Visualization of Freezing Process *in situ* upon Cooling and Warming of Aqueous Solutions

Anatoli Bogdan[1,2,3*], Mario J. Molina[4], Heikki Tenhu[2], Erminald Bertel[1], Natalia Bogdan[5] & Thomas Loerting[1]

[1]Institute of Physical Chemistry, University of Innsbruck, Innrain 52a, A-6020, Innsbruck, Austria.

[2]Laboratory of Polymer Chemistry, Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014, Helsinki, Finland.

[3]Department of Physical Sciences, University of Helsinki, P.O. Box 64, FI-00014, Helsinki, Finland.

[4]Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093-0356, USA.

[5]Faculty of Medicine, University of Helsinki, P.O. Box 63, FIN-00014, Helsinki, Finland.

Legends for videos in SI

1. Video 1: The fast and slow freezing and subsequent melting of 20wt% CA (citric acid).

   Video 1: Video 1 (10.8 MB) demonstrates the fast and slow freezing of 20wt% CA upon cooling. The slow freezing occurs in FCS_2 and is terminated by the onset of the liquid-FCS_2-glass transition at ~208K. Upon warming, the slow freezing recommences above the reverse glass-liquid-FCS_2 transition at ~208K and proceeds to ~230K. Above ~230K ice only melts. Temperature change is seen in the left bottom corner.

2. Video 2: The formation of FCS_2 in front of the advancing IF/FCS_1 front in freezing 40wt% CA.

   Video 2: Video 2 (4.22 MB) demonstrates the formation of FCS_2 in front of the advancing IF/FCS_1 front during the freezing of 40wt% CA. In the left upper corner, the FCS_2/air borderline moves when the IF/FCS_1 front propagates.

3. Video 3: The freezing of 58wt% CA from multiple ice nucleating events.

   Video 3: Video 3 (3.99 MB) demonstrates that 55wt% CA freezes from multiple ice nucleating events. Dark dots are ice crystals formed by vapour deposition on the outer side of a cover glass.

4. Video 4: The fast and slow freezing and subsequent melting of 40wt% sucrose.

   Video 4: Video 4 (15.8 MB) demonstrates the fast ta slow freezing of 40wt% sucrose upon cooling. The slow freezing occurs in FCS_2 and is terminated by the onset of the liquid-FCS_2-glass transition at ~230K. Upon warming, the slow freezing recommences above the reverse glass-liquid-FCS_2 transition at ~230K and proceeds to ~245K. Above ~245K ice only melts.

5. Video 5: Simultaneous freezing and ice melting upon warming of 62wt% CA.

   Video 5: Video 5 (6.95 MB) demonstrates simultaneous slow freezing in FCS_2 and ice melting in FCS_1 upon warming of 62wt% CA previously cooled to 173K. The freezing starts at ~220K and proceeds to ~240K. Ice melting in FCS_1 starts at ~233K and is seen as the increasing brightness of IF/FCS_1. Between ~233K and ~240K the freezing in FCS_2 and melting in FCS_1 proceed simultaneously.