

Supplementary Information:
Hierarchical clustering analysis of hydrogen
bond networks in aqueous solutions

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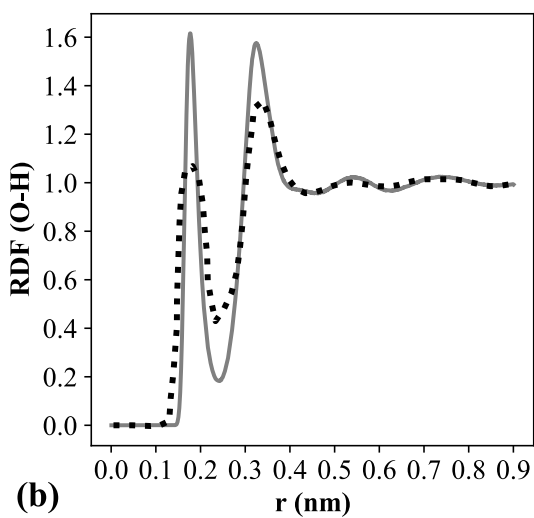
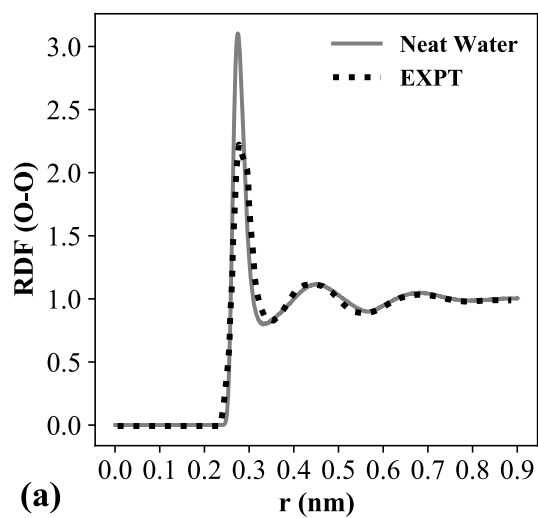
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1 Molecular Dynamics Simulation Results

Table S1. Molecular Dynamics Simulations Results

| Water molecule | Ion pair | Concentration | | Density (g/cm^3) | | D_{water} ($\times 10^{-9}m^2/s$) | |
|----------------|----------|---------------|--------------|----------------------|--------------------|---------------------------------------|------------------------------|
| | | (mol/L) | (mol/kg) | MD | Expt. | MD | Expt. |
| 19641 | 0 | 0 | 0 | 0.998 | 0.995 ² | 2.71 | 2.7 ² (305 K) |
| 19641 | 381 | 1.05 | 1.01 | 1.037 | 1.039 ³ | 2.32 | 2.17 ¹ (1.0 M) |
| 19641 | 794 | 2.12 | 1.98 | 1.071 | 1.069 ³ | 1.96 | 2.02 ¹ (2.0 M) |
| 19641 | 1241 | 3.22 | 2.91 | 1.106 | 1.100 ³ | 1.64 | 1.87 ¹ (3.0 M) |
| 19641 | 1727 | 4.32 | 3.80 | 1.137 | - | 1.38 | 1.71 ¹ (4.0 M) |



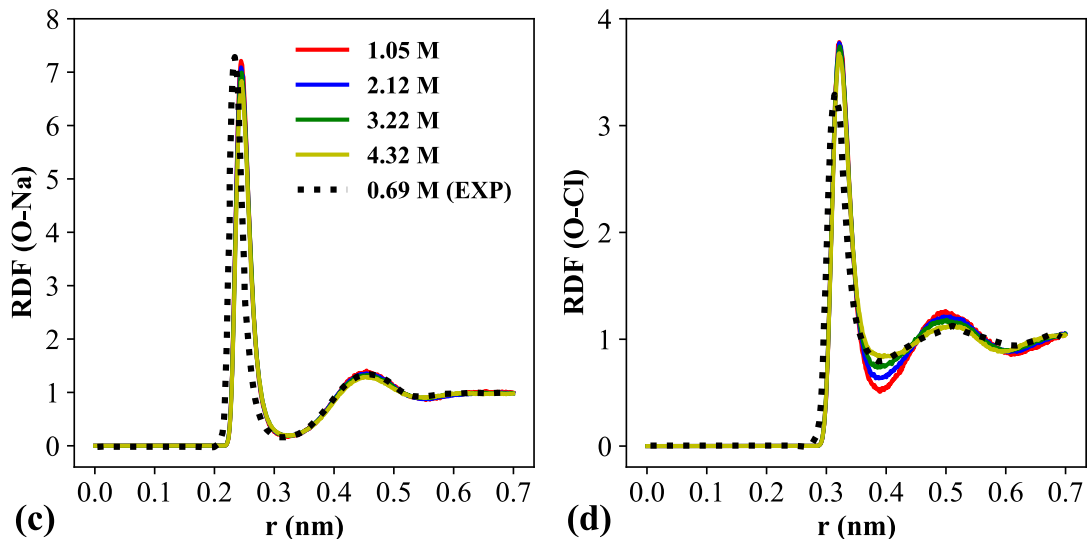


Figure S1. Radial distribution function (RDF) (a) between oxygen and oxygen, (b) between oxygen and hydrogen, (c) between oxygen atom and sodium cations and (d) between oxygen atom and chloride anions in neat water and NaCl solutions compared with experimental values^{4,5}.

2 Lifetime data

Table S2. Lifetime of rings in neat water and 1.05 M, 2.12 M, 3.22 M, 4.32 M NaCl solutions.

| Ring size | Neat | NaCl solutions | | | |
|-----------|-------|----------------|--------|--------|--------|
| | water | 1.05 M | 2.12 M | 3.22 M | 4.32 M |
| 4 | 78.3 | 73.3 | 71.2 | 67.4 | 64.7 |
| 5 | 92.7 | 87.7 | 83.6 | 79.2 | 74.6 |
| 6 | 83.0 | 78.2 | 74.7 | 71.0 | 67.1 |
| 7 | 70.0 | 66.4 | 64.2 | 61.7 | 59.0 |
| 8 | 56.7 | 54.9 | 53.5 | 52.2 | 51.0 |
| 9 | 48.6 | 47.5 | 46.9 | 46.1 | 45.4 |

Table S3. Lifetime of fragments in neat water and 1.05 M, 2.12 M, 3.22 M, 4.32 M NaCl solutions.

| Fragment size | Neat | NaCl solutions | | | |
|---------------|-------|----------------|--------|--------|--------|
| | water | 1.05 M | 2.12 M | 3.22 M | 4.32 M |
| 5 | 39.0 | 37.7 | 37.1 | 36.5 | 35.8 |
| 6 | 50.4 | 48.3 | 47.0 | 45.3 | 44.1 |
| 7 | 51.1 | 49.1 | 47.5 | 46.0 | 44.6 |
| 8 | 54.4 | 52.3 | 50.2 | 48.9 | 46.8 |
| 9 | 47.8 | 45.9 | 44.8 | 43.6 | 42.3 |
| 10 | 45.6 | 44.3 | 42.8 | 42.0 | 41.2 |
| 11 | 45.8 | 43.5 | 43.1 | 41.8 | 43.1 |
| 12 | 46.4 | 43.0 | 42.4 | 39.3 | 43.4 |

Table S4. Lifetime of clusters in neat water and 1.05 M, 2.12 M, 3.22 M, 4.32 M NaCl solutions.

| Cluster size | Neat water | NaCl solutions | | | |
|--------------|------------|----------------|--------|--------|--------|
| | | 1.05 M | 2.12 M | 3.22 M | 4.32 M |
| 5 | 33.8 | 33.3 | 33.3 | 33.9 | 33.8 |
| 6 | 37.6 | 38.1 | 39.3 | 39.1 | 39.2 |
| 7 | 36.3 | 37.2 | 38.2 | 39.0 | 39.2 |
| 8 | 36.2 | 37.3 | 38.4 | 39.4 | 39.6 |
| 9 | 34.3 | 35.2 | 35.8 | 36.3 | 36.0 |
| 10 | 32.2 | 33.0 | 32.9 | 33.3 | 33.4 |
| 11 | 30.7 | 31.5 | 31.7 | 32.3 | 31.8 |
| 12 | 30.0 | 30.6 | 30.6 | 31.0 | 31.6 |
| 13 | 29.5 | 29.9 | 30.2 | 31.0 | 30.3 |
| 17 | 27.6 | 27.9 | 28.1 | 28.1 | 28.3 |
| 25 | 25.8 | 26.0 | 26.0 | 26.2 | 26.0 |
| 33 | 25.3 | 25.4 | 25.4 | 25.4 | 25.4 |
| 41 | 25.1 | 25.2 | 25.1 | 25.1 | 25.3 |
| 49 | 25.1 | 25.1 | 25.0 | 25 | 25 |
| 57 | 25.0 | 25.1 | 25.0 | 25 | 25 |
| 65 | 25.0 | 25 | 25 | 25 | 25 |
| 73 | 25.0 | 25 | 25 | 25 | 25 |

REFERENCES

1. Müller KJ, Hertz HG. A parameter as an indicator for water-water association in solutions of strong electrolytes. *J Phys Chem.* 1996;100(4):1256-1265. doi:10.1021/jp951303w
2. Berendsen HJC, Grigera JR, Straatsma TP. The missing term in effective pair potentials. *J Phys Chem.* 1987;91(24):6269-6271. doi:10.1021/j100308a038
3. Yue S, Panagiotopoulos AZ. Dynamic properties of aqueous electrolyte solutions from non-polarisable, polarisable, and scaled-charge models. *Mol Phys.* 2019;117(23-24):3538-3549. doi:10.1080/00268976.2019.1645901
4. Soper AK, Bruni F, Ricci MA. Site-site pair correlation functions of water from 25 to 400 °C: Revised analysis of new and old diffraction data. *J Chem Phys.* 1997;106(1):247-254. doi:10.1063/1.473030
5. Mancinelli R, Botti A, Bruni F, Ricci MA, Soper AK. Hydration of sodium, potassium, and chloride ions in solution and the concept of structure maker/breaker. *J Phys Chem B.* 2007;111(48):13570-13577. doi:10.1021/jp075913v