

Electronic Supplementary Information

Molecular dynamics study of the nano-aggregation in asphaltene mixtures: effects of the N, O and S heteroatoms.

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The tables S1, S3 and S6 herein reported are also found concatenated in the main-body of the text, Table 2.

The other tables, S2, S4 and S5, present the relative concentrations of the studied mixture of asphaltenes.

1 Aggregation within homogeneous boxes

1.1 Effect of the heteroatom

Asphaltene 1	Asphaltene 2	E_i (kcal.mol ⁻¹)	L.-J. contribution
A13	A13	56.2	86
A23	A23	52.2	81
A33	A33	57.0	84
A43	A43	58.9	85
A53	A53	54.0	82
AAC	AAC	45.8	73

Table S1 Interaction energies calculated for PA3- and CA22-type dimer molecules and Lenard-Jones terms contributions to the total energy.

2 Aggregation within heterogeneous boxes

2.1 Effect of the heteroatom

Table S2 presents the constitution of the simulated mixtures.

Label	A13	A23	A13	A33	A23	A33
Mix 1a	20%	80%	20%	80%	20%	80%
Mix 1b	40%	60%	40%	60%	40%	60%
Mix 1c	60%	40%	60%	40%	60%	40%
Mix 1d	80%	20%	80%	20%	80%	20%

Table S2 Mixture of asphaltene molecules with –CH₃ lateral chain-end in order to study the effect of different heteroatoms on the aggregation within the same class of asphaltenes.

Asphaltene 1	Asphaltene 2	E_i (kcal.mol ⁻¹)
A13	A23	40.9
A13	A33	37.4
A23	A33	46.7

Table S3 Interaction energies calculated for PA3- and CA22-type dimer molecules.

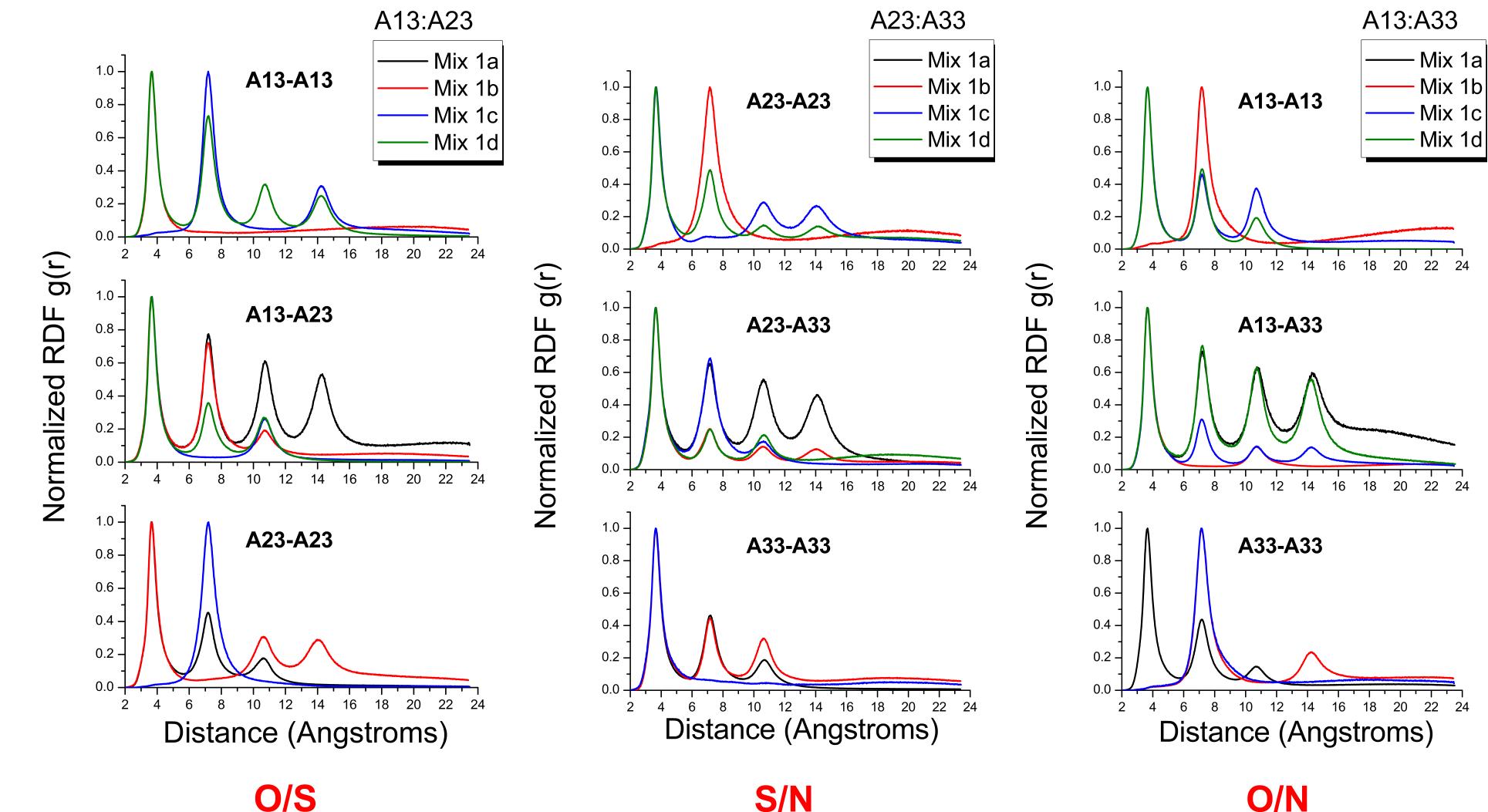


Figure S1 Effect of the mixture of asphaltene molecules with $-\text{CH}_3$ lateral chain-end.

2.2 Effect of chain-end

Label	A11	A13	AAA	AAC
Mix-2a	20%	80%	20%	80%
Mix-2b	40%	60%	40%	60%
Mix-2c	60%	40%	60%	40%
Mix-2d	80%	20%	80%	20%

Table S4 Mixture of asphaltene molecules varying the relative concentrations of lateral chain-ends within each class.

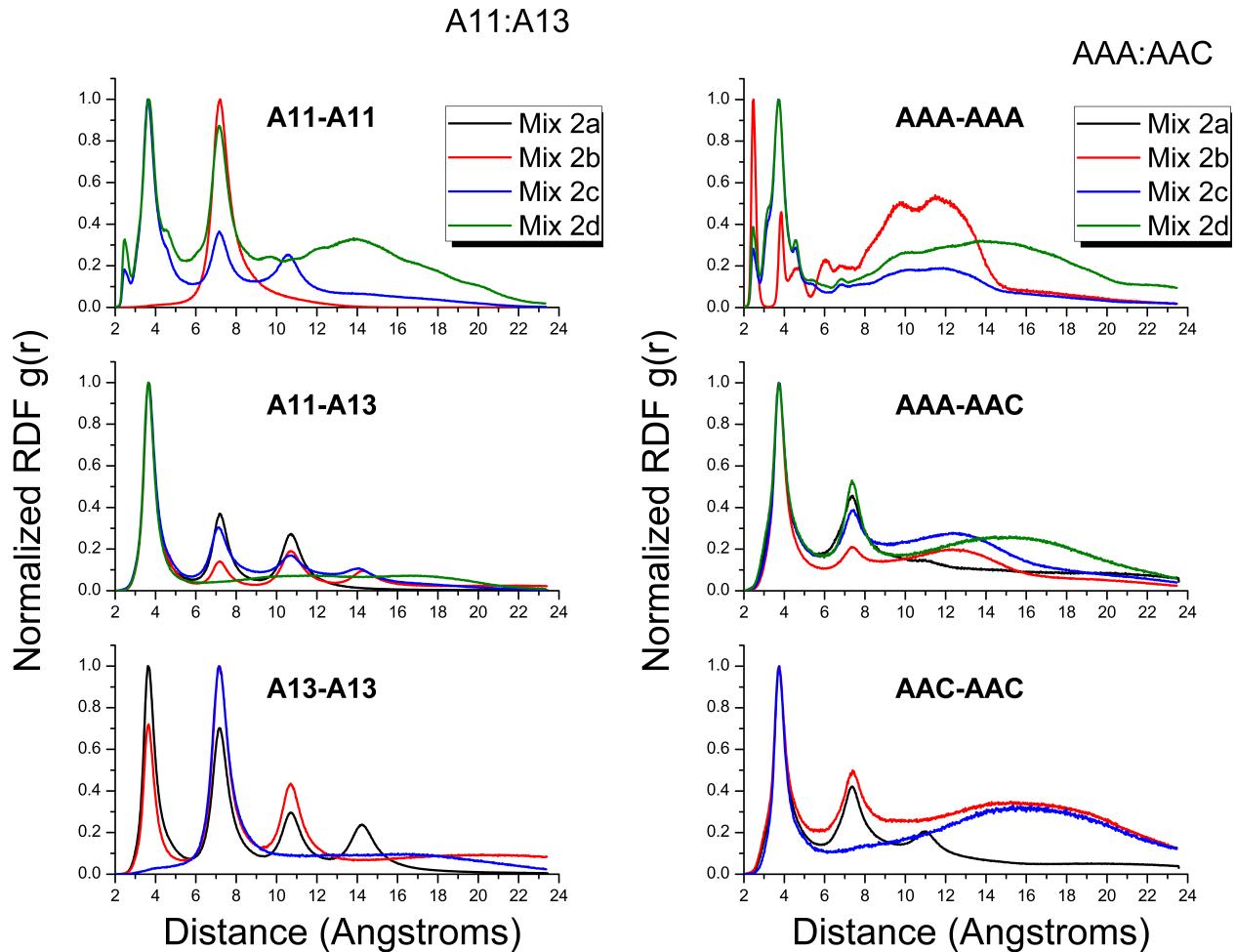


Figure S2 Effect of the chain-end on the aggregation within heterogeneous boxes.

3 Aggregation within *super-heterogeneous* boxes

Label	A13	AAC	A23	AAC	A33	AAC
Mix-3a	20%	80%	20%	80%	20%	80%
Mix-3b	40%	60%	40%	60%	40%	60%
Mix-3c	60%	40%	60%	40%	60%	40%
Mix-3d	80%	20%	80%	20%	80%	20%

Table S5 Mixture of asphaltene molecules with -CH₃ lateral chain-end in order to study the effect of different asphaltene classes on the aggregation.

Asphaltene 1	Asphaltene 2	E_i (kcal.mol ⁻¹)
A13	AAC	42.2
A23	AAC	47.4
A33	AAC	35.2

Table S6 Interaction energies calculated for PA3- and CA22-type dimer molecules.

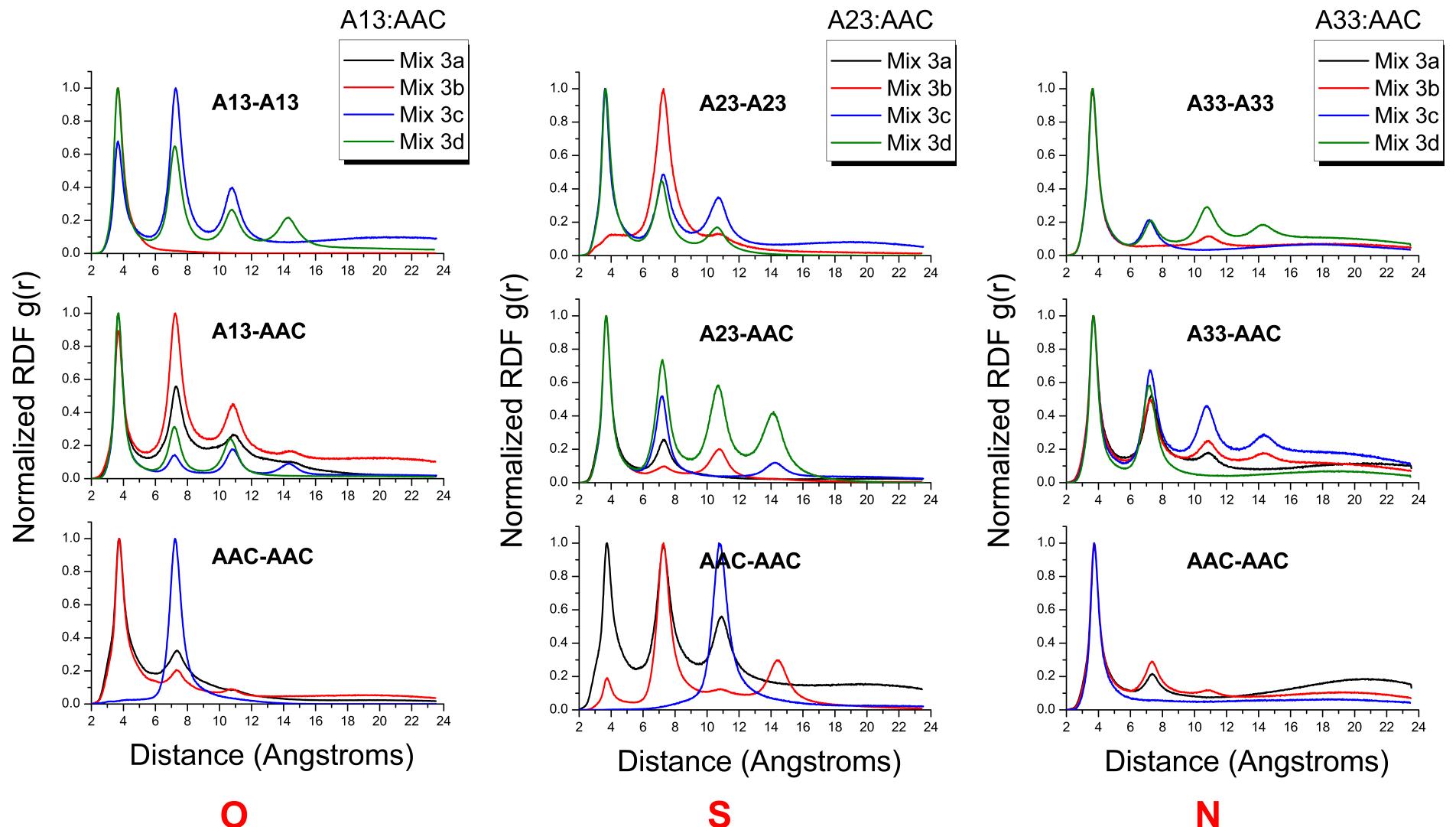


Figure S3 Effect of the heteroatom and of the asphaltene type on the aggregation mechanism.