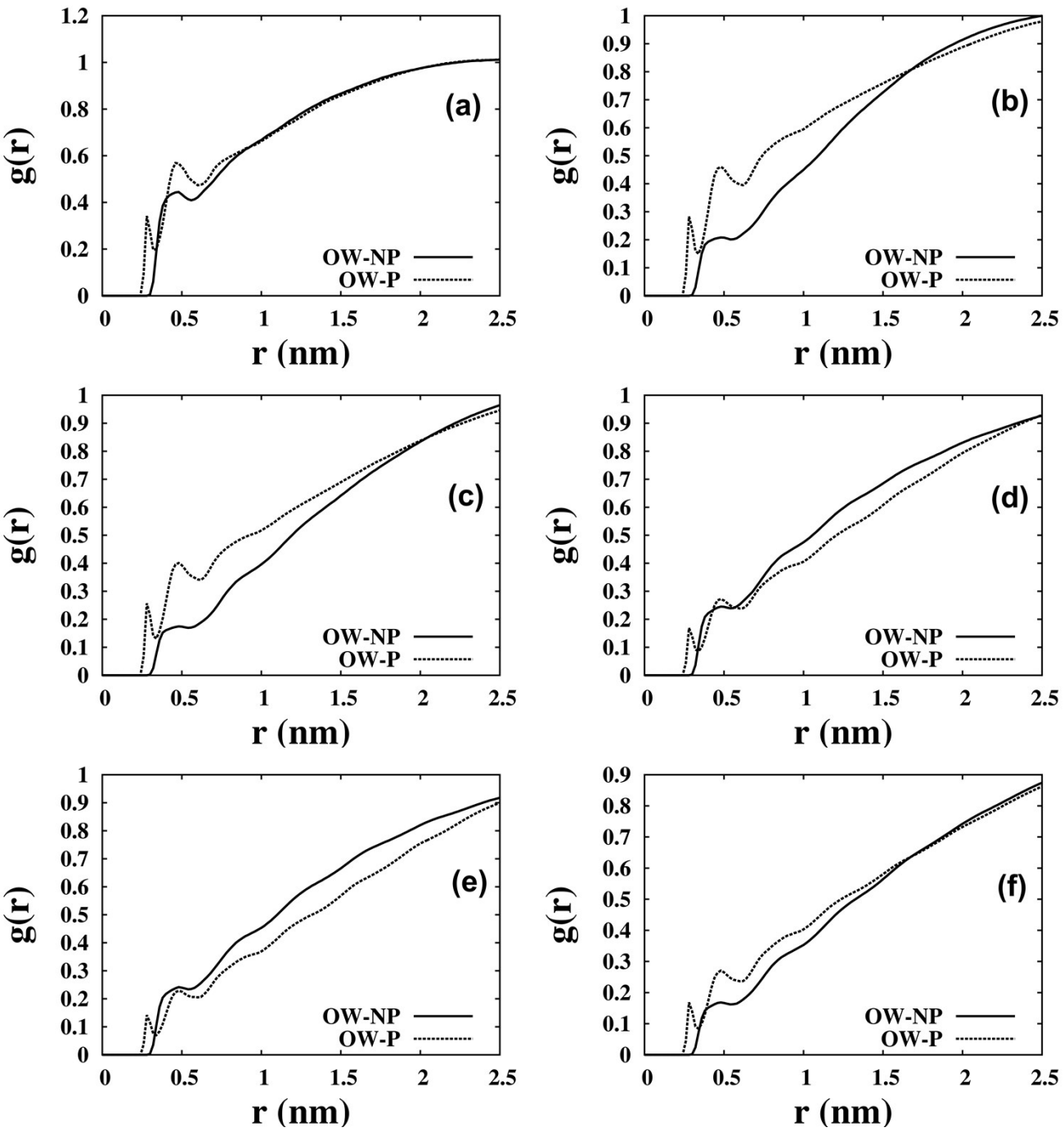

Figure 9S. Radial distribution functions (RDF's) for water oxygen (OW) atoms with respect to the polar and non-polar parts of surfactant in ternary solution at different concentration of $C_{10}E_8$ surfactant. (a) 0.016 gmol/lit (b) 0.042 gmol/lit (c) 0.068 gmol/lit (d) 0.094 gmol/lit (e) 0.12 gmol/lit (f) 0.14 gmol/lit.

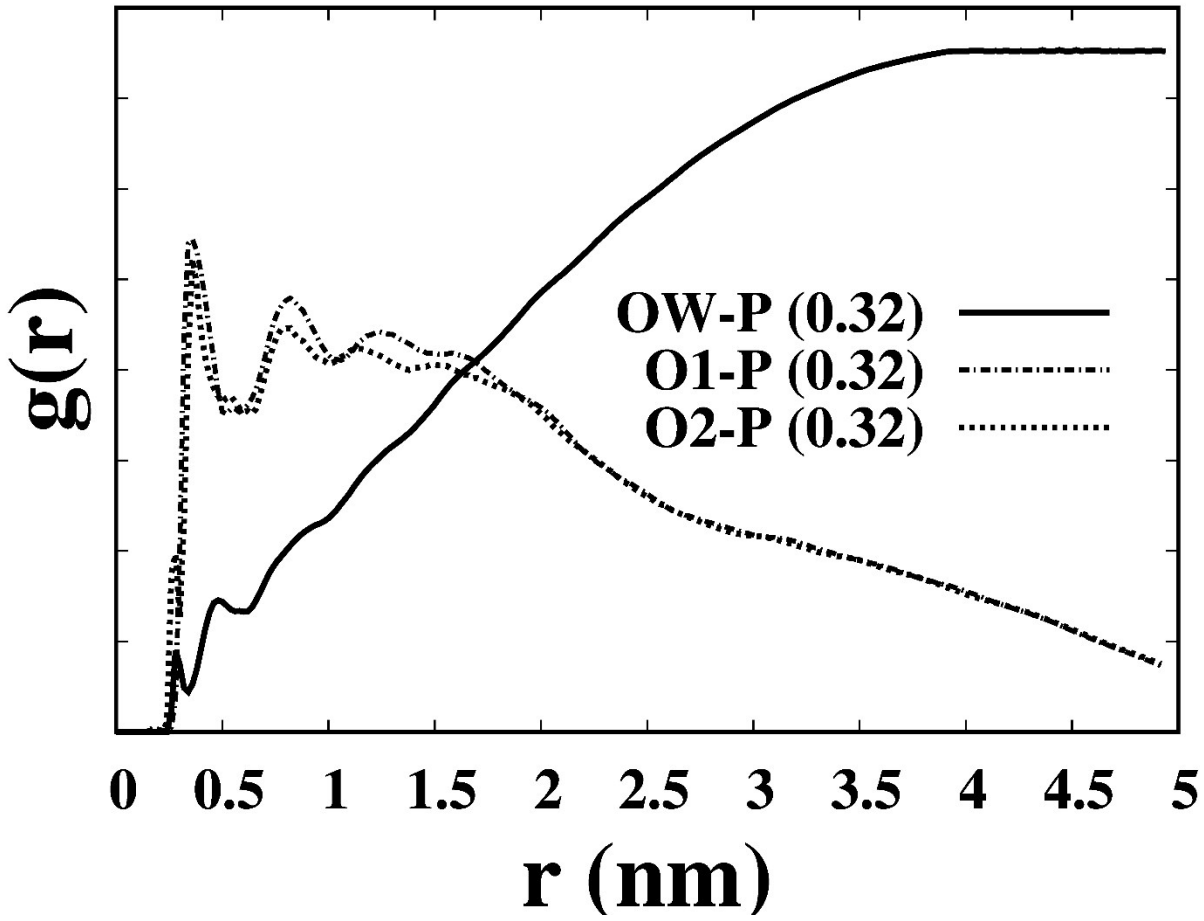

Figure 10S. (RDF's) of different oxygens with polar parts (P) of the surfactant at C_s=0.32 gmol/lit in ternary solution.

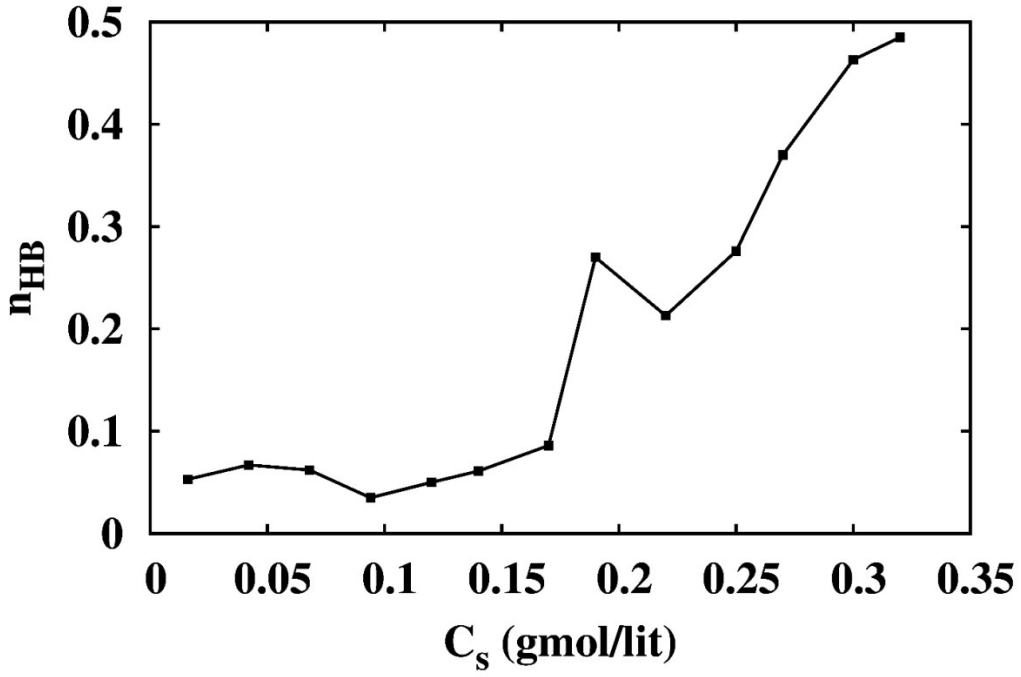

Figure 11S. Represents the number of hydrogen bonds between groups (OS, HS) of the surfactant and (O1) of PAA.

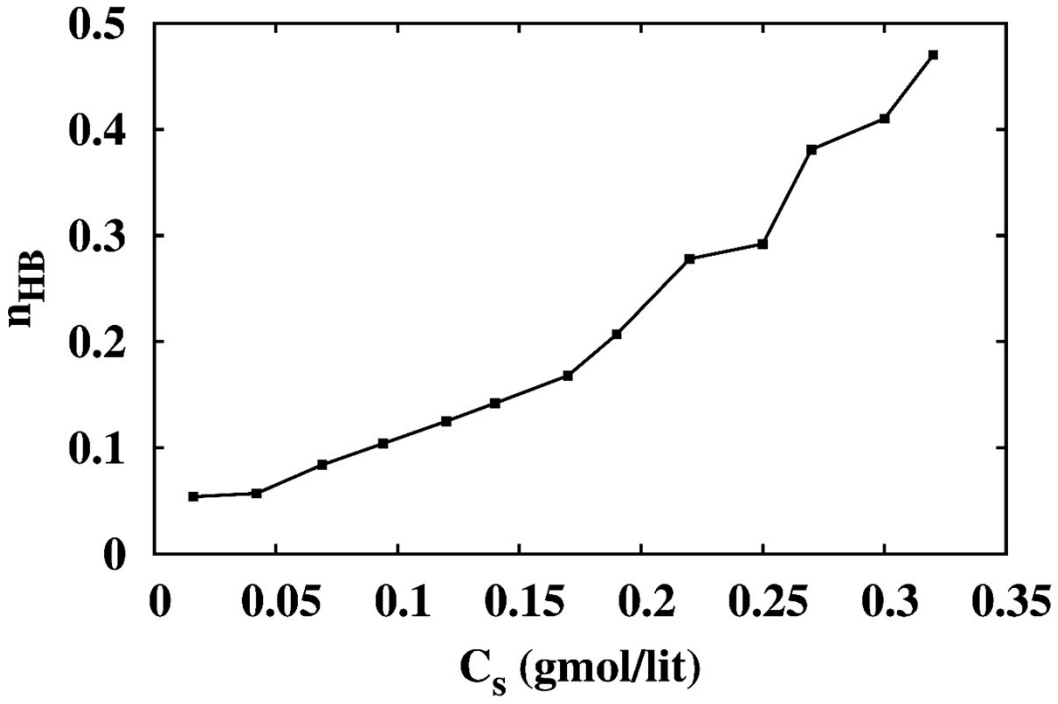

Figure 12S. Represents the number of hydrogen bonds between groups (OS, HS) of the surfactant and (O2) of PAA.

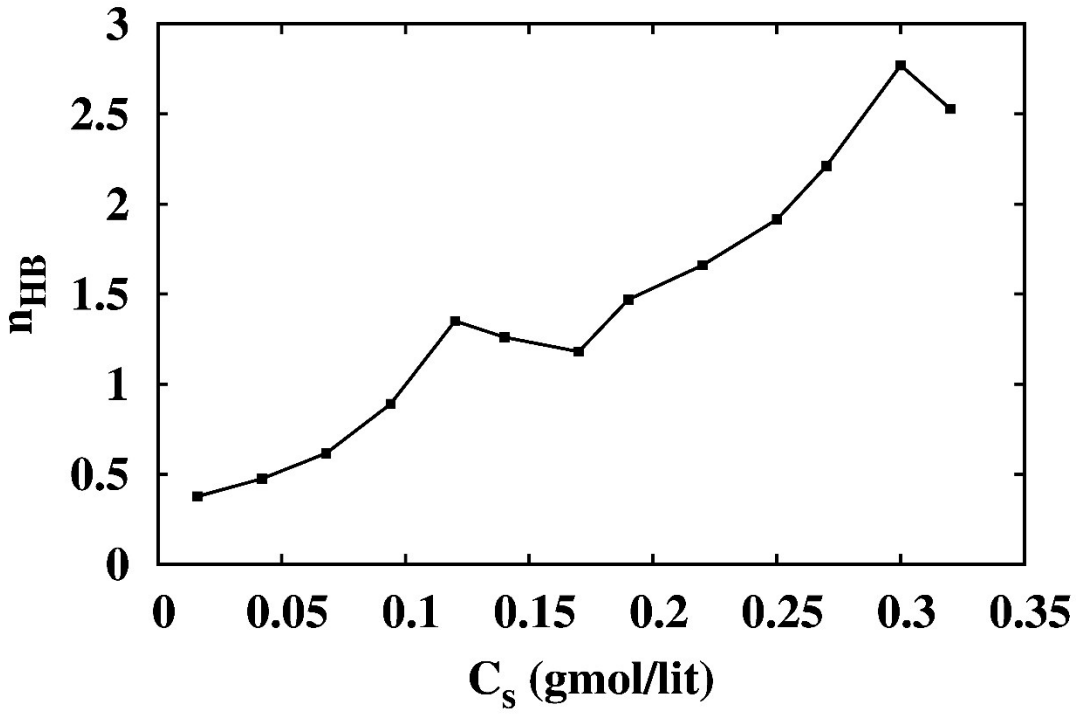

Figure 13S. Represents the number of hydrogen bonds between groups (OS) of the surfactant and (O2, HA) of PAA

Table. 1S. Tacticity sequence of the polymer chains.

S.No.	Chain tacticity sequence of dyads	Dyad ratio (%)	Triad ratio (%)			
		M	R	RM	MM	RR
S1	M-M-M-M-R-M-R-R-R-R-R-M-M-R-R-R-M-M-R-R-M-R-R-R-R-M-R-R-M-R	0.44	0.56	0.46	0.19	0.35
S2	M-R-R-R-R-M-M-R-R-M-M-R-R-R-R-M-M-R-R-R-R-M-M-M-M-R-R-M-M	0.45	0.55	0.36	0.25	0.39

Table 2S. Intermolecular distance in lamellar aggregates.

Aggregation no. N_{agg}	Intermolecular distance in ternary system (nm)	Intermolecular distance in binary system (nm)	h_{lam} (nm) Ternary system	d_{lam}(nm) Ternary system	h_{lam} (nm) Binary system	d_{lam} (nm) Binary system
29	0.29	-	3.8	2.8	-	-
37	0.33	-	3.8	3.0	-	-
45	0.38	0.40	4.1	3.3	3.8	2.9
53	0.40	0.42	3.8	3.5	3.8	3.2
61	0.44	0.45	3.8	3.8	4.1	3.5
69	0.46	0.48	4.2	4.2	3.9	3.9
77	0.49	0.50	3.8	4.6	3.8	4.8
85	0.55	0.54	4.2	5.0	3.9	5.1
93	0.57	0.58	3.9	5.3	3.9	5.4
101	0.58	0.60	3.8	5.5	4.2	5.6

Table 3S. Force field parameters used for PAA in MD simulations.

Non-bonded parameters			
Group	Charge (q)	C6(KJ nm6/mol)	C12 (KJ nm12/mol)
CH_3 (C1)[a)]	0	0.00961380	2.664624×10^{-5}
CH_2 (C1)	0	0.00746841	3.396558×10^{-5}
CH (C2*)	0	0.00606841	9.70225×10^{-5}
Carboxylic acid C (CA)	0.33	0.00234062	4.937284×10^{-6}
=O (O1)	-0.45	0.00226195	1×10^{-6}
O (O2)	-0.288	0.00226195	1.505529×10^{-6}
H (HA)	0.408	0	0
SPC water O (OW)	-0.82	0.00226173	2.634129×10^{-6}
H (HW)	0.41	0	0

Bonded parameters					
Bond type	$b_{i,0}$ [1)] (nm)	k_{ib}[2)] x 10^{-6} (KJ/mol nm4)	Angle type	$\theta_{i,0}$[3)] (°)	$k_{i\theta}$[4)] (KJ/mol rad2)
C1-C2	0.153	7.15	C1-C2-C1	111	530
CA-O2	0.136	16	C2-CA-O2	115	610
CA-O1	0.123	10.2	C2-CA-O1	121	685
O2-HA	0.1	15.7	O2-CA-O1	124	730
OW-HW	0.1	0.345	CA-O2-HA	109	450
			HW-OW-HW	109.47	383

Torsion parameters		
Torsion type	$\varphi_{i,0}$[5)] (degrees)	$k_{i\varphi}$[6)] (KJ/mol)
C1-C2-CA-O2	0	1
C2-CA-O2-HA	180	16.7
C1-C2-C1-C2 (Ryckaert-bellemans)	$C_0 = 8.397$, $C_1 = 16.785$, $C_2 = 1.134$, $C_3 = -26.316$, $C_4 = 0$,C5 = 0	

Table 4S. Force field parameters used for $C_{10}E_8$ in MD simulations.

Non-bonded parameters					
Group	Charge (q)	C6(KJ nm6/mol)	C12 (KJ nm12/mol)		
CH_3 (C1)	0	0.00961380	2.664624×10^{-5}		
CH_2 (C2-C7)	0	0.00746841	3.396558×10^{-5}		
CH_2 (C8-C16)	0.25	0.00746841	3.396558×10^{-5}		
CH_2(C17)	-0.265	0.00746841	3.396558×10^{-5}		
O(O1-O5)	-0.5	0.00226195	1.505529×10^{-6}		
OS	-0.7	0.00226195	1.505529×10^{-6}		
HS	0.435	0	0		
Bonded parameters					
Bond type	$b_{i,0}$ [1] (nm)	k_{ib}[2] x 10^{-6} (KJ/mol nm4)	Angle type	$\theta_{i,0}$[3] (°)	$k_{i\theta}$[4] (KJ/mol rad2)
C-C	0.153	7.15	C-C-C	109.5	285
C-O	0.136	10.2	C-C-O	115.0	50
O-H	0.100	15.7	C-O-C	109.5	380
			O-C-C	121.0	685
			C-C-O	109.5	450
Torsion parameters					
Torsion type	$\varphi_{i,0}$[5] (degrees)		$k_{i\varphi}$[6] (KJ/mol)		
C-C-C-C (Ryckaert-bellemans)	$C_0 = 8.397$, $C_1 = 16.785$, $C_2 = 1.134$, $C_3 = -26.316$, $C_4 = 0$, $C5 = 0$				
C-C-C-O	0		5.92		
C-C-O-C	0		3.77		
O-C-C-O	0		2.09		

Table 5S. Enthalpy values with fluctuations.

C_s (gmol/lit)	$\Delta H_{S\text{-}W}$ (PAA-$C_{10}E_8$)[a)]	$\Delta H_{S\text{-}W}$ ($C_{10}E_8$) [a)]	ΔH_{SP} [a)]	ΔH_{Conf} [a)]	$\Delta H_{P\text{-}S\ bind}$ [a)]	ΔH_{agg} (PAA-$C_{10}E_8$) [a)]	ΔH_{agg} ($C_{10}E_8$) [a)]	ΔH_{Form} [a)]
0.016	-1908.05 ±91.58	-1549.25 ±76.99	1643.14 ±78.87	381.15± 18.47	-2269.63 ±115.71	-999.78± 46.24	-792.02± 32.47	-1526.44 ±67.51
0.042	-3399.09 ±146.16	-2997.76 ±135.86	1788.43 ±81.62	229.37± 12.31	-4142.05 ±172.54	-1828.88 ±76.47	-1566.40 ±68.05	-2559.28 ±103.85
0.068	-4211.94 ±197.34	-4081.68 ±176.56	1891.83 ±85.13	97.29± 6.41	-5854.18 ±263.44	-2726.18 ±112.61	-2310.72 ±96.51	-3289.55 ±138.31
0.094	-4951.72 ±202.52	-4769.53 ±206.83	1989.48 ±83.43	-312.19± 14.42	-7691.81 ±320.34	-3817.62 ±171.37	-3112.80 ±132.61	-3881.37 ±185.42
0.119	-5919.84 ±260.42	-5684.84 ±252.15	2179.08 ±88.24	-454.84± 19.10	-9653.46 ±427.46	-4476.02 ±209.84	-3802.66 ±184.28	-4655.87 ±193.67
0.14	-6945.40 ±281.85	-6369.23 ±277.48	2219.05 ±91.52	-736.14± 31.67	-11034.5 ±463.27	-5319.60 ±222.61	-4670.74 ±196.18	-5556.32 ±251.28
0.17	-7392.41 ±312.26	-7071.41 ±331.85	2325.24 ±97.64	-848.61± 39.03	-13247.3 ±543.14	-6633.57 ±291.88	-5552.43 ±241.53	-5913.92 ±248.37
0.19	-8833.63 ±351.48	-8276.44 ±371.61	2448.25 ±94.28	-1208.54 ±50.06	-15427.2 ±684.51	-7848.33 ±366.26	-6437.01 ±291.10	-7066.90 ±325.21
0.22	-9539.72 ±385.47	-9274.52 ±412.33	2626.46 ±105.87	-1334.37 ± 66.16	-17124.5 ±734.27	-8668.11 ±389.34	-7492.28 ±348.43	-7471.77 ±311.51
0.25	-10132.2 ±440.18	-9817.56 ±431.95	2774.40 ±119.29	-1483.42 ±62.85	-19273.3 ±843.49	-9567.89 ±408.73	-8595.80 ±335.91	-7945.72 ±363.43
0.27	-11127.3 ±494.51	-10764.3 ±458.08	2859.79 ±116.45	-1781.63 ±84.61	-21566.7 ±887.34	-10561.2 ±433.16	-9652.43 ±408.81	-8901.79 ±372.18
0.30	-12376.9 ±552.47	-11057.8 ±508.66	2987.26 ±127.84	-2094.34 ±89.47	-23263.6 ±964.58	-11620.3 ±528.34	-10865.5 ±489.67	-9401.52 ±451.57
0.32	-12582.4 ±616.42	-12260.2 ±555.64	3139.37 ±148.61	-2182.18 ±97.61	-25316.2 ±1134.81	-12546.8 ±584.67	-11729.1 ±538.46	-9905.95 ±462.27

a) Units of enthalpies are kJ/mol

Equations used for obtaining the straight line fits to the values of eccentricity and aspect ratio are given below. These equations are taken from (W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.P. Flannery. *Numerical recipes in C, The art of scientific computing.* Cambridge university press, USA.)

x_i = Aggregation number, y_i = eccentricity or aspect ratio, σ_i = fluctuations in eccentricity or aspect ratio, a = slope of line, b = intercept of line, σ_a = error in slope and σ_b = error in intercept.

$$S = \sum_{i=1}^{N} \frac{1}{\sigma_i^2} \quad (12)$$

$$S_x = \sum_{i=1}^{N} \frac{x_i}{\sigma_i^2} \quad (13)$$

$$S_y = \sum_{i=1}^{N} \frac{y_i}{\sigma_i^2} \quad (14)$$

$$S_{xx} = \sum_{i=1}^{N} \frac{x_i^2}{\sigma_i^2} \quad (15)$$

$$S_{xy} = \sum_{i=1}^{N} \frac{x_i y_i}{\sigma_i^2} \quad (16)$$

$$\Delta = S * S_{xx} - (S_x)^2 \quad (17)$$

$$a = \frac{S * S_{xy} - S_x S_y}{\Delta} \quad (18)$$

$$b = \frac{S_{xx} * S_y - S_x S_y}{\Delta} \quad (19)$$

$$\sigma_a = \frac{S}{\Delta} \qquad (20)$$

$$\sigma_b = \frac{S_{xx}}{\Delta} \qquad (21)$$

In the line equation of eccentricity the % error in slope is 0.061 and % error in intercept in 0.45.

In the line equation of aspect ratio % error in slope is 0.074 and % error in intercept in 0.22.

s