Supporting Information

Mesoscopic Probes in Asphaltenes Nanoaggregate Structure: From Perpendicular to Paralleled Orientation at the Water-in-Oil Emulsions Interface

Jinhui Chen [a], Jinliang Chen [b], Chuheng Zhong[c], Shouyu Chen [a], Bowen Chen[d],

Shenwen Fang[e], Wenjun Xiang[f]*

[a]China University of Geosciences (Wuhan),Wuhan 430074,China.

[b]Management Center of Sustainable Development Research Institute of Yellow River Delta, Dongying, Shandong, 257091, China.

[c]Ecole Centrale de Nantes, pays de la loire 44000 NANTES, France.

[d]Université Laval, 3 Avenue Des Sciences-Humaines, Sainte-Foy, Québec, Canada.

[e]College of Chemistry and Chemical Engineering, Southwest University of Petroleum, 8 Xindu Avenue, Xindu District, Chengdu, Sichuan 610500, P. R. China.

[f]School of Chemistry and Chemical Engineering, Sichuan University of Arts and Science, Dazhou, Sichuan 635000, China.

Keywords Dissipative Particle Dynamics; Asphaltenes; Nanoaggregate Structures, Emulsion Stability;

*To whom correspondence should be addressed:

E-mail: fangwen1228@yahoo.com.cn

Telephone number：+8602883037346

Fax number：+8602883037346

Present Addresses: 8 Xindu Avenue, Xindu District, Chengdu, Sichuan 610500, P. R. China

Bead-bead interaction parameters.

The most important parameter in DPD method is the conservative repulsive force which can be determined by the equation: $a_{ij} = a_{ii} + 3.27\chi_{ij}$,[36,41] where a_{ii} = 78.0 with the mapping of three water molecules perbead.[41,42]The values of χ_{ij} can be calculated from the solubility parameters following the equation: $\chi_{ij} = \frac{\nu_{ij}}{RT}(\delta_i - \delta_j)^2$,[42] where ν_{ij} is the average of molar volumes of two beads; δ_i and δ_j are the solubility parameters of component i and j, respectively. The Hansen solubility parameters were listed in **Table S1**. Thus, the conservative repulsive forces in DPD simulations were calculated with above two equations, as shown in **Table S2**.

Table S1. Hansen Solubility Parameters $(J/cm^3)^{1/2}$and molar volume (cm^3/mol) at 298K[40,43]

molecule	Hansen Solubility Parameter $(J/cm^3)^{1/2}$	Molar Volume (cm^3/mol)
water (W)	47.81	18.00
benzene (B)	18.51	89.40
butane (H)	14.10	101.4
thiourea(T)	33.01	72.8

Table S2. Parameters of Conservative Force

bead	water (W)	benzene (B)	butane (H)	thiourea(T)
water(W)	78.0			
benzene (B)	138.7	78.0		
butane (H)	161.9	80.4	78.0	
thiourea(T)	91.10	100.5	119.1	78.0

The calculation of diffusion coefficient and interlayer distance of asphaltenes.

The diffusion coefficients *D*, calculated from the slopes of the mean square displacements (MSD) in the long time limit using follow equation: [46]

$$D = \frac{1}{2N_d}\lim_{t\to\infty}\frac{d}{dt}\sum_{i=1}^{N}\left[\left|\mathbf{r}_i(t) - \mathbf{r}_i(t)\right|^2\right] \quad (1)$$

where N_d is the dimensionality (N_d = 3 for the simulations),$r_i(t)$ and [$|r_i(t)- r_i(0)|^2$] are the position and squared displacement of given molecules at time t, respectively. The simulation results of mean square displacements were given in **Figure S1a**. By calculating the slope of mean square displacements versus time, the diffusion coefficients D can be calculated, as shown in **Figure S1a**. The diffusion coefficient of diluted asphaltene in toluene is 3.41∼5.73× 10^{-10} m^2s^{-1}.

The radial distribution function is computed for all pairs of beads or centroids in the set which are closer than the cutoff value. Thus, it could illustrate the interlayer distance between asphaltenes in aggregation process.[35] Radial distribution function can be calculated using following equation[33,35,37]

$$g_{ij}(r) = \frac{\langle \Delta N_{ij}(r \to r + \Delta r) \rangle}{4\pi \cdot r^2 \Delta r N_i N_j} \quad (2)$$

where $\{\Delta N_{ij}(r \to r+\Delta r)\}$ is the ensemble averaged number of j around i within a shell from r to $r+\Delta r$, V is the system volume, N_i and N_j are number of i and j, respectively. We take the first peak of radial distribution function as interlayer distance. As shown in **Figure S1b,** the interlayer distance value from DPD simulations is about 5.05 Å in our calculation.

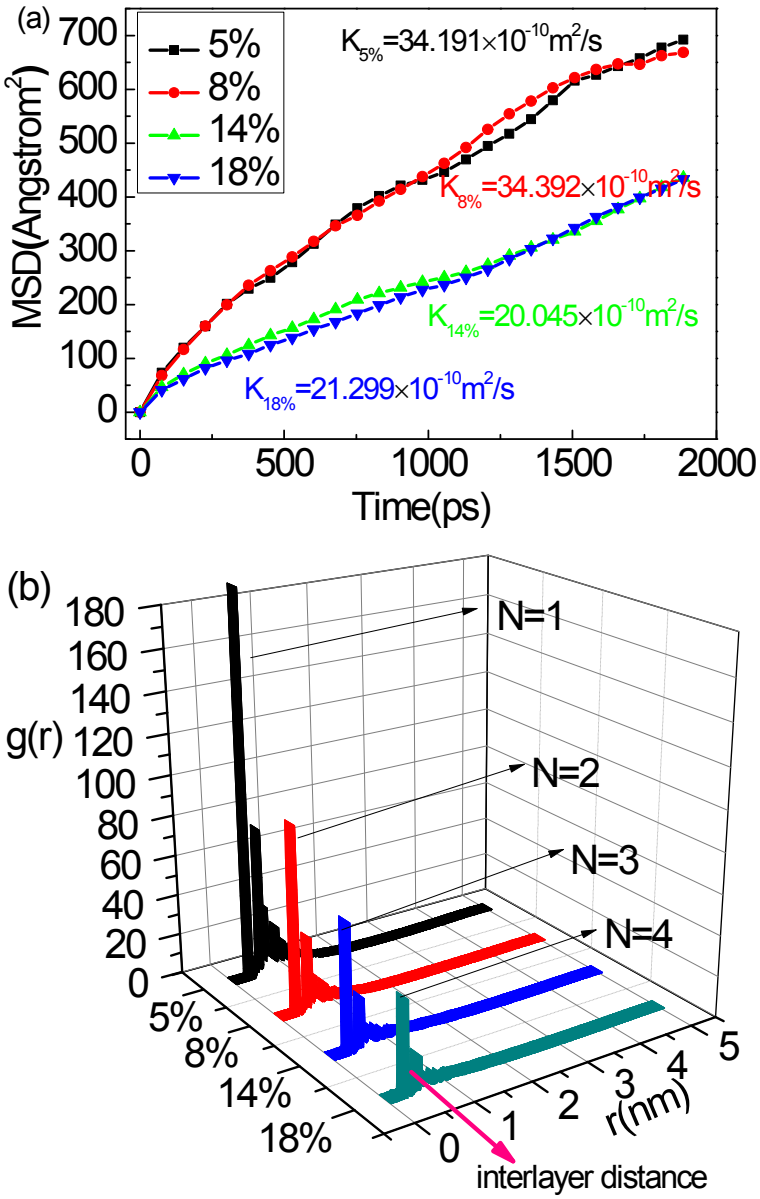


Figure S1. (a) The MSD of asphaltenes at different concentrations in toluene and (b) the radial distribution functions of asphaltenes at different concentrations in toluene.

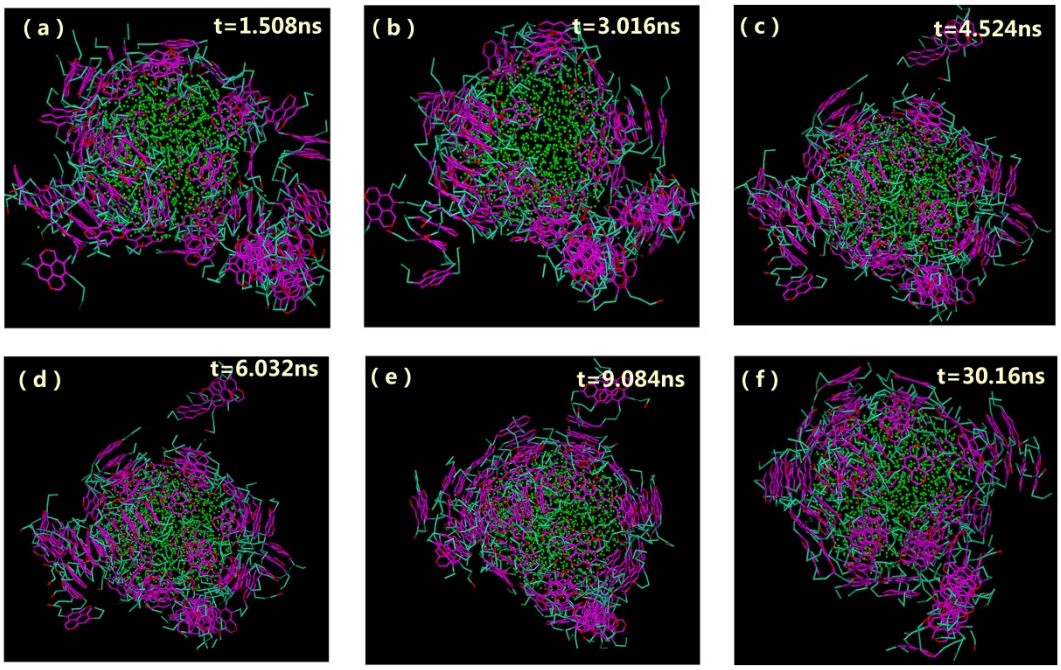
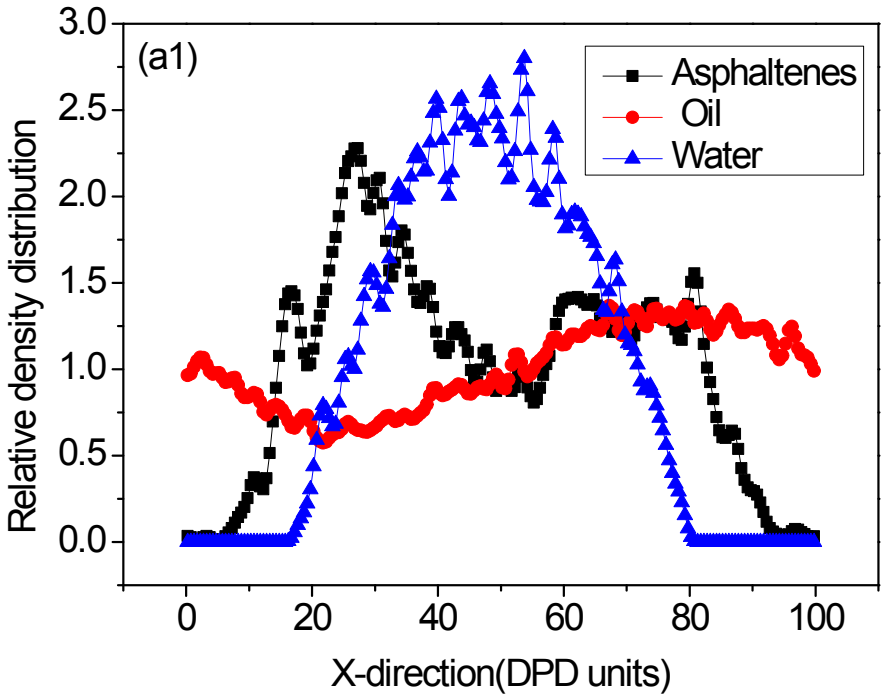
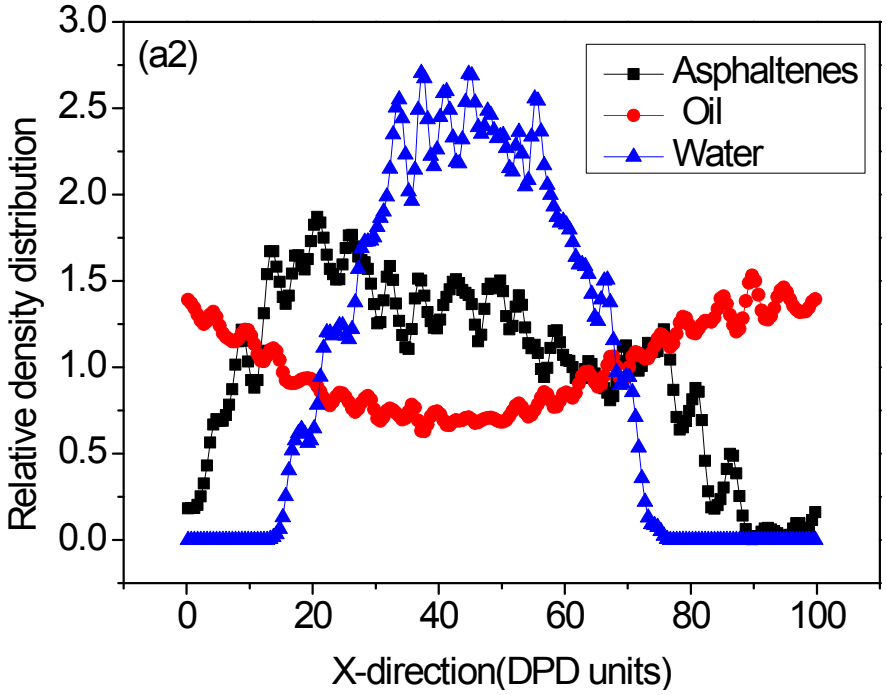
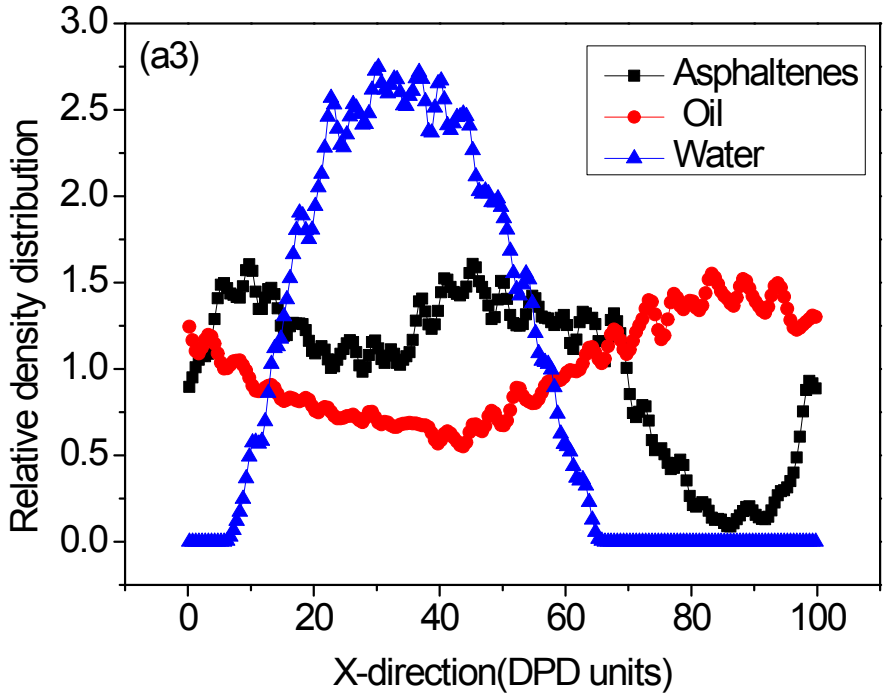
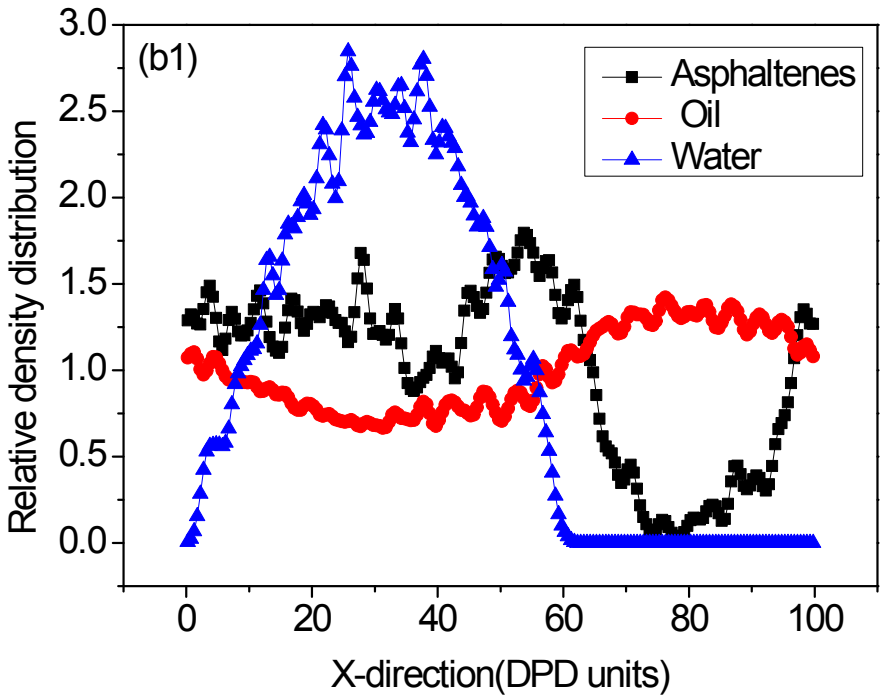


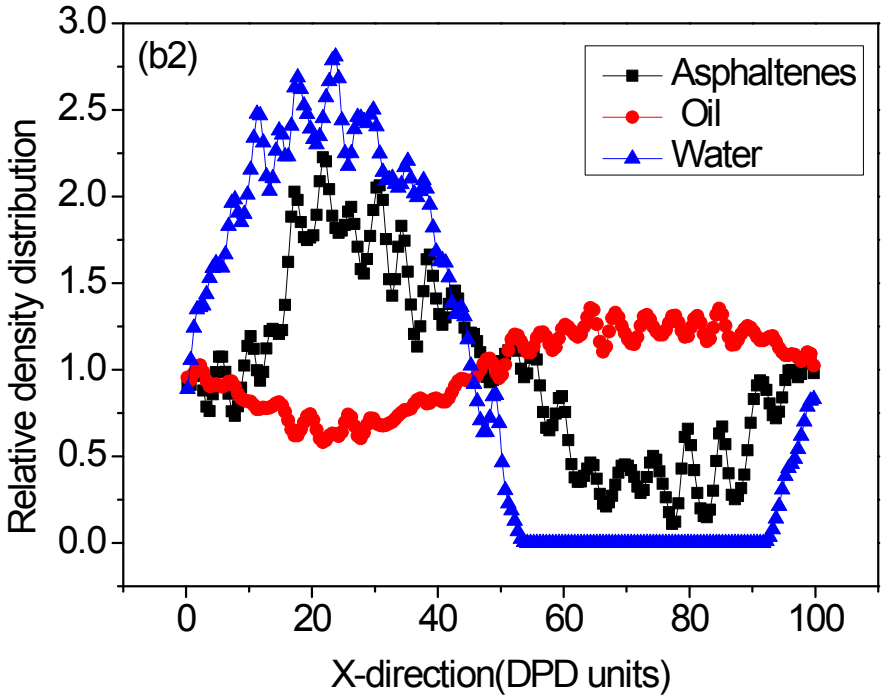
Figure S2. Morphologies of water-in-oil emulsions at different simulation time with the concentrations of 20% model C asphaltenes. Different beads in simulations are represented by different colors as can be illustrated from Figure 1f (the same as below). The toluene molecules are suppressed for clarity.

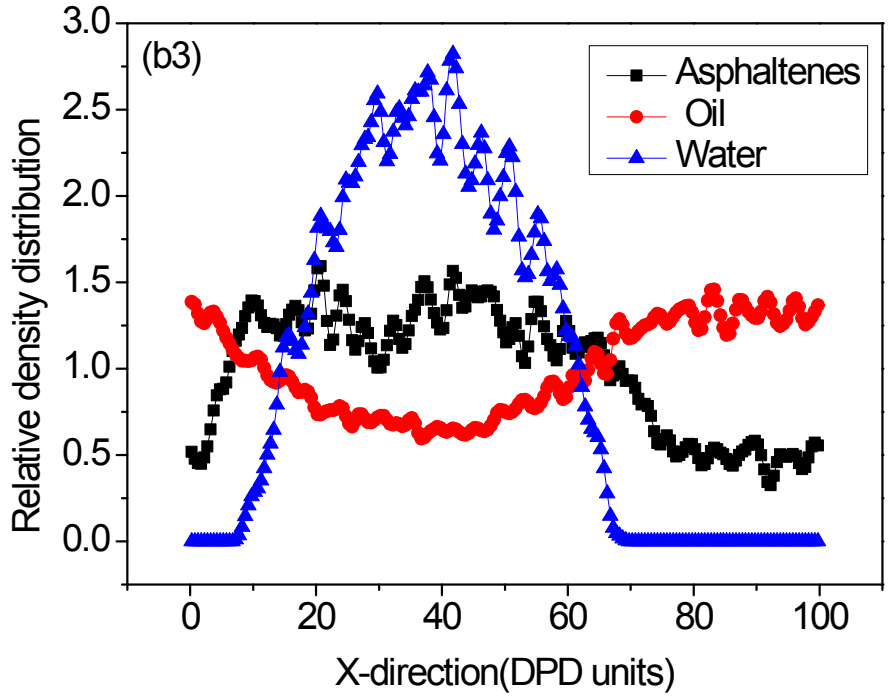


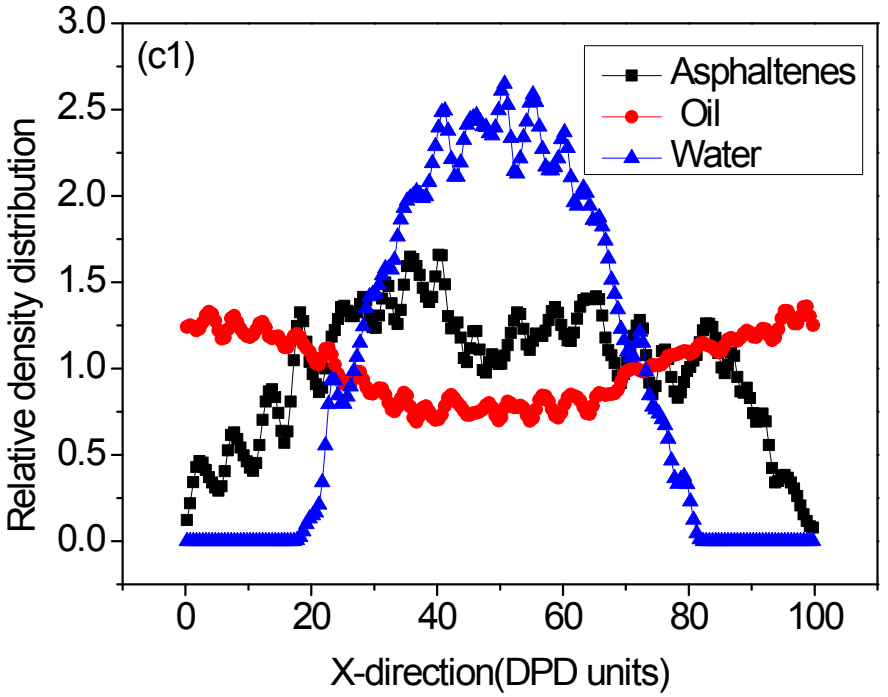

(a2)
Asphaltenes
Oil
Water
Relative density distribution
X-direction(DPD units)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100


(a3)
Asphaltenes
Oil
Water
Relative density distribution
X-direction(DPD units)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100


(b1)
Asphaltenes
Oil
Water
Relative density distribution
X-direction(DPD units)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100


(b2)
Asphaltenes
Oil
Water
Relative density distribution
X-direction(DPD units)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100


(b3)
Asphaltenes
Oil
Water
Relative density distribution
X-direction(DPD units)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100


(c1)
Asphaltenes
Oil
Water
Relative density distribution
X-direction(DPD units)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100

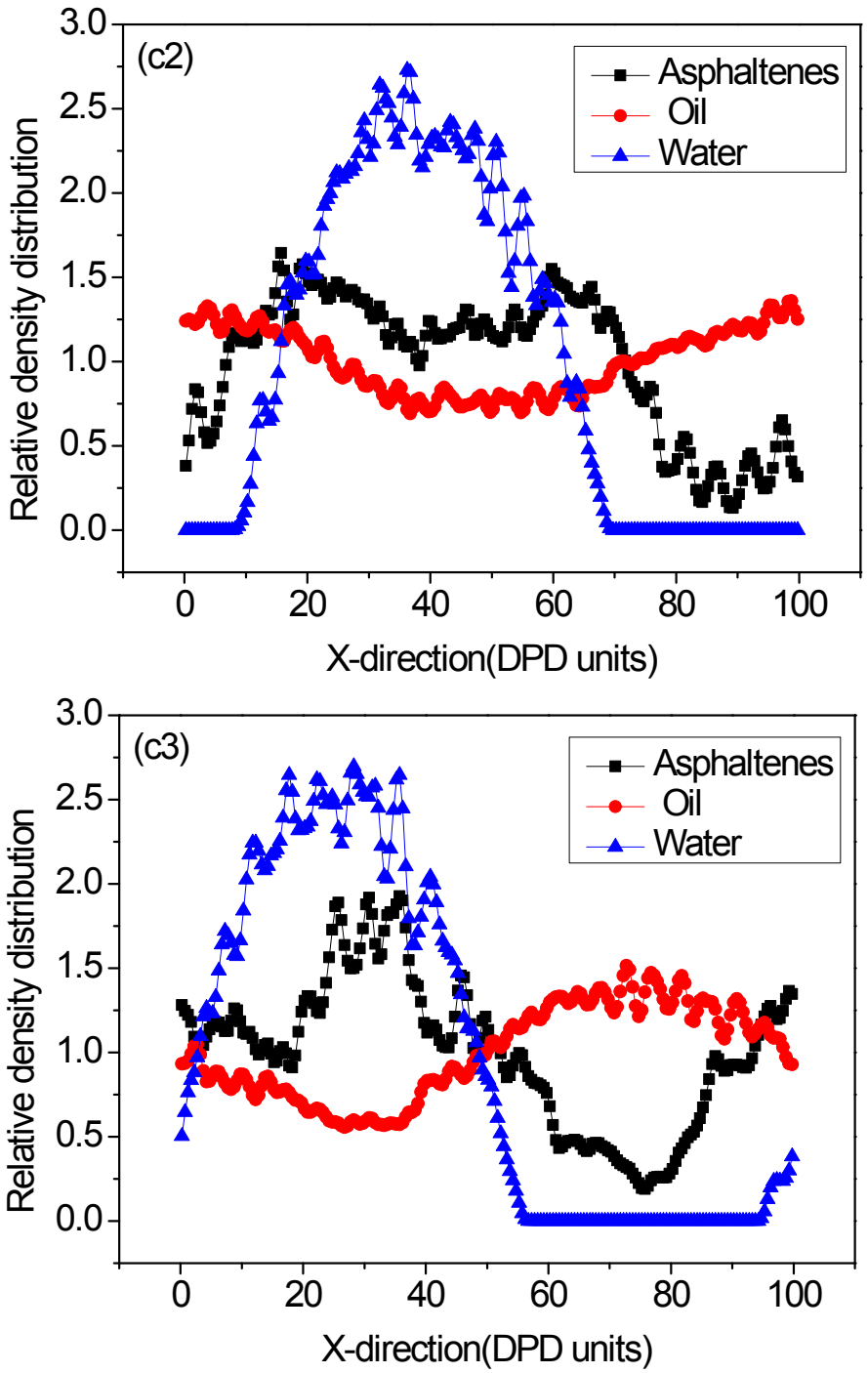


Figure S3. Relative density profiles for different asphaltene models at different concentrations. Asphaltenes of *Model A* were used: (a1) 15%, (a2) 20%, (a3) 25%; Asphaltenes of *Model B* were used: (b1) 15%, (b2) 20%, (b3) 25%; Asphaltenes of *Model C* were used: (c1) 15%, (c2) 20%, (c3) 25%. The toluene molecules are suppressed for clarity.