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Anomalous phase transition behavior of dilute electrolyte solutions in nanoconfinement under cryogenic environment

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The impact of confined spaces on the phase transition of water or electrolyte solutions has garnered considerable interest due to their widespread occurrence in natural processes and technological applications. [1-3] Specifically, phenomena such as freezing, melting, and vapor condensation have been extensively studied. Recently, there has been growing attention towards the phase transition of aqueous solutions, as they represent situations closer to natural and realistic scenarios than pure water.[4-5]

Notably, electrolyte solutions exhibit a slight variation from pure water, wherein an ice-salt phase separation occurs at low temperatures. The phase transition starts when ice or salt precipitates and continues until the eutectic point is reached. The eutectic point, being the lowest temperature at which a liquid solution can exist, remains constant regardless of the initial molality, and decreases with decreasing pore radius.[4] Anomalous behavior in confinement arises when the initial concentration is significantly diluted. In all studies involving a dilute solution in confinement, the thermal signal of ice and salt crystallization at the eutectic point was not observed, neither in bulk nor in the pore.[3,5]

In this work, we conducted a systematic calorimeter measurement to analyze the influence of salt molality, pore filling extent, and pore size on the transition routine of CaCl_2 and NaCl solution. The results indicate that in situations with fewer salts, such as smaller pores, dilute solutions, or lower filling degrees, only water freezing at the beginning is detected, and the eutectic transition is absent due to the lack of available free ions for crystallization in the pore center. Conversely, the eutectic transition could be well detected in the solution with a larger amount of salts. This may be attributed to the uneven distribution of cations and anions in pores[6]

Reference

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