

Supporting Information for

**Acidic Conditions Impact Hydrophobe Transfer
Across the Oil-Water Interface in Unusual Ways**

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1. Density profile of chloride anions in different systems

In the main text, we discuss the features of density profiles of the two different cations in the acid and salt systems. Although the two systems share the same anion, the behavior of the anion in different systems is different. Upon comparing the density profiles of the chloride anion in the two systems, it is clear that there is an enhanced density of anion near the interface for the acid system, while this is not seen in the salt system. While the hydronium achieves its highest density at $z_{\text{GDI}} \approx -0.5 \text{ \AA}$, the chloride anion reaches its maximum density at $z_{\text{GDI}} \approx -3.0 \text{ \AA}$. The difference in the position of reaching the highest density for the cation and anion indicates that the enhanced density of the anion is not because that the anion is attracted to the interface in the acid system, but because of the Columbic interaction between the anion and the hydronium at the interface. When it comes to the salt system, there is no enhanced cation density at the interface, and the anion itself does not have an affinity to the water-oil interface. Therefore, the density of the anion starts to drop at $z_{\text{GDI}} \approx -7.0 \text{ \AA}$. Actually, this means that the anion is repelled by the water-oil interface.

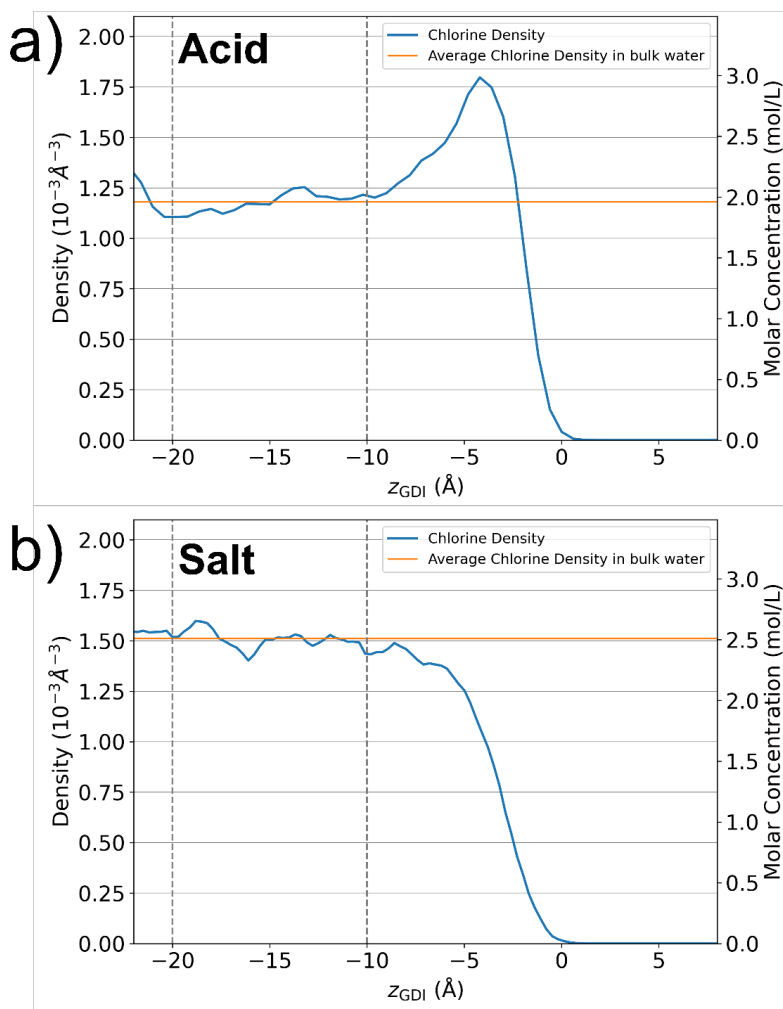


Figure S1. Density profiles of chloride anions in the (a) acid and (b) salt systems.

2. Potential of Mean Force for the Association between Hydronium and Neopentane

To quantitatively describe the association interaction between hydrated proton and neopentane, it is possible to calculate the potential of mean force (PMF) as a function of the distance between hydronium structure and neopentane. According to the reversible work theorem,¹ the PMF can be directly computed from inversion of the radial distribution function (RDF) $g(r)$ using the following equation

$$\text{PMF}(r) = -k_{\text{B}}T \ln g(r) \quad (\text{S1})$$

where k_{B} is the Boltzmann constant, T is the temperature of the system, and $\ln g(r)$ is the natural logarithm of $g(r)$.

Due to the fact that the RDF in an interfacial system cannot fully represent the true interaction around each species, we instead use the modified RDF from the main text and the PMF results are shown in Figure S2.

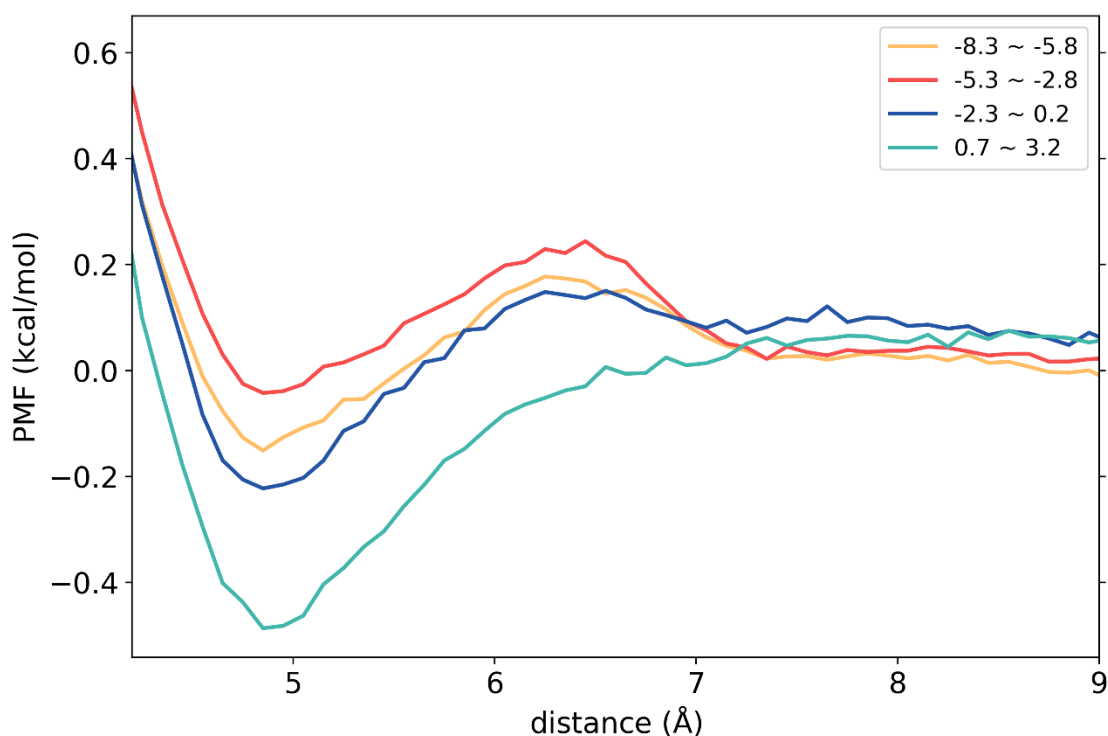


Figure S2. Potential of mean force (PMF) of the association between the hydronium and neopentane as a function of the distance between them. The legends show the position where the neopentane molecule is biased relative to the GDI of water.

3. Radial Distribution Functions (RDFs) between Neopentane and Anion

The distribution of the anion around the neopentane is different in the acid and the salt systems, due to the different distribution of the cations and the Columbic interaction between cations and anions.

In the acid system, the primary peaks are enhanced by the attraction of the surrounding hydronium. One interesting observation is that the tail of the RDF in region $z_{\text{GDI}} = -8.3 \sim -5.8 \text{ \AA}$ is higher than 1. This can be attributed to the enhanced anion density near the interface, as shown in the Figure 1(a).

For the salt system, the primary peaks of the anion are lower than those in the acid system, but higher than the primary peaks of the Na^+ . Due to the anisotropic orientation of interfacial water molecules with dangling hydrogen bonds,² there is a slight absorption of anions near the neopentane/water interface, which results in the slightly higher anion RDF peaks than the cation.

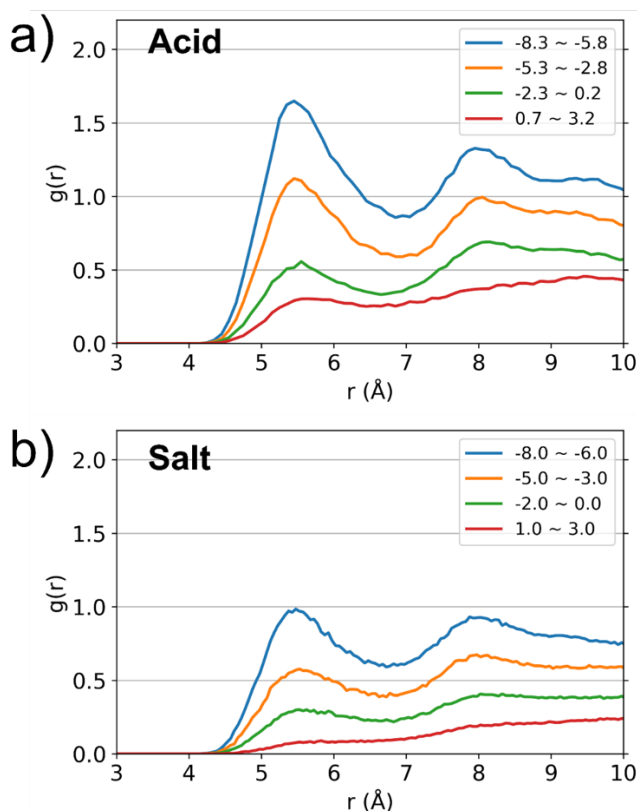


Figure S3. Original RDFs between the central carbon (CC) of the neopentane molecule and chloride anions in the (a) acid and (b) salt systems when the neopentane molecule is biased in different regions. The legends show the position where the neopentane molecule is biased at relative to the GDI of water.

SUPPLEMENTAL REFERENCES

1. Chandler, D., *Introduction to Modern Statistical Mechanics*. Oxford University Press: New York, 1987.
2. Du, Q.; Freysz, E.; Shen, Y. R., Surface Vibrational Spectroscopic Studies of Hydrogen Bonding and Hydrophobicity. *Science* **1994**, *264*, 826-828.