

Supporting Information

Effects and mechanisms of anion and cation on the gelation of nanosilica sol by all-atom molecular dynamics simulation: Promotion or Inhibition?

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1. Definition of hydrogen bond type and calculation of formation probability

Table S1 showed the hydrogen bond types formed by Si(OH)₄, Si(OH)₃O⁻ with the hydroxyl groups on the silica surface and the definitions of the hydrogen bonding donors and acceptors. The naming rule for hydrogen bonds is that the surface hydroxyl atom comes first and the solution component atom comes second, connected by "~" in between. Table S2 showed the calculation of hydrogen bond formation probability.

Table S1. Hydrogen bond types and definitions

Name	Donor	Definition of donor	Acceptor	Definition of acceptor
slab_H~sol_O	slab_H	Surface silicon hydroxyl H	sol_O	Solution silicon hydroxyl O
slab_H~sol_O ⁻	slab_H	Surface silicon hydroxyl H	sol_O ⁻	Solution ionized silanol O ⁻
slab_O~sol_H	sol_H	Solution silicon hydroxyl H	slab_O	Surface silicon hydroxyl O
slab_O~sol_H	sol_H	Solution silicon hydroxyl H	slab_O ⁻	Surface ionized silanol O ⁻

Table S2. Calculation of hydrogen bond formation probability

Model	Hydrogen bonding type	Number of donors (pc)	Number of acceptors (pc)	Number of hydrogen bonds (pc)	Hydrogen bond formation probability
Q2	slab_O~sol_H	(208+58)*2	776	N1	N1/532
	slab_O ⁻ ~sol_H	1006	120	N2	N2/120
	slab_H~sol_O	776	(208+58)*2	N3	N3/532
	slab_H~sol_O ⁻	776	58	N4	N4/58
Q3	slab_O~sol_H	(208+58)*2	384	N1	N1/532
	slab_O ⁻ ~sol_H	1006	64	N2	N2/64
	slab_H~sol_O	384	(208+58)*2	N3	N3/532
	slab_H~sol_O ⁻	384	58	N4	N4/58

Note: The data in the table are obtained from the number of donors and acceptors corresponding to hydrogen bonds in the statistical model.

2. Distribution of each component of the solution and formation of hydrogen bonds in the no-added salt system

The Q2 and Q3 models of the no-added slat system were simulated separately, and the concentration distribution of each component in the z -direction (Fig. S1A, C) and the hydroxyl H and O on the surface along the z -direction (Fig. S1B, D). For the Q2 model, the ionization of the surface silicon hydroxyl caused a large number of negatively charged R-Si-O⁻ groups, which attracted free Na⁺ (replacing H⁺ in the

simulated system) in solution, and Na^+ was adsorbed considerably on the silica surface to form a double electric layer. The strong hydrogen bonding interaction between the silicon hydroxyl group on the surface and $\text{Si}(\text{OH})_4$ caused $\text{Si}(\text{OH})_4$ to be adsorbed in large quantities on the surface (Fig. S1A, black line). The concentration of Na^+ near the surface was substantially larger than $\text{Si}(\text{OH})_4$ because the electrostatic attraction between ions was much stronger than the hydrogen bonding between hydroxyl. Part of $\text{Si}(\text{OH})_3\text{O}^-$ accumulated in the double layer due to the electrostatic attraction with Na^+ on the surface. Since Na^+ readily entered the voids on the crystal surface, thus two concentration peaks of Na^+ appear near the silica surface. Additionally, the distribution of hydrogen and oxygen on the silica surface, as shown in Fig. S1B, differed in that more hydrogen atoms were inside the crystal, and a smaller number extended into the solution.

The adsorption trend of the Q3 model was similar to that of the Q2 model. Still, fewer hydroxyl groups on the surface of silica in the Q3 model resulted in weaker attraction to Na^+ ions at the same ionization degree. As a result, the concentration of Na^+ in the double layer was lower, and the diffusion layer was more extensive. The surface of Q3 had weaker electrostatic repulsion to $\text{Si}(\text{OH})_4$ and electrostatic attraction to $\text{Si}(\text{OH})_3\text{O}^-$ than that of Q2, so a large amount of $\text{Si}(\text{OH})_4$ was adsorbed on the surface of silicon dioxide, and $\text{Si}(\text{OH})_3\text{O}^-$ tended to aggregate in silicic acid solution. In addition, the hydroxyl H atoms on the surface of the Q3 model extended more toward the solution (Fig. S1D, black line) and were more likely to be in contact with solution components.

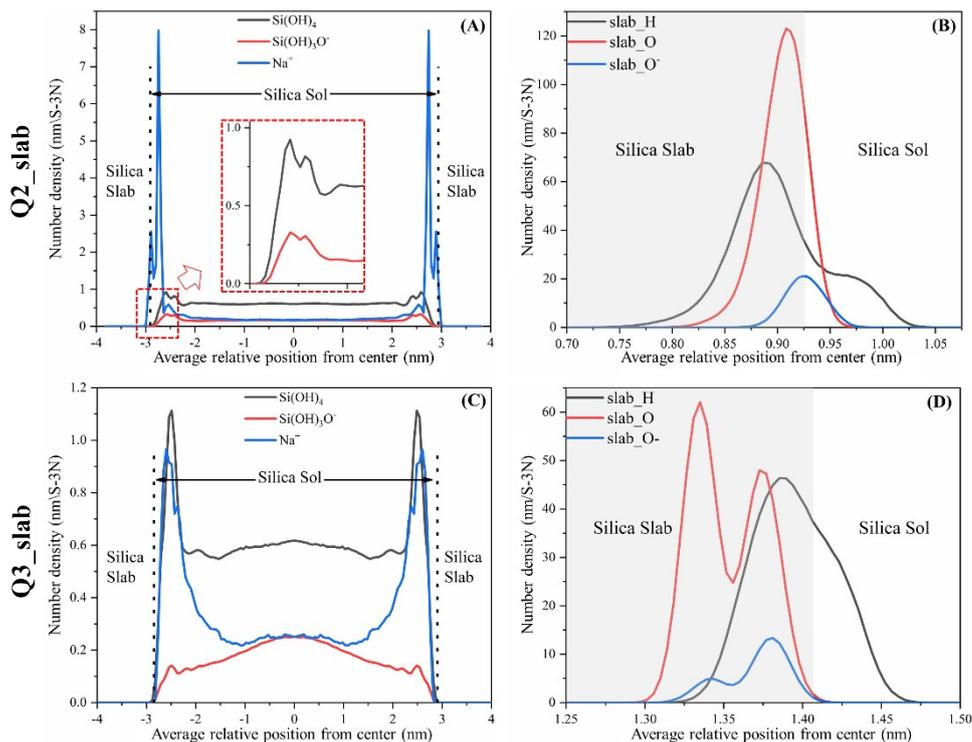


Fig. S1. The concentration distribution of Si(OH)₄, Si(OH)₃O⁻, and Na⁺ in the *z*-direction (A, C) and the concentration distribution of hydroxyl H atoms and O atoms on the silica surface (B, D) in the no-added salt system

The formation probabilities and lifetimes of four different hydrogen bonds (slab_O~sol_H, slab_O~sol_H, slab_H~sol_O, and slab_H~sol_O⁻) were calculated and shown in Fig. S2. The silicon hydroxyl groups on the surface of the Q2 model and the solution silicon hydroxyl groups primarily formed three hydrogen bond types: slab_O~sol_H, slab_O~sol_H, and slab_H~sol_O. slab_H~sol_O⁻ hydrogen bonds were challenging to develop due to the stronger electrostatic attraction between Si(OH)₃O⁻ and Na⁺ in the electric double layer, which caused Si(OH)₃O⁻ from being preferentially distributed near the electric double layer and prevented it from approaching the silanol on the surface. The three hydrogen bond formation probabilities followed the order slab_O~sol_H > slab_O~sol_H > slab_H~sol_O, with slab_O~sol_H and slab_H~sol_O from the same pair of hydroxyl groups but having different formation probabilities. This phenomenon was related to the distribution of hydroxyl H and hydroxyl O on the surface, where only a small amount of hydroxyl H on the surface of Q2 extended into the solution (Fig. S1B). Most of the hydroxyl H

faced towards the silica crystal, exposing hydroxyl O to the solution environment and facilitating the formation of slab_O~sol_H.

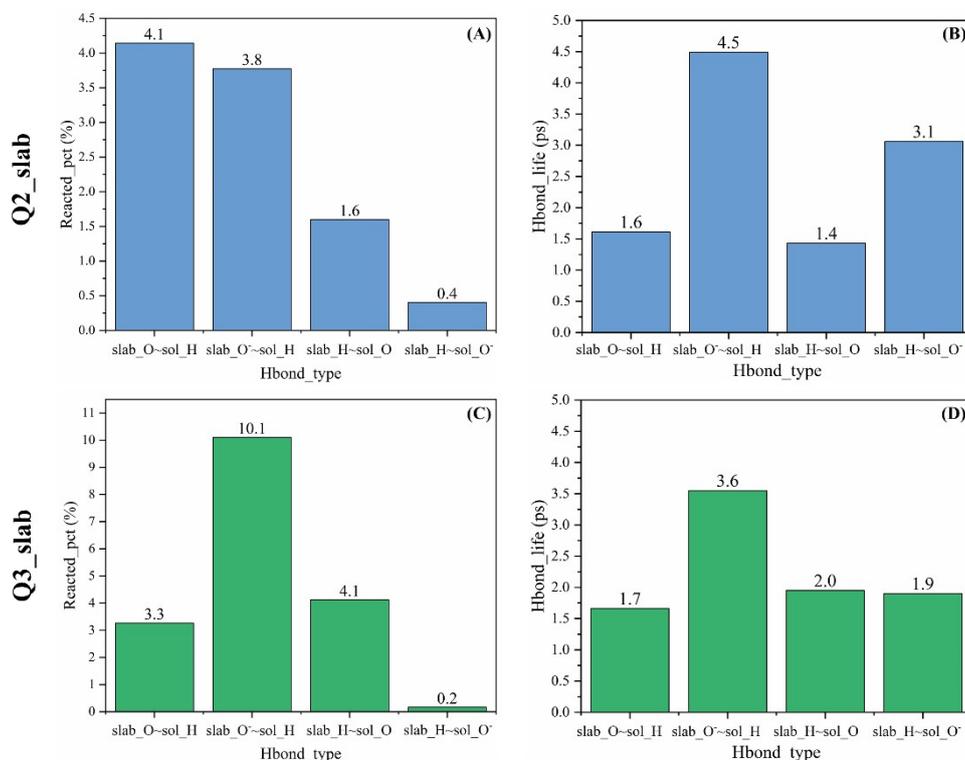


Fig. S2. The hydrogen bond formation probability (A, C) and hydrogen bond lifetime (B, D) on silica surface without salt-added system, (A, B: Q2 model; C, D: Q3 model)

In the Q3 model with weaker electrostatic interactions, the number of cations on the silica surface decreased due to the small number of hydroxyl groups present. This had two effects: (1)The sodium ions concentration around the silica slab group decreased, making it more likely for $\text{Si}(\text{OH})_4$ to approach the slab_O⁻ group and increasing the formation probability of slab_O~sol_H hydrogen bonds. (2)The attraction and repulsion between $\text{Si}(\text{OH})_3\text{O}^-$ and $\text{Si}(\text{OH})_4$ on the surface was weakened, leading to a decrease in the HBP of slab_O~sol_H related to $\text{Si}(\text{OH})_3\text{O}^-$ and an increase in the HBP of slab_H~sol_O related to $\text{Si}(\text{OH})_4$. In addition, the hydrogen on the surface in the Q3 model tended to extend into the solution (Fig. S1D), and the oxygen was more difficult to interact with $\text{Si}(\text{OH})_4$, resulting in a higher probability of slab_O~sol_H formation and an easier formation of slab_H~sol_O.

The slab_O~sol_H hydrogen bond had a longer lifetime than the other three

hydrogen bonds, indicating that this bond was more stable. Compared to the Q3 model, the HBL of slab_O~sol_H and slab_H~sol_O bonds in the Q2 model was shorter, while the HBL of slab_O~sol_H and slab_H~sol_O bonds was longer. It was worth noting that there was no relationship between the HBP and HBL. For instance, the probability of slab_H~sol_O in the Q3 model was the smallest among the four hydrogen bonds, at only 0.2%, but its lifetime was the longest (1.9 ps).

To summarize, the primary hydrogen bonds in the salt-free silica sol were slab_O~sol_H, slab_O~sol_H, and slab_H~sol_O. The most easily formed and longest-lasting hydrogen bond is slab_O~sol_H. The main difference between the Q2 and Q3 models was that the electric double layer in the Q3 model had weaker repulsion to Si(OH)₄ and weaker attraction to Si(OH)₃O⁻, making it easier for Si(OH)₄ to adsorb to the surface. As a result, the probability of slab_O~sol_H bond formation in the Q3 system increased significantly compared to the Q2 system. The surface hydrogen of the Q3 model was more likely to be exposed to the solution, making it easier to form slab_H~sol_O hydrogen bonds.

3. Distribution and hydrogen bond formation of each component of the Q3 system with different concentrations of cationic salts

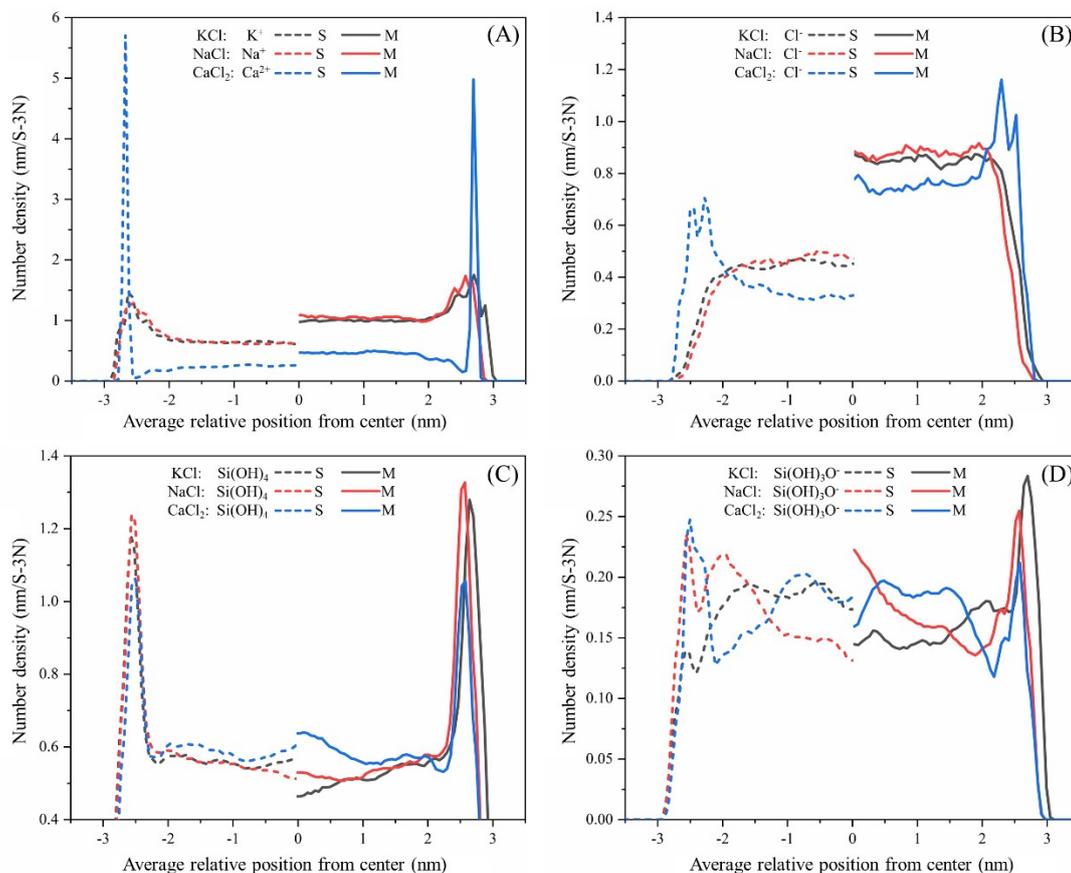


Fig. S3. The concentration distribution of each species in the z-direction of the Q3 system added with different cationic salts: (A) K⁺, Na⁺, Ca²⁺; (B) Cl⁻; (C) Si(OH)₄; (D) Si(OH)₃O⁻ (The dotted line and the solid line represent the concentration distribution of the components when the addition amount is small (S) and medium (M) respectively.)

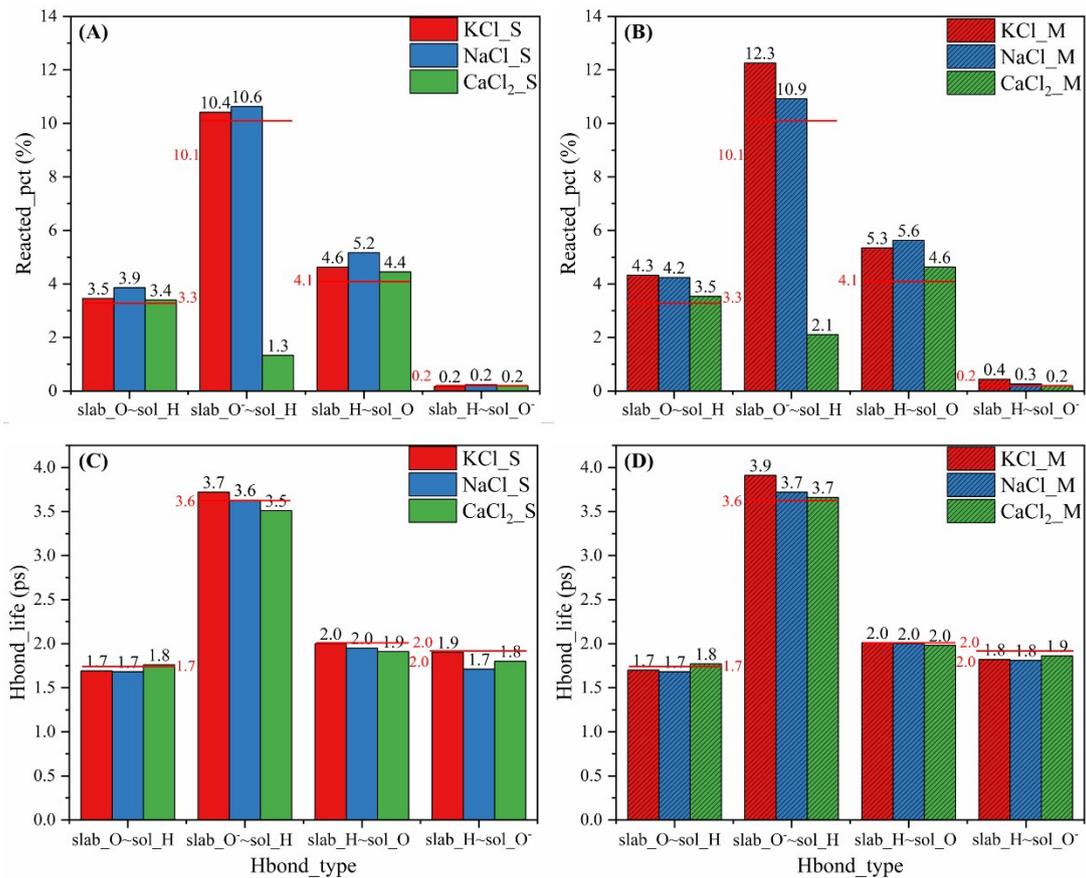


Fig. S4. The HBP (A and B) and the HBL (C and D) in the Q3 system with small (S) and medium (M) amounts of KCl, NaCl, and CaCl₂ added (The red horizontal solid line is the HBP or HBL of the no-added anion system.)

4. Distribution and hydrogen bond formation of each component of Q3 system with different concentrations of anionic salts

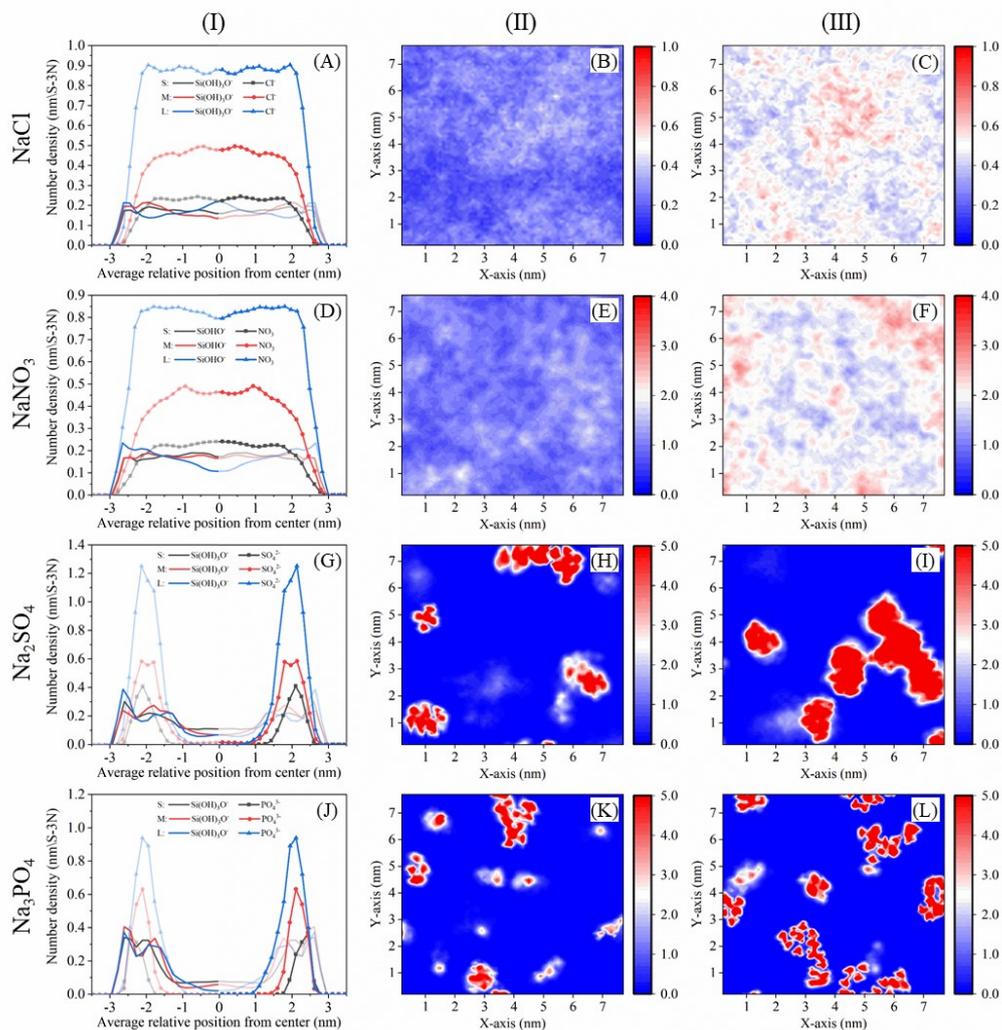


Fig. S5. In the Q3 system with different concentrations of anions added, the concentration distribution of $\text{Si}(\text{OH})_3\text{O}^-$ and anions in the z -direction (I) and the density distribution of anions in the XY plane (II: addition amount is medium (M); III: addition amount is large (L).)

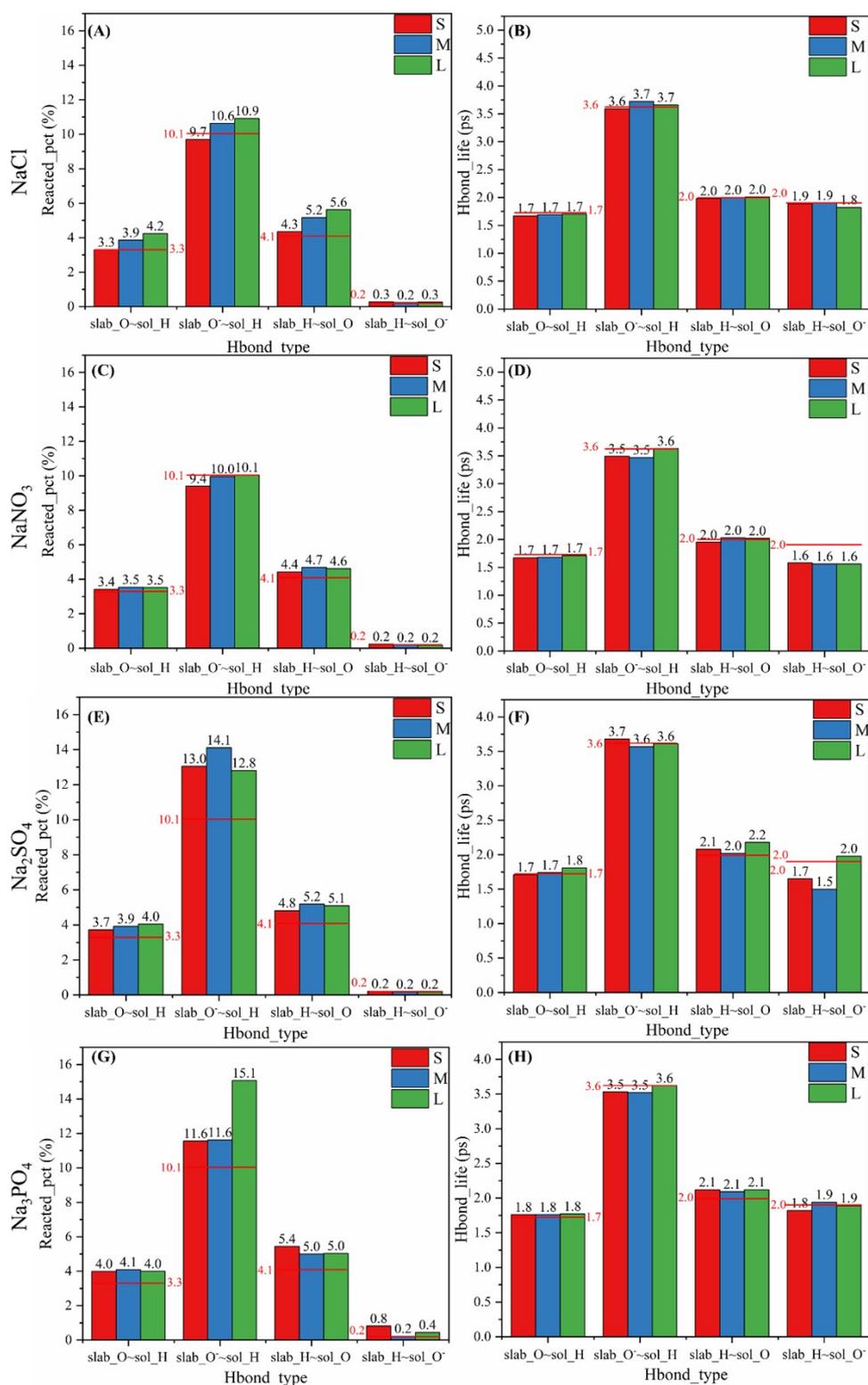


Fig. S6. HBP (A, C, E, G) and HBL (B, D, F, H) in the Q3 system with different concentrations of anions (The red horizontal solid line is the HBP or HBL of the no-added anion system, S/M/L stands for small/medium/large amounts of salt added.)