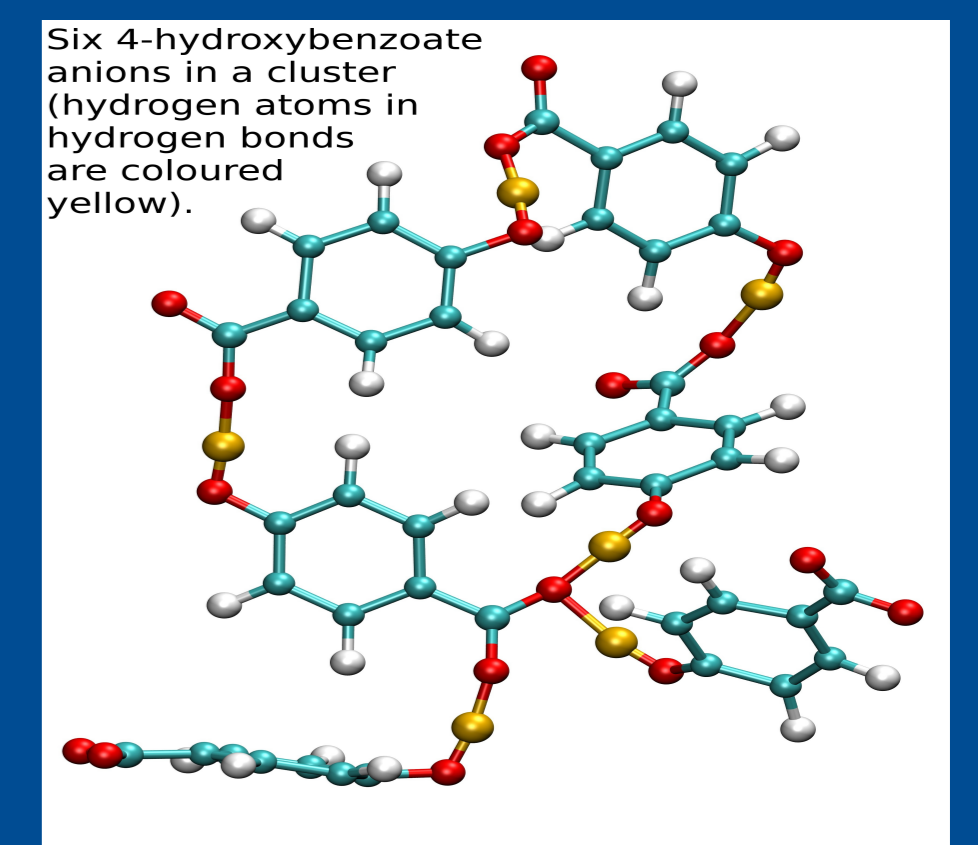


Clustering of Hydroxybenzoates in Aqueous Solutions and their Effect on the Micellisation of Dodecyltrimethylammonium Chloride: A Molecular Dynamics Simulation Study

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1 Motivation

Hydroxybenzoic (HB) acid can be found in three different geometric isomers which differ in relative positions of the carboxylic and hydroxylic group (Figure 1): 2-hydroxybenzoic (*o*-HB), 3-hydroxybenzoic (*m*-HB), and 4-hydroxybenzoic (*p*-HB) acid. Different structure of the HB isomers results in different values for certain hydrodynamic properties such as the self-diffusion coefficient. The mobility of HB anions is ranked in the order *o*-HB > *m*-HB > *p*-HB, which was ascribed to differences in the solvation of each HB isomer [1]. Furthermore, the presence of HB salts largely influences the thermodynamics of the self-assembly of cationic surfactants, such as dodecyltrimethylammonium chloride (DTAC), and also the structure of the resulting micelles [2]. At sufficiently high concentration of *o*-HB rod-like micelles are formed, while in the presence of *p*-HB only spherical aggregates were observed. *m*-HB displays an intermediate behaviour [3]. Our goal is to understand these differences on the molecular level.

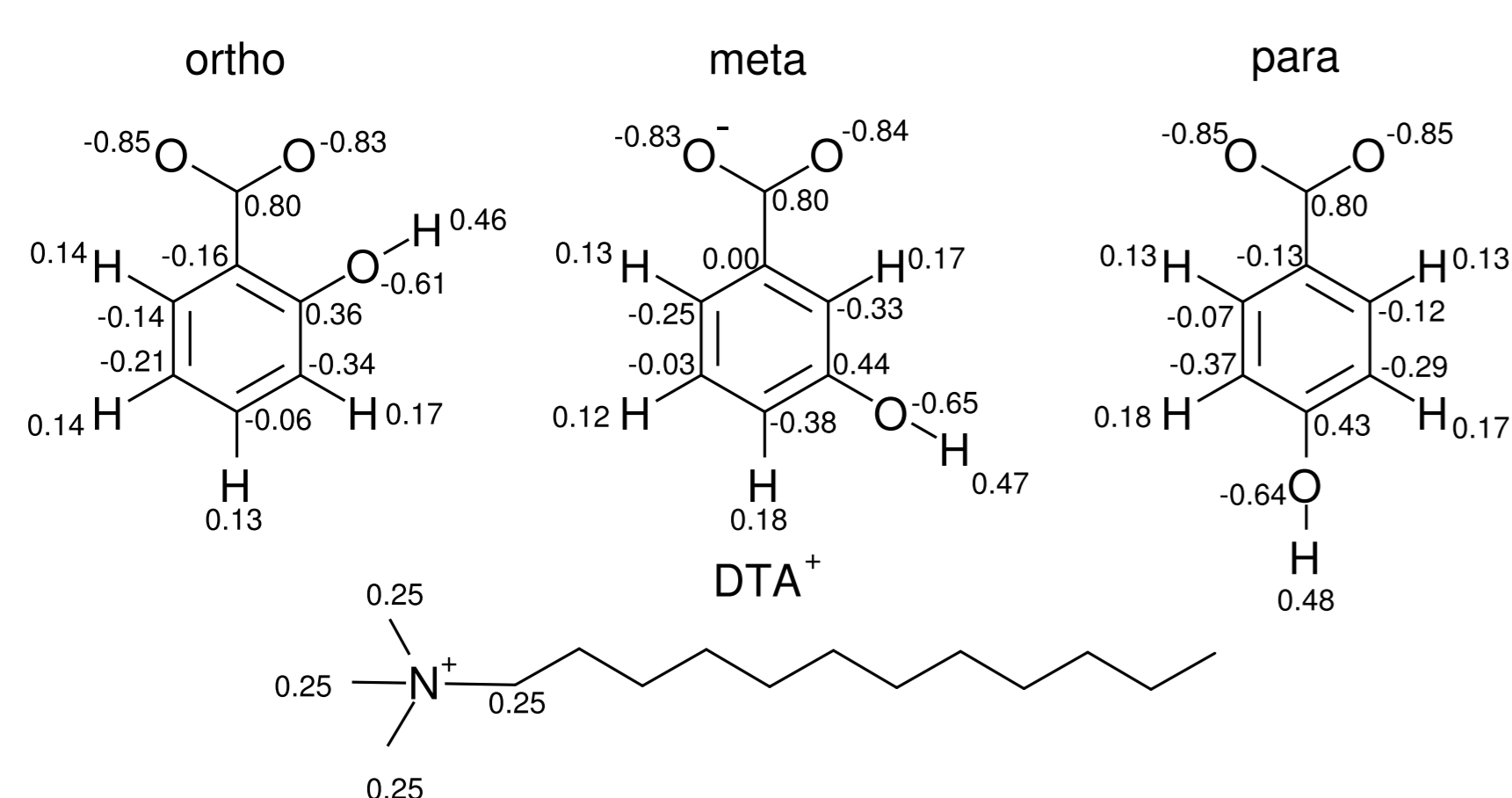


Figure 1: Structures and partial charges of all three hydroxybenzoate isomers and DTAC⁺.

2 Simulation details

• Molecular Dynamics with LAMMPS [4] package. GROMOS96 45a3 forcefield with SPC or SPC/E water model. PPPM for long-range electrostatics. Partial charges for hydroxybenzoate anions were calculated with B3LYP/6-31G** in PBF solvent model with Schrödinger software [5]. For DTAC they were taken from the literature [6].

• NaHB solution:

- Systems with one ion pair (Na⁺ and HB⁻) per 120 water molecules (216 NaHB pairs, $\rho = 1.002 \text{ g/cm}^3$) and one ion pair per 1000 water molecules (27 NaHB ion pairs, $\rho = 0.997 \text{ g/cm}^3$). Cubic periodic simulation box at 298.15 K.
- 3 5 ns NVE production runs at the lower concentration (55mM) started from different initial configurations. 45 ns NVT production run at the higher concentration (0.46M).

• Micellar systems:

- The system was initially a long cylindrical micelle spanning the *z* dimension of a periodic rectangular box comprising 180 DTAC⁺, 180 Cl⁻, 180 NaHB and 15000 water molecules at 1 atm and 298.15K.
- 80ns NPT production run with an anisotropic pressure coupling. *Z* dimension of the box was allowed to rescale independently of *x* and *y* dimensions.

3 Aqueous solutions of NaHB

Table 1: Calculated self-diffusion coefficients ($D / 10^{-10} \text{ m}^2 \text{ s}^{-1}$) for HB anions. Data for the low concentration SPC/E *ortho* system are missing due to very poor statistics. Experimental values were taken from the literature [3].

Isomer	Simulations		Experiment [3]	
	Low c (0.055 M)	High c (0.46 M)	c=1 mM	Inf. dil.
<i>ortho</i>	13.9 ± 0.4	9.5 ± 0.3	9.3 ± 0.4	9.18 ± 0.01
<i>meta</i>	13.1 ± 0.8	8.7 ± 0.5	8.6 ± 0.3	7.90 ± 0.01
<i>para</i>	11.7 ± 0.5	7.9 ± 0.1	7.7 ± 0.4	7.17 ± 0.01

Table 2: The number of intermolecular hydrogen bonds and all hydrogen bonds formed per HB anion.

Conc.	Isomer	SPC water		SPC/E water	
		Intermol.	Total	Intermolecular	Total
0.055M	<i>o</i> -HB	0	4.26 ± 0.04	0	4.44 ± 0.04
	<i>m</i> -HB	0.01	4.54 ± 0.04	0.01	4.71 ± 0.04
	<i>p</i> -HB	0.01	4.70 ± 0.04	0.02	4.91 ± 0.04
0.46M	<i>o</i> -HB	0.58	3.82 ± 0.02	0.5	4.03 ± 0.01
	<i>m</i> -HB	0.39	4.18 ± 0.02	0.26	4.45 ± 0.03
	<i>p</i> -HB	0.58	4.13 ± 0.01	0.39	4.46 ± 0.02

• MD simulations can correctly rank HB isomers according to their self-diffusion coefficient, *o*-HB > *m*-HB > *p*-HB (Table 1). In SPC/E water, which has lower self-diffusions coefficient, the mobility of HB anions is lower.

• At the lower concentration there is little or no clustering and the formation of hydrogen bonds with water determines the isomer's mobility. At the higher concentration clustering is significant and contributes to the mobility of the isomer. *m*-HB and *p*-HB forms approximately the same number of H-bonds, but in the case of *p*-HB more of them are intermolecular and the isomer is less mobile (Table 2).

• *o*-HB predominantly forms cyclic dimers. *m*-HB and especially *p*-HB can form larger aggregates of various shapes, such as rings and chains, and sizes. The largest observed cluster consisted of 17 *p*-HB molecules in SPC water.

5 Conclusions

MD simulations with the GROMOS96 45a3 force field and the SPC (SPC/E) water can correctly discriminate HB isomers on the basis of their mobility. At the lower concentration hydrogen bonding with water determines the mobility of the isomer (less H-bonds, higher mobility) while at the higher concentration clustering must also be considered. Clusters are formed via hydrogen bonds between HB molecules. *o*-HB predominantly forms cyclic dimers, while *m*-HB and especially *p*-HB can form larger aggregates of various shapes and sizes, including rings and chains. We can also conclude that *o*-HB stabilizes a long cylindrical DTAC micelle the most. In its presence there is the highest short-range order of DTA unimers. *o*-HB also penetrates deepest into the micellar core and has a strong preferential orientation with respect to the main micellar axis. These results agree with experimental observations and can be ascribed to the fact that the *ortho* isomer is the most amphiphilic (ie. has a distinguishable hydrophobic and hydrophilic region).

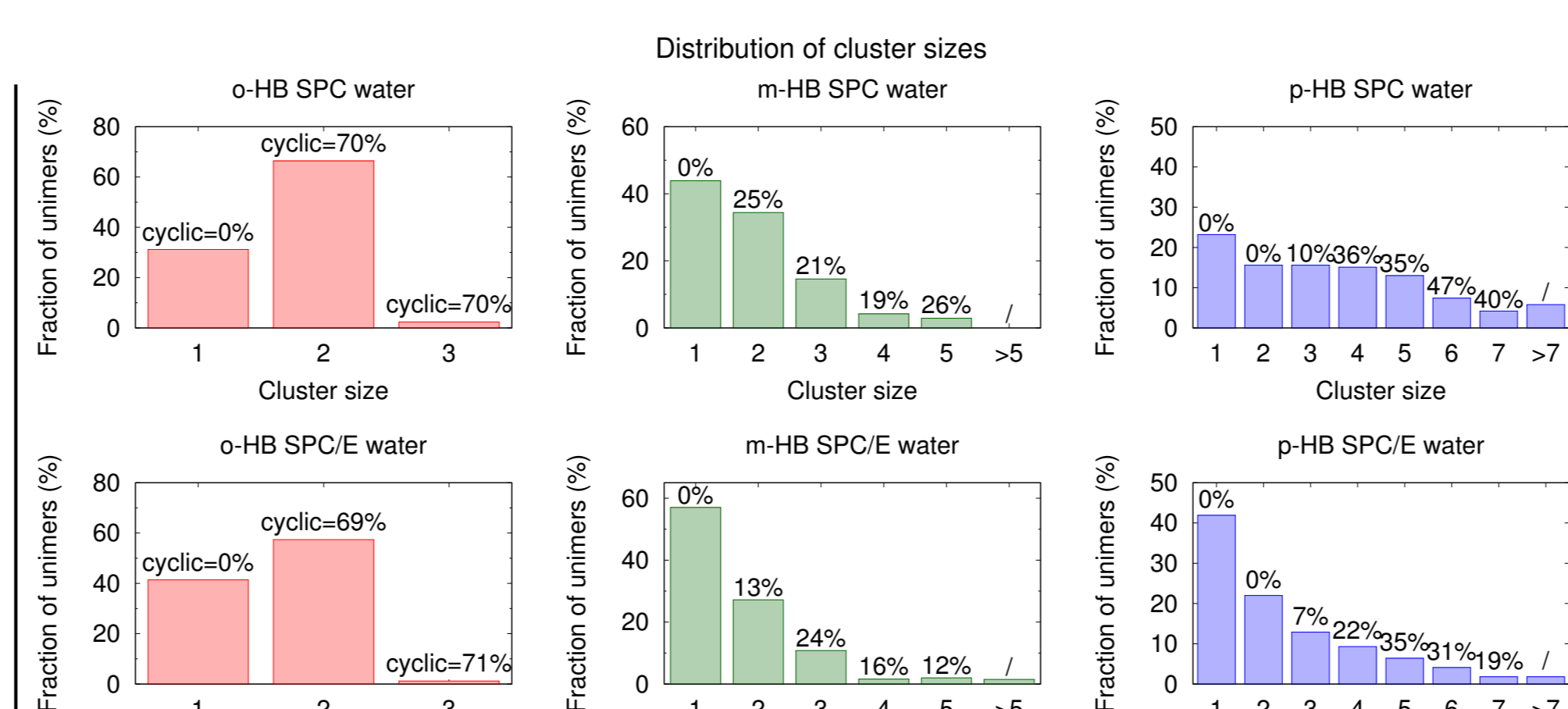


Figure 2: Distribution of cluster sizes. Cluster is termed cyclic if the number of intermolecular bonds in the cluster is the same or larger than the cluster size.

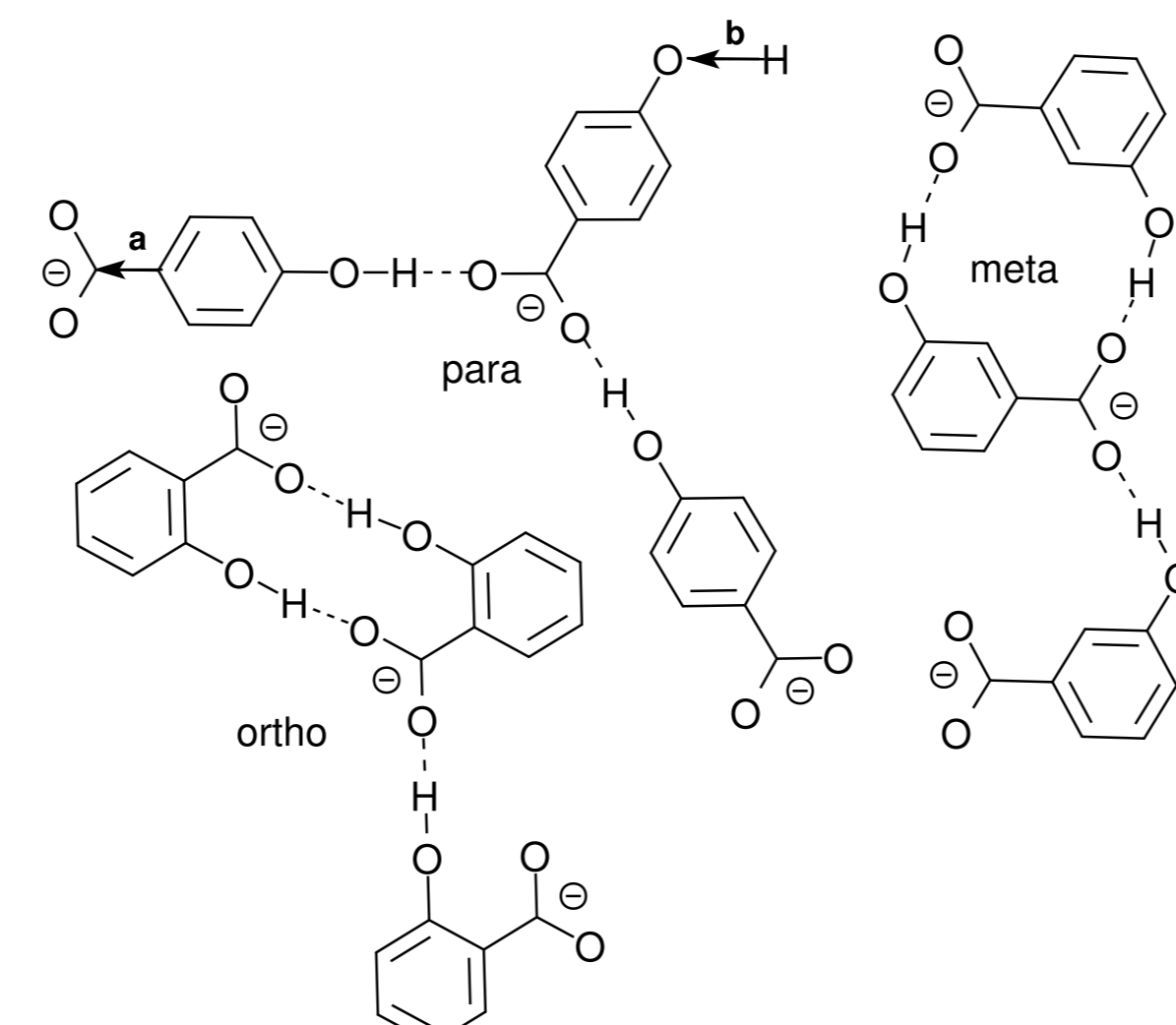


Figure 3: Possible hydroxybenzoate anion cluster geometries as suggested by pair distribution and angle distribution functions (presented in [7]). Drawings are not to scale.

4 Micellar systems (SPC water)

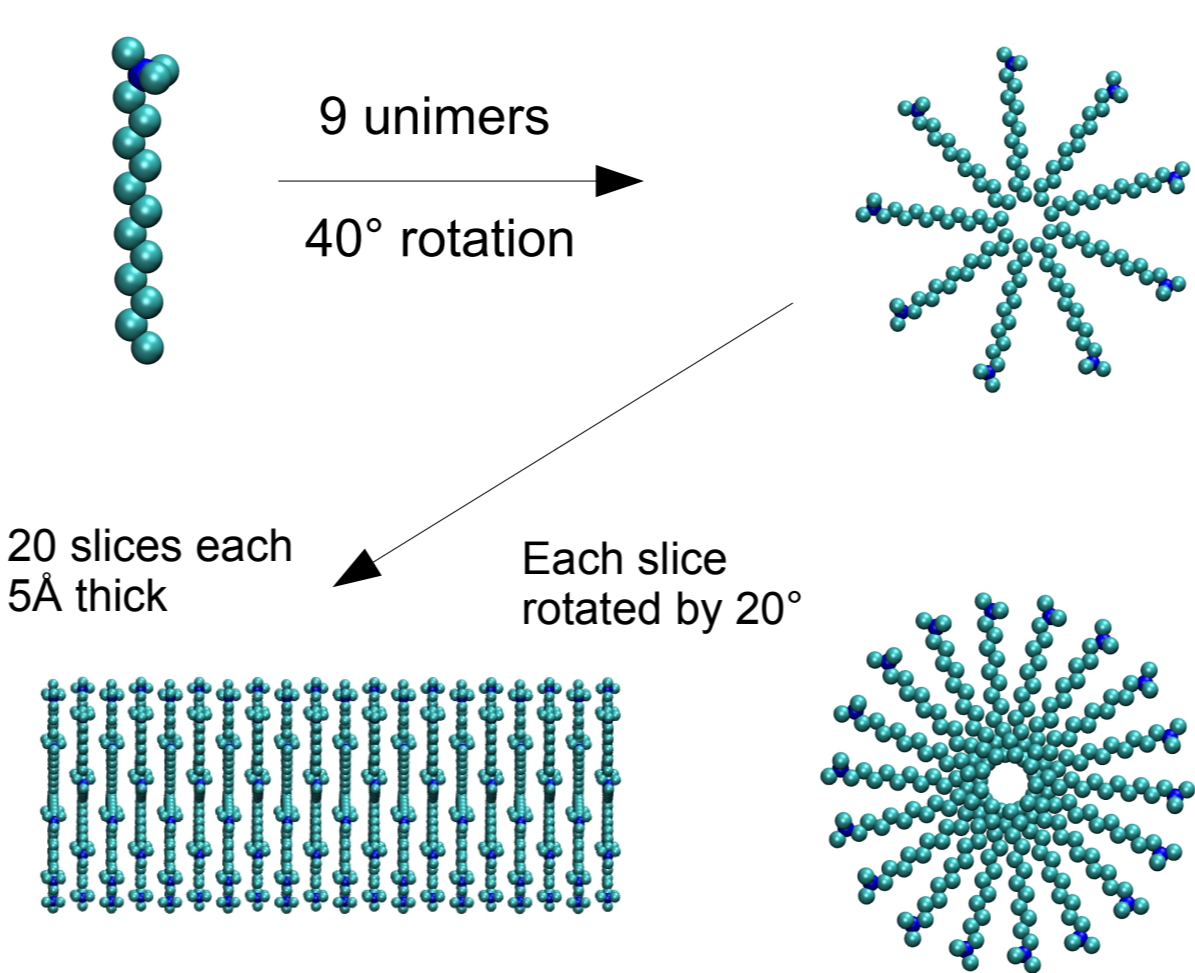


Figure 4: Assembly of the initial micelle.

Table 3: Geometric properties of stable cylindrical micelles after an 80 ns production run: Added salt, box dimensions (L_x), number of unimers per unit length (n_L), radius of the micelle (R_{th}), volume per unimer (v), area per headgroup (a_0).

Salt	$L_{x,y}$ [Å]	L_z [Å]	n_L [Å ⁻¹]	R_{th} [Å]	v [Å ³]	a_0 [Å ²]
<i>o</i> -HB	84.274	78.130	2.304	18.906	487.1	51.5
<i>m</i> -HB	79.256	88.339	2.038	17.891	493.2	55.1
<i>p</i> -HB	78.291	90.539	1.988	17.525	485.1	55.4

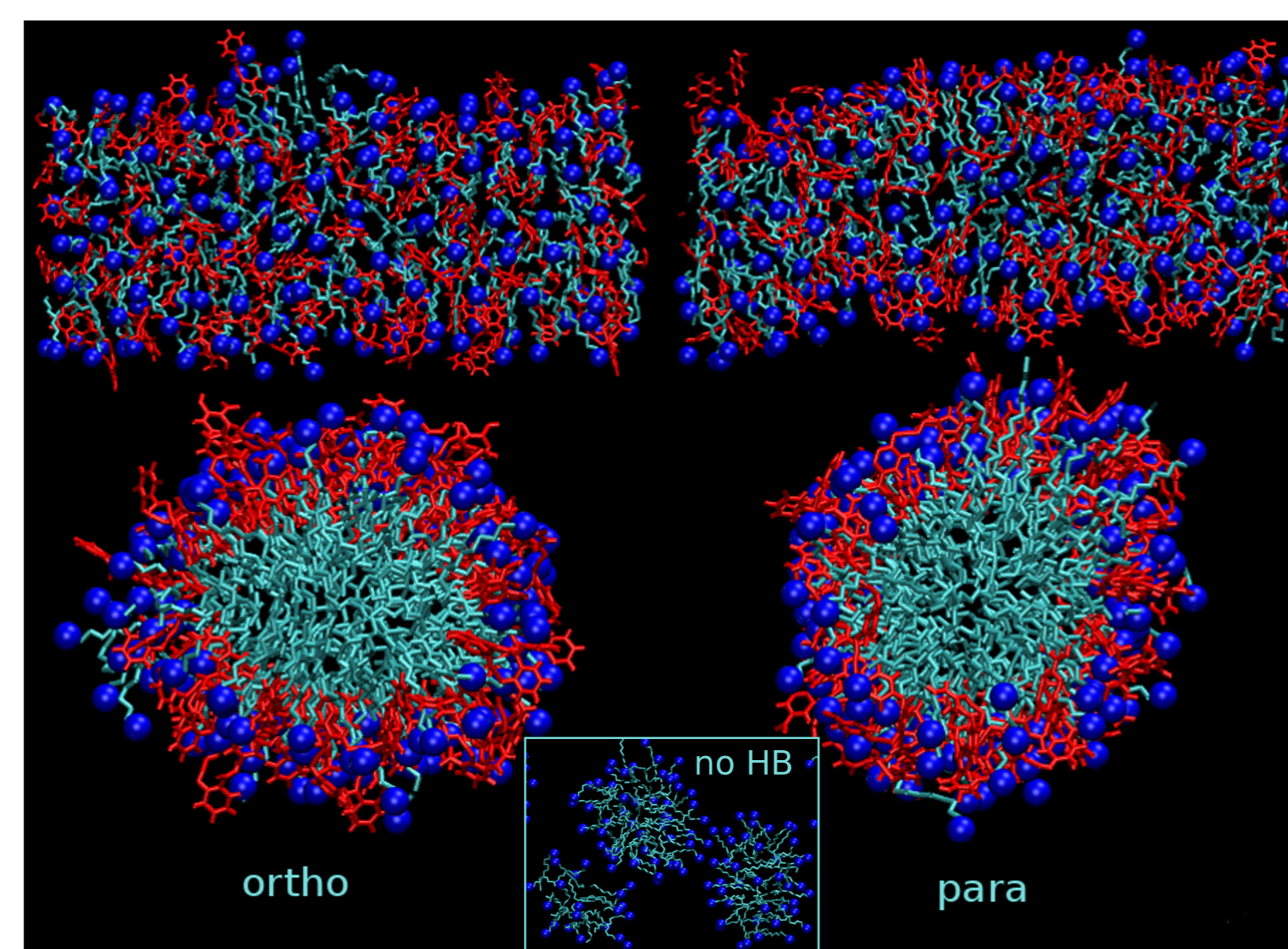


Figure 5: Snapshot of stable cylindrical DTAC micelles in the presence of *o*-HB (left) and *p*-HB (right) after an 80 ns run. HB atoms are coloured red and surfactant headgroups are represented as blue balls. In the box in the middle there are spherical DTAC micelles which are a result of the disintegration of the initial cylindrical micelle in pure water.

• In Table 3 there are geometrical properties of the stable cylindrical micelles after an 80 ns production run. In the case of *o*-HB the unimers are most densely packed (highest n_L), the micelle is thickest (highest R_{th}) and has the lowest area per surfactant molecule. This shows that *o*-HB stabilizes cylindrical micelles more than the other two isomers.

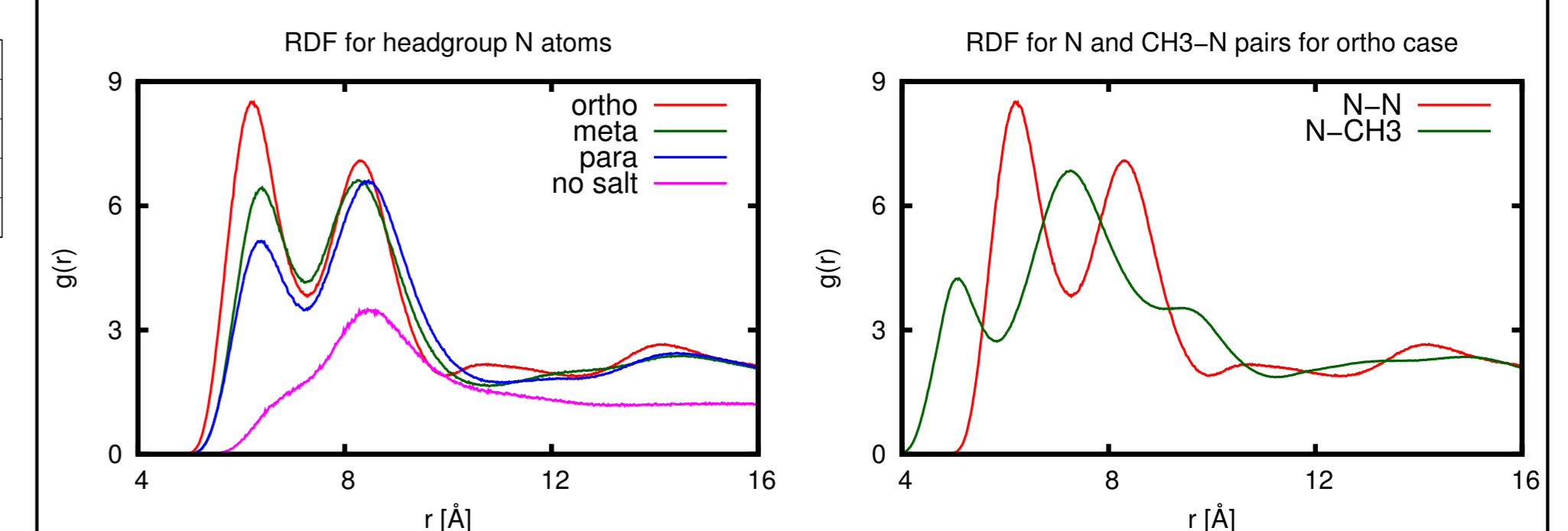


Figure 6: RDF for surfactant nitrogen atoms (left) and surfactant nitrogen atoms to headgroup CH₃ groups (right). Notice how the second peak of the green curve fits nicely between the two highest peaks of the red curve.

• NaHB induces strong coordination of the headgroups, especially *o*-HB (Figure 6 left, first peak). We can treat this structure as a quasi-2D hexagonal lattice. A Wigner-Seitz cell with lattice constant b ($a_0 = \sqrt{3}b^2/2$, $b = 7.7 \text{ Å}$ for the *o*-HB case) can be used. Then the 2nd neighbour (position of the 3rd peak in Figure 6 left) equals $\sqrt{3}b$ (13.4 Å for the *o*-HB case).

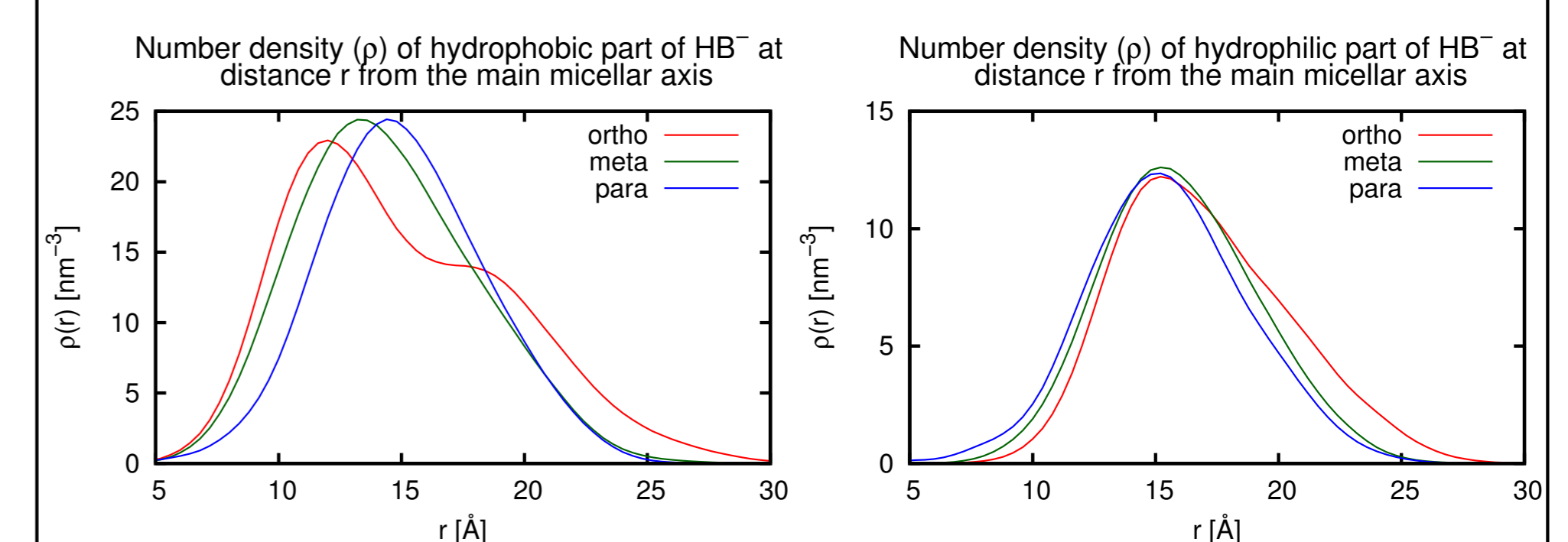


Figure 7: Number densities of the hydrophobic and hydrophilic part of HB⁻ anions as a function of distance from the main micellar axis.

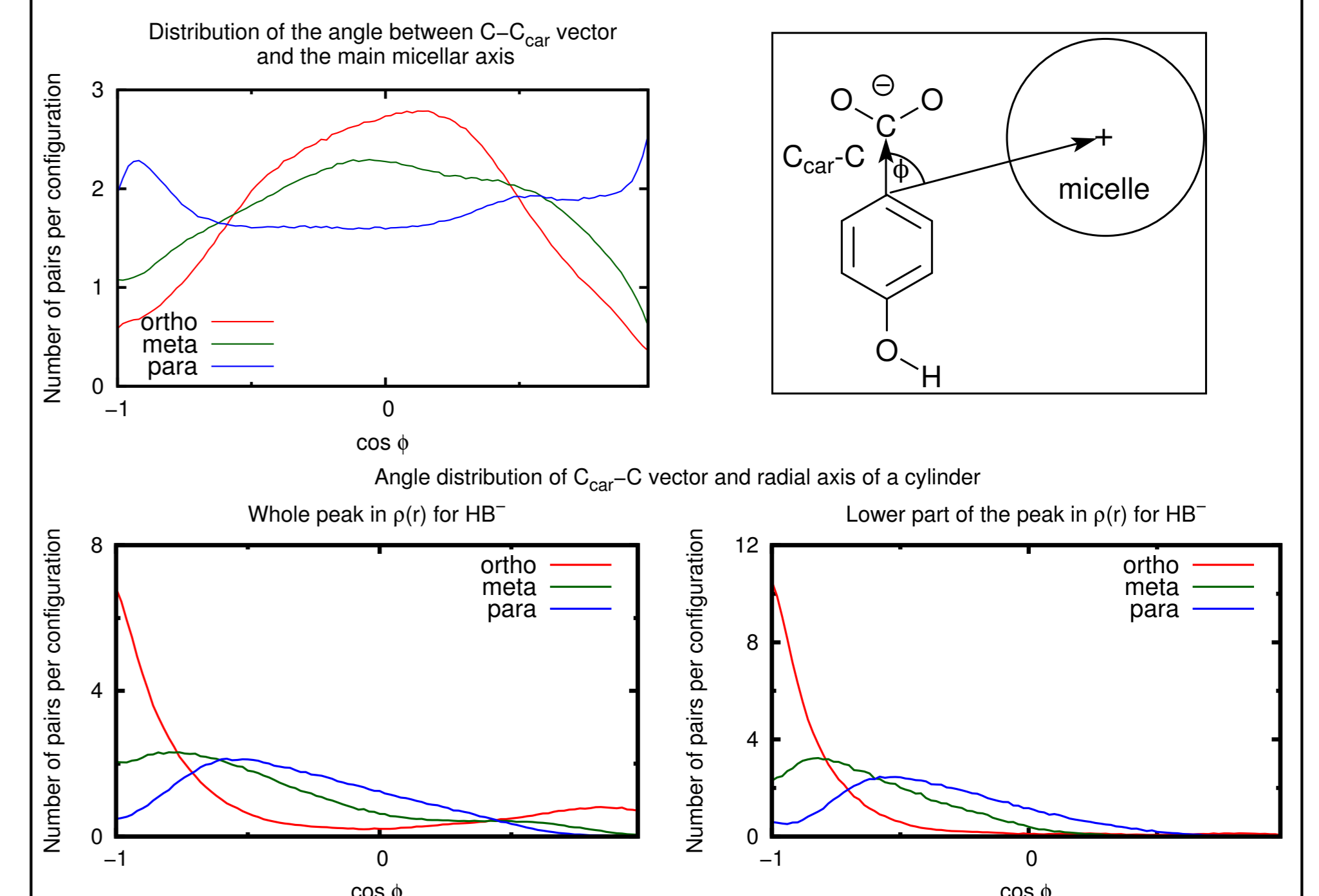


Figure 8: Distributions of the cosine of the angle between C-C_{car} bond and different micellar axes. The lower part of the figure shows the distributions of the cosine of the angle depicted in the drawing for the whole peak in Figure 7 left, and the lower part (up to 15 Å) of the same peak. *o*-HB has two preferential orientations depending on the distance from the main micellar axis.

• *o*-HB penetrates deeper into the micellar core than the other two isomers and has, due to its highest amphiphilicity, a greater tendency for a preferential orientation with respect to the micelle than *m*-HB or *p*-HB.

References

- [1] M. Bešter-Rogač, J. Chem. Eng. Data **56**, 4965 (2011).
- [2] B. Šarac *et al.*, Colloid Polym. Sci. **289**, 1597 (2011).
- [3] B. Šarac, G. Mériquet, B. Ancian, and M. Bešter-Rogač, Langmuir **29**, 4460 (2013).
- [4] <http://lammps.sandia.gov>.
- [5] A. Bochevarov *et al.*, Int. J. Quantum Chem. **113**, 2110 (2013).
- [6] Z. Wang and R. G. Larson, J. Phys. Chem. B **113**, 13697 (2009).
- [7] J. Gujt, Č. Podlipnik, M. Bešter-Rogač, and E. Spohr, Phys. Chem. Chem. Phys. **16**, 19314 (2014).