

Biophysical Journal, Volume 97

Supporting Material

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Supporting Material:

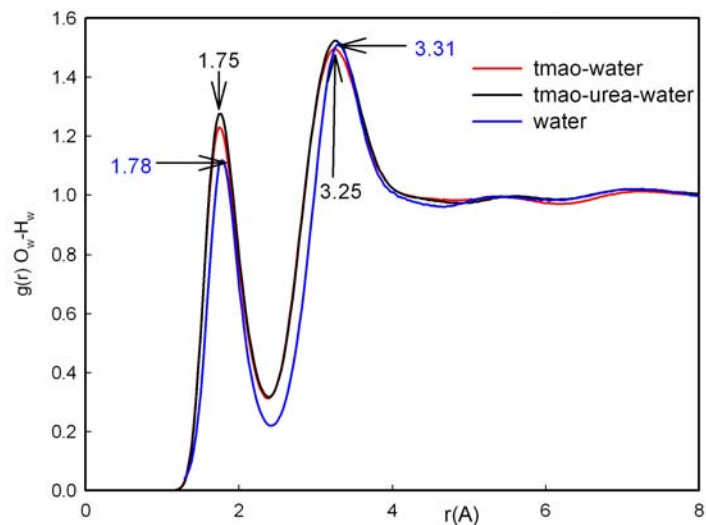


FIGURE S1 PPDF of the water hydrogens around the water oxygens, $g(r)_{O_w-H_w}$ in pure water (1) and aqueous solutions of TMAO and 1:1 TMAO-urea.

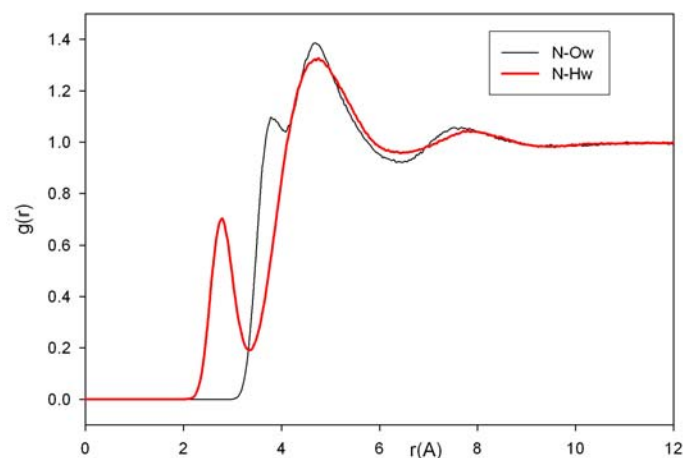


FIGURE S2 Partial pair distribution of the water oxygens ($g(r)_{N-O_w}$) and water hydrogens $g(r)_{N-H_w}$ around the nitrogen atom of TMAO. The first maximum in the N-H_w distribution is at too large a distance (2.79 Å) to correspond to a hydrogen bond.

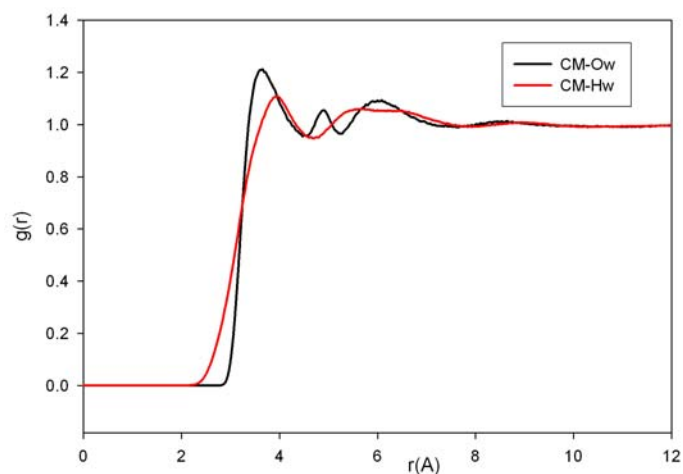


FIGURE S3 Partial pair distribution functions of the water oxygens ($g(r)_{\text{CM-Ow}}$) and water hydrogens ($g(r)_{\text{CM-Hw}}$) around the methyl carbons of TMAO. The absence of any peak at distances shorter than the CM-Ow peak confirms the preferential orientation of the water oxygens towards the methyl groups, which maximizes the formation of hydrogen bonds.

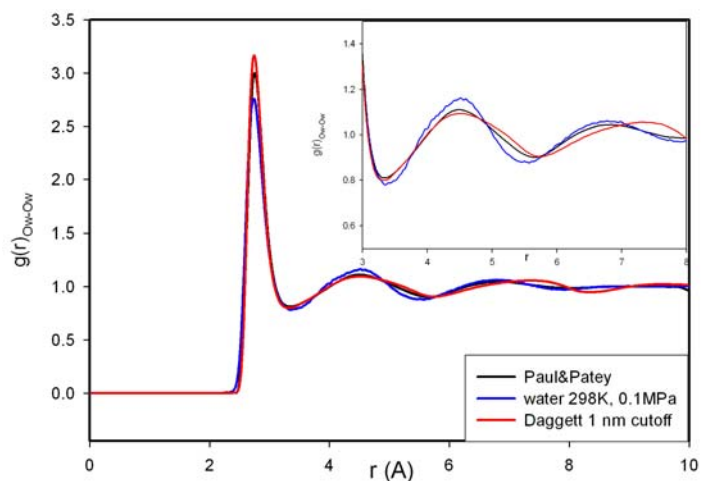


FIGURE S4 Partial pair distribution of the water oxygens in pure water obtained by MD using the SPC/E model (Paul and Patey, private communication) and the F3C model (Beck and Daggett, private communication) and the curve obtained by isotopic substitution. Note that the curve of the Daggett group displayed here is the correct one for comparison with TMAO/water.

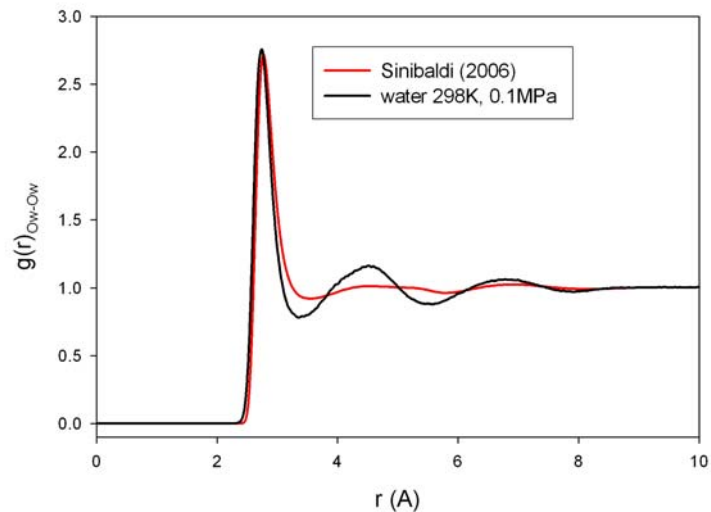


FIGURE S5 Partial pair distribution of the water oxygens in pure water obtained by MD using the TIP3P model (2) and the curve obtained by isotopic substitution.

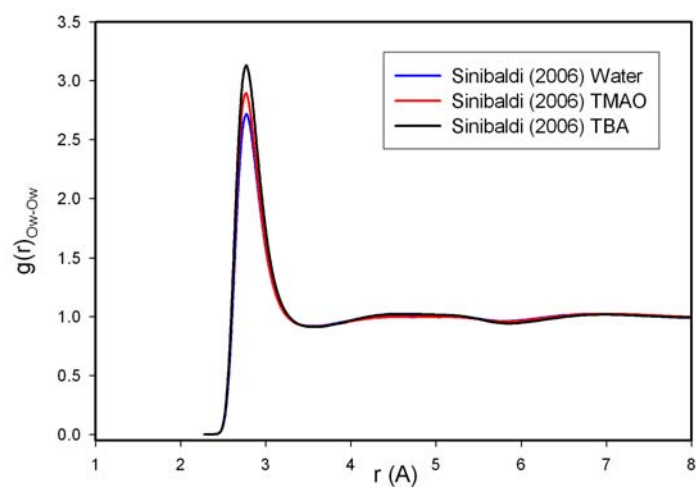


FIGURE S6 Partial pair distribution of the water oxygens ($g(r)_{Ow-Ow}$) in pure water and in TMAO (mole fraction: 0.05) or TBA solution (mole fraction: 0.05) obtained by MD using the TIP3P model for water (2).

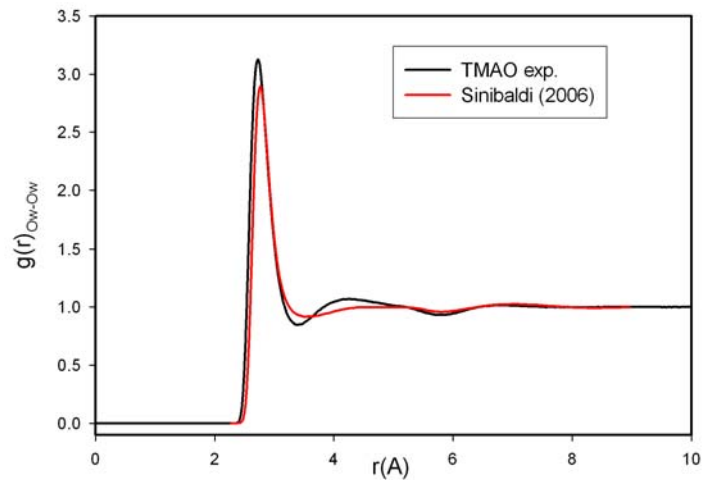


FIGURE S7 Partial pair distribution of the water oxygens in a TMAO solution (mole fraction TMAO: 0.05) (2) and equivalent curve obtained by isotopic substitution.

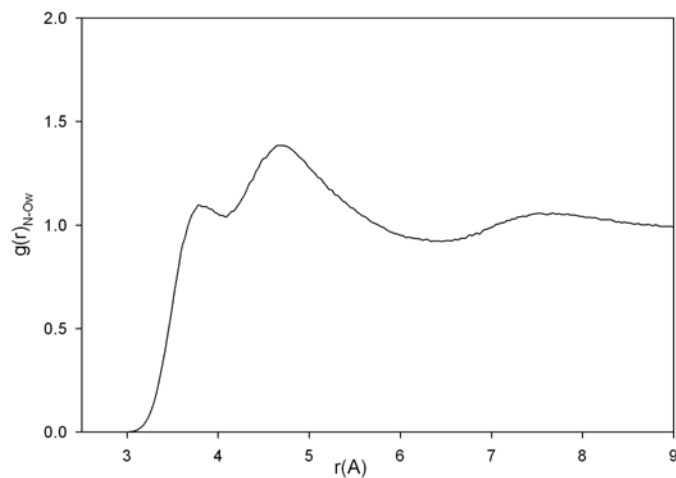


FIGURE S8 Partial pair distribution function of water oxygens around the nitrogen atom ($g(r)_{N-Ow}$) of TMAO (mole fraction TMAO:0.05) obtained by isotopic substitution. These results should be compared with Figure 4(b) of Sinibaldi et al. (2).

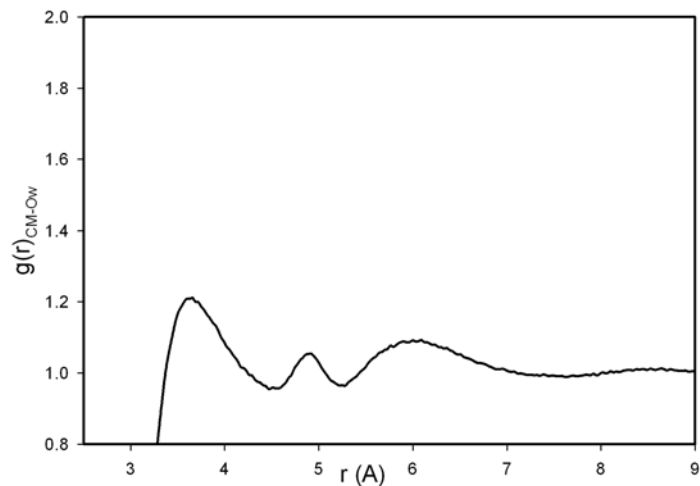


FIGURE S9 Partial pair distribution function of water oxygens around the methyl carbons ($g(r)_{\text{CM-O}_w}$) of TMAO (mole fraction TMAO:0.05) obtained by isotopic substitution. These results should be compared with Figure 4(d) of Sinibaldi et al. (2).

The features of the CM-O_w distribution for TBA of Sinibaldi et al. (2) resemble those of the experimental curves for TBA (3) and for TMAO (Fig. S9). The first shell in the TBA simulations is at 3.58 \AA , compared to 3.74 \AA (3) in the experimental data whereas the value for TMAO is 3.10 \AA compared with an experimental value of 3.93 \AA .

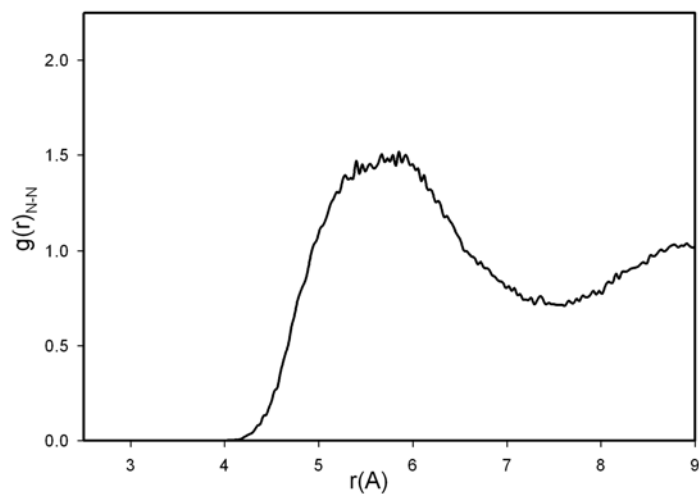


FIGURE S10 Partial pair distribution function of the nitrogen atoms $g(r)_{N-N}$ in TMAO (mole fraction TMAO:0.05) obtained by isotopic substitution. These results should be compared with Figure 4(f) of Sinibaldi et al. (2).

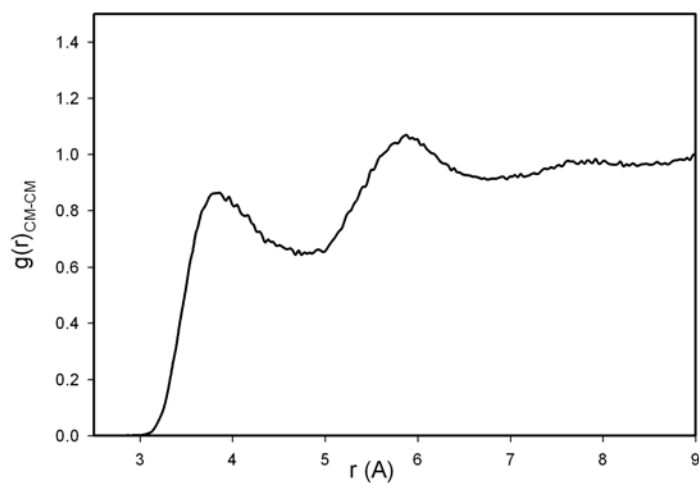


FIGURE S11 Partial pair distribution of the TMAO methyl carbons, $g(r)_{CM-CM}$ obtained by isotopic substitution TMAO (mole fraction TMAO:0.05). This figure should be compared with figure 4(h) of Sinibaldi et al. (2).

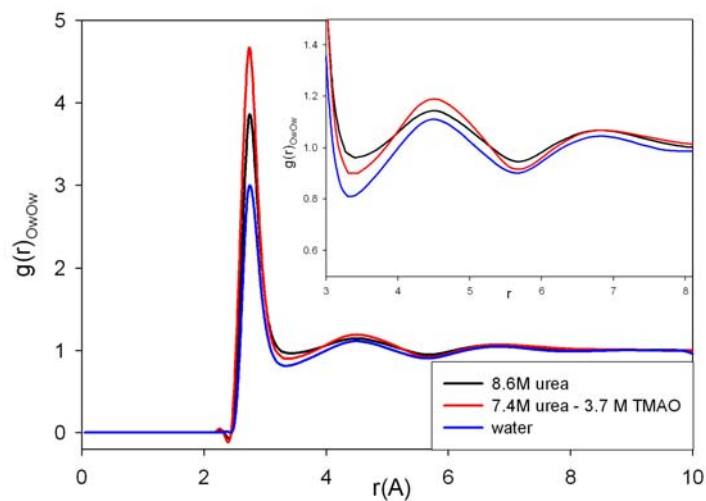


FIGURE S12 MD simulations for 8.6M urea, 7.4M urea - 3.7M TMAO and pure water (4) (Paul and Patey, private communication).

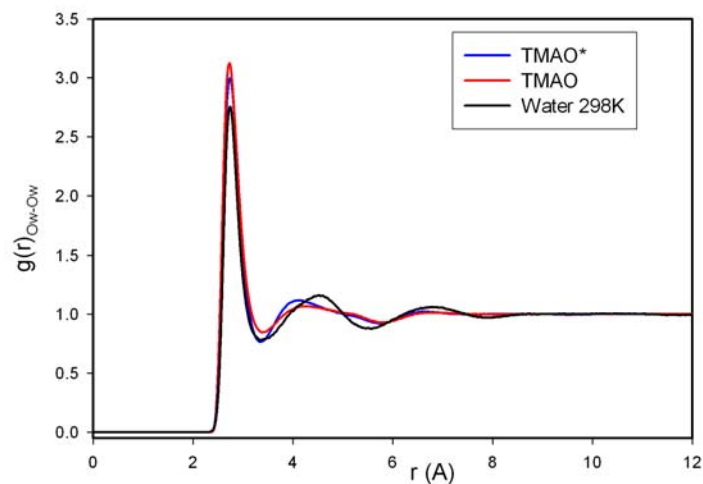


FIGURE S13 Comparison of the partial pair distribution of the water oxygen atoms in a TMAO solution (mole fraction TMAO: 0.05) obtained by the EPSR method using the two sets of charges in Table 2 and the curve for pure water (1). The label of the curve corresponding to the second set of charges (5, 6) is marked with an asterisk.

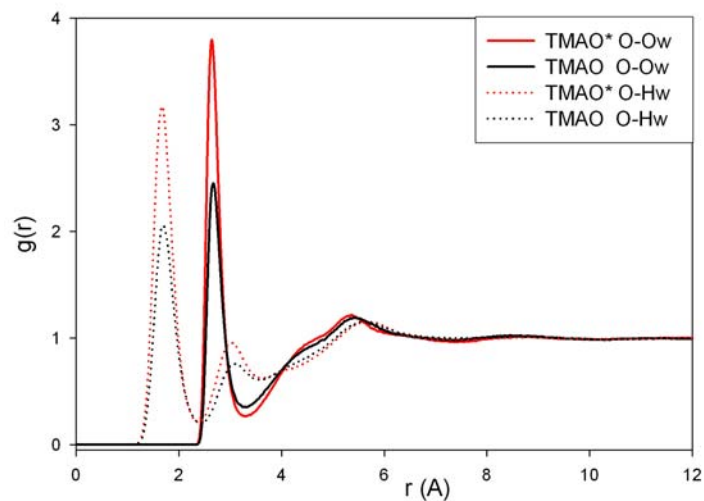


FIGURE S14 Comparison of partial pair distribution involving the oxygen atom of TMAO in a TMAO solution (mole fraction TMAO: 0.05) obtained by the EPSR method using the two sets of charges in Table 2. The label of the curves corresponding to the second set of charges (5, 6) is marked by an asterisk.

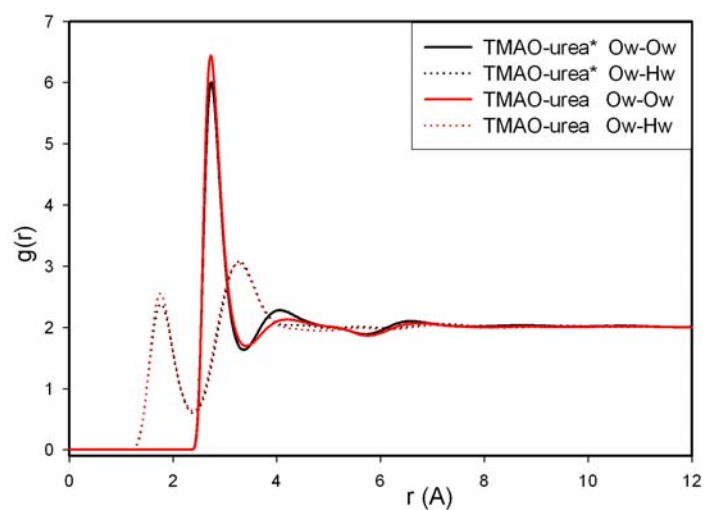


FIGURE S15 Comparison of partial pair distribution involving the oxygen atoms of water in a 1:1 TMAO-urea solution (mole fraction TMAO: 0.05) obtained by the EPSR method using the two sets of charges in Table 2. The label of the curves corresponding to the second set of charges (5, 6) is marked by an asterisk.

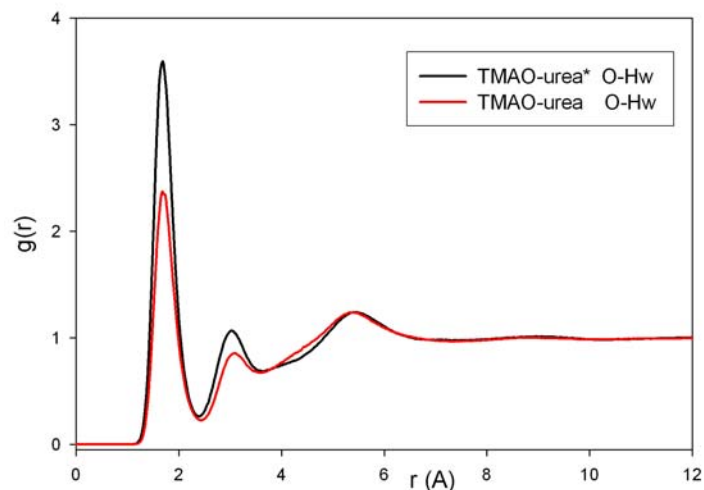


FIGURE S16 Comparison of partial pair distribution of water hydrogen atoms around the oxygen atom of TMAO in a 1:1 TMAO-urea solution (mole fraction TMAO: 0.05) obtained by the EPSR method using the two sets of charges in Table 2. The label of the curve corresponding to the second set of charges (5, 6) is marked by an asterisk.

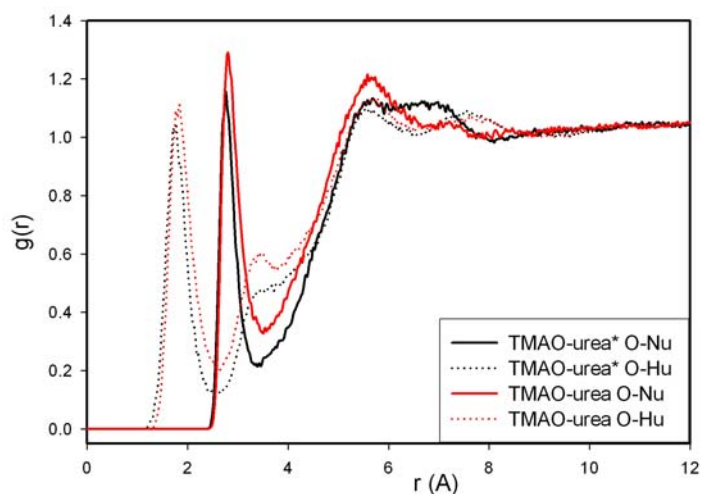


FIGURE S17 Comparison of the PPDFs involving the oxygen atom of TMAO for a 1:1 TMAO solution obtained by EPSR using the two sets of charges in Table 2. The labels of the curves calculated with the second set of charges (5, 6) are marked with an asterisk.

References:

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