

Interfacial Free Energy Study of KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ Aqueous Solutions at Deeply Supersaturated States

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The measurement of the interfacial free energy for aqueous solutions is one of the most important and challenging experimental works in better understanding crystallization and its theoretical model developments. Here, we report the crystal-liquid interfacial free energy of extremely highly supersaturated aqueous KH_2PO_4 (KDP) and $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP) solutions using combining the electrostatic levitation (ESL) technique with real-time Raman spectroscopy measurement. On a levitated droplet without any mechanical contact, the natural evaporation of water molecules results in the high increase of supersaturation level (S). In this report, the supersaturation values of KH_2PO_4 (KDP) and $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP) solutions increase up to ~ 4 times higher than their well-known characteristic solubility limit level ($S=1$). Such high supersaturation indicates that maximally supersaturated solutions should exhibit only one or two water molecules per ion. In-situ measurement of solution droplets could reveal the unprecedentedly high interfacial free energy values based on classical nucleation theory, which explains the stability of a nucleus by a competition between chemical potential energy ($\Delta\mu$) and an interfacial free energy. Both solutions reveal unprecedented interfacial free energy values (e.g., ~ 37 mJ/m² for ADP ($S=3.9$)). These interfacial free energy values are much higher than the previously reported data and indicate an extremely high nucleation barrier in extremely supersaturated KDP and ADP solutions. This present work paves a new way of experimental measurement the solid-liquid interfacial free energy and provide valuable clues in theoretical calculation and modeling of crystallization in aqueous solution.