Water Molecule Transfer Equilibrium between Hydrated Li^+ and Mg^{2+} to Reveal the Lithium Separation Mechanism

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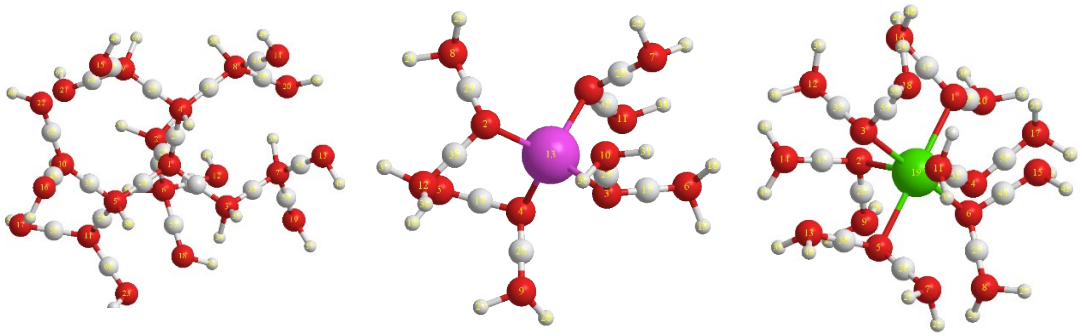
1. Estimation of the water/Mg^{2+} ratio in high magnesium bittern

In high - magnesium systems, the concentration of magnesium chloride often reaches 4 - 5 $mol \cdot L^{-1}$. For instance, in the bittern from solar saltworks, a typical concentration of magnesium chloride is 4.60 $mol \cdot L^{-1}$. Without considering the hydration of lithium and other existing particles, the water/ion ratio of magnesium can be calculated as 10.57. The following is the detailed calculation process: The density of the solution was determined by the gravimetric method to be 1.314 $g \cdot mL^{-1}$. The molar masses of $MgCl_2$ and water are 95.39 $g \cdot mol^{-1}$ and 18.00 $g \cdot mol^{-1}$, respectively. Assuming a volume of 1 L for the high - magnesium bittern, its mass is 1314 g. The mass of $MgCl_2$ is calculated as 4.60 mol × 95.39 $g \cdot mol^{-1}$ = 438.79 g, and the mass of water is 1314 g - 438.79 g = 875.21 g. Consequently, the water - to - magnesium ratio is calculated as (875.21 g ÷ 18.00 $g \cdot mol^{-1}$) ÷ (438.79 g ÷ 95.39 $g \cdot mol^{-1}$) = 10.57.

Moreover, in a typical study, the second hydration sphere of the magnesium ion needs to be considered. A maximum hydration number of 18 for magnesium is taken into account. When considering the second hydration spheres of lithium and water, a maximum hydration number of 12 for lithium and 22 for water are incorporated into this study.

2. Initial guess and optimized structures

The typical initial guessed structures are illustrated in Figure_S1, while the optimized structures are presented separately in Figure_S2. The numbers assigned to the oxygen atoms correspond to the sequential addition of water molecules. The optimized structures reveal that as the number of hydration water molecules increases, water - ring trimers and tetramers become increasingly prevalent in the hydration shells of lithium and magnesium ions. Additionally, pentamer and hexamer rings are observed within larger water clusters. Overall, these structures are reasonable and consistent with the principles reported in the literature.



$(H_2O)_n$ $Li(H_2O)^+_n$ $Mg(H_2O)^{2+}_n$

Figure S1. Initial guess of $(H_2O)_n$ $Li(H_2O)^+_n$ and $Mg(H_2O)^{2+}_n$

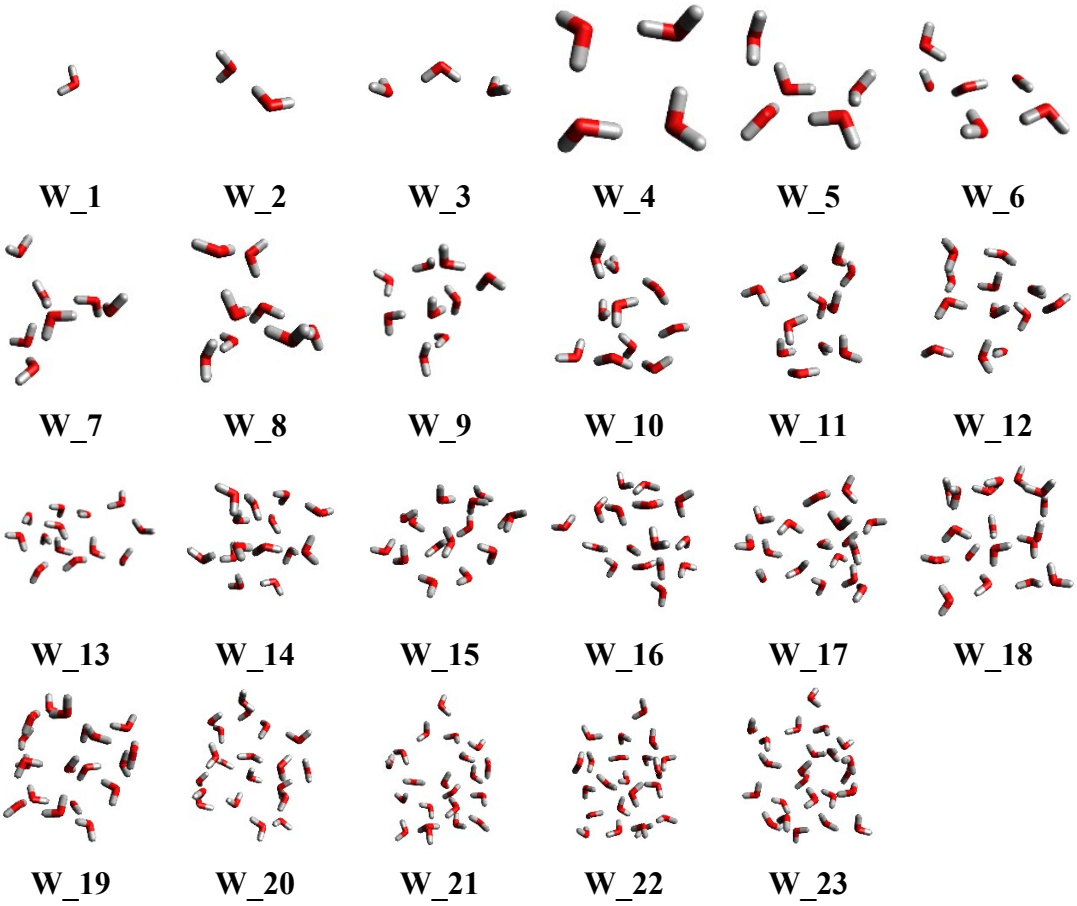


Figure S2. Optimized structures of $(H_2O)_n$

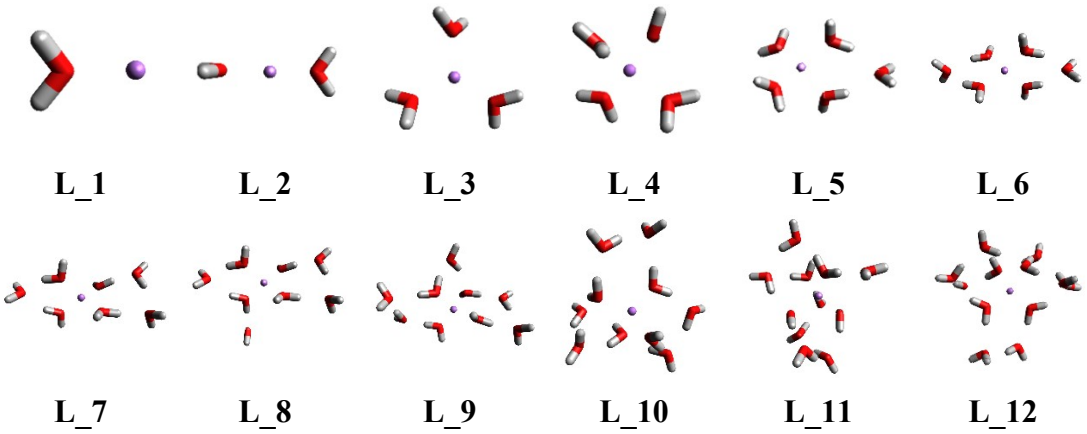


Figure S3. Optimized structures of $Li(H_2O)_n^+$ clusters

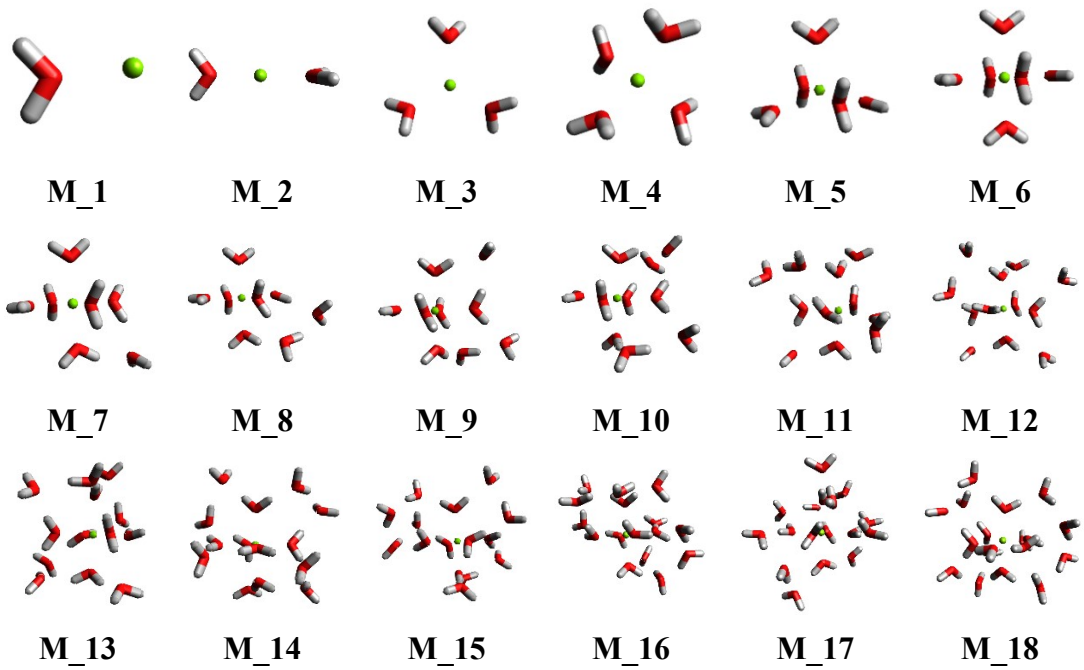


Figure S4. Optimized structures of $Mg(H_2O)^{2+}_n$ clusters