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Motivation:

- OZPN and OZPN hydrates exhibit low aqueous solubility and there is interest in studying the mechanism of anhydrate to hydrate formation given the potential impact on performance and stability of OZPN.
- The structural similarities between the OZPN forms (I and II) and corresponding dihydrates (DD and DB) direct the different hydration outcomes under 93% RH after 180 days [1].
- We studied the transformation of OZPN I to OZPN DD in stirred and non-stirred aqueous conditions (Fig. 1). The templating effect is lost in stirred conditions and kinetic polymorphs (OZPN DB) is formed.
- Direct observation of OZPN DD nucleation on the surface of OZPN I suggests non-classical nucleation mechanism inluding formation of dense clusters (Fig. 2) [2].

Research question:

What is the mechanism of clusters formation?

Method and Results

Brownian Microscopy:

- A laser illuminates a 500 μm solution layer at an oblique angle such that the incident beam avoids the lens of a microscope positioned above the sample, Fig. 4a.
- The Brownian trajectories (Fig 4d) of the clusters are tracked by comparing the locations of the individual clusters in a sequence of images collected at a rate 30 s⁻¹ (Fig 4 b, c).
- The diffusion coefficients $D$ (Fig. 4e) of the individual clusters are computed from the trajectories of the Brownian motion of the imaged cluster.
- The clusters sizes are determined using the Einstein–Stokes relation $R = kT/6πηD$.
- The resulting size distribution, shown in Fig. 4f, is relatively symmetric and narrow: the cluster radii vary from 30 to 90 nm, with a mean at about 35 nm.

Identification of clusters and the response to varying EtOH concentration

- The cluster radius is independent of the solution concentration and steady in time for up to three hours, Fig. 5a.
- The fraction of the solution volume occupied by the cluster population $\phi$ increases with $C_{\text{EtOH}}$ and solution age, Fig. 5b. The growth of $\phi$ is consistent with slow maturation of the cluster phase.
- The cluster radius $R$ is independent of the EtOH concentration in the range 20 – 90 %, Fig. 6a.
- Dependence of $\phi$ on $C_{\text{EtOH}}$ in a complicated non-monotonic fashion, Fig. 6b.

The thermodynamics parameters of OZPN crystallization from EtOH/H₂O mixtures

- Solubility dependence on temperature plotted in van't Hoff coordinates provide information about solution thermodynamics:
  
  \[ \Delta H_{\text{vap}} = -RT \ln K = RT \ln C_s \]

  \[ \Delta S_{\text{vap}} = \left( \Delta H_{\text{vap}} - \Delta H_{\text{sub}} \right)/T \]

- At 20% EtOH three water molecules that are associated with OZPN set free upon incorporation of OZPN and two other water molecules incorporate into the crystal
- The low magnitude of $\Delta H$ at 20% EtOH, Fig. 8b, corresponds to mild repulsion between the OZPN molecules in the solution.
- At $C_{\text{EtOH}}$ 30% and above stronger intermolecular repulsion occurs due to the hydration shells of the polar nitrogen groups of OZPN.

Conclusions:

- The variations of $H^0$ solution is parallel to those of $\phi$.
- This synchronized behavior suggests that stronger repulsion between the solute OZPN molecules, indicated by higher $H^0$, drives the volume $\phi$.
- In agreement with the transient dimer [4,5] model of cluster formation, the cluster population volume and the fraction of solute captures in the clusters are determined by the solution thermodynamics.
- We propose that a transient dimer, which may be akin to the centrosymmetric dimer SC0 present in most of the 60 known OZPN crystal structures, may underlie cluster formation.

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