The Observation of Molecular Symmetry Evolutions in Extremely Supersaturated Aqueous Solution

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In the present study, we report the measurement of the solution structures of KH_2PO_4 (KDP) and $NH_4H_2PO_4$ (ADP) in extremely high supersaturation by using the-state-of-the-art, a combination of electrostatic levitation (ESL) and synchrotron X-ray scattering, which gives almost ***one*** or ***two water molecules per ion*** at maximum supersaturation. The structural evolution of both KDP and ADP aqueous solutions could be successfully obtained as a function of supersaturation using in-situ synchrotron x-ray scattering. Our results reveal that both solutions have $(H_2PO_4^-)_2$ dimer unit block as the solute structure, even at low concentrations, which has been indirectly predicted in the gas phase by calculation, but differs from general expectations in solution studies. Interestingly, we find that the solute structure abruptly changes at high supersaturation in KDP solution, which is accompanied by molecular symmetry breaking in H_2PO_4 ions from C_{2v} to C_1 as supersaturation increases. Such solution-solution transition has not been observed in ADP solution. Moreover, the structural evolution of the solutes in KDP solution shows different H_2PO_4 liking process from that in ADP solution, although they have the same crystal structure at room temperature. This manifests the existence of two different solute structures, depending on the degree of supersaturation in the KDP solution. We also find that molecular symmetry and its structural evolution of the solute can affect the pathways of the early-stage nucleation, which explains the different pathways of KDP crystal formation. The present work paves a new way of studying the solute structure and its evolution in highly supersaturated solutions, and sheds light on the microscopic origin of Ostwald's step rule.