Thermodynamic Studies of Secondary Nucleation in Microgravity

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Secondary Nucleation (SN) is a nucleation phenomenon which takes place at the surface of the nuclei formed by primary nucleation. Therefore, the rate of SN is a direct function of the population and size distribution of these nuclei. Since primary nucleation always precedes SN an understanding of primary nucleation is crucial in understanding of SN. The most common type of primary nucleation occurring in practical applications is Heterogeneous Primary Nucleation (HPN). HPN happens due to the presence of dissolved impurities or solid surfaces (such as dust, dirt, container walls, solid templates). Therefore, the study of HPN can be considered the first step in the study of SN and will be addressed in this report.

A unique replication of the microgravity environment can be achieved in ground-based research by employing the Electrodynamic Levitator Trap (ELT) technique. The study of the dependence of HPN phenomenon on factors such as supersaturation, presence of convective flows implies, first of all, investigation of the relative importance and role of these factors on the HPN. This can be achieved only by virtue of experiments allowing separation of one dependence from another. The only experimental technique capable of accomplishing this goal is the ELT technique. This technique allows containerless confinement of microdroplets of supersaturated solutions. T he three major advantages which make the ELT technique so attractive for the study of metastable state and nucleation, including the HPN, are:

A. the absence of container walls which usually serve as a major source of heterogeneities triggering uncontrollable SN;
B. the levitation of small volumes of the initially purified solutions; and,
C. the suppression of convective flows.

The first advantage is self-explanatory. The second advantage can be understood if one specifies the probability $P(x=K)$ to have exactly K impurities in volume V_0 (V_0 is the microdroplet volume), where x is the corresponding random variable. Assuming that the random variable x has the Poisson distribution, the probability $P(x = K) = \lambda^K e^{-\lambda} /K!$, $\lambda = N_{tot} V_0 /V$, where N_{tot} is the total number of impurities in the initial solution volume V. Therefore, the probability to have K impurities inside of the microdroplet is the sharply decreasing function of the microdroplet volume V_0. The third advantage is again due to small solution volumes levitated. There is simply not enough room for the convective flows to develop since convection flows are proportional to the microdroplet radius R as $R^{3/2}$ or R^3. Therefore, even comparing with regular μl-size solution drops, the approximately 10^3 or 10^6 factor difference in sizes between the μl-size drops and pl-size levitated microdroplets would essentially reduce the convection effects in the levitated microdroplets.

Based on the foregoing, employment of the ELT technique allows a unique opportunity in the study of HPN phenomenon under microgravity conditions. For the first time it is possible to completely separate major factors, effecting the HPN phenomenon, such as the solution supersaturation and the presence of impurities in the convection-free environment. In addition to that the ELT technique allows us to investigate the relative importance of these factors in the HPN phenomenon by controlling number of impurities in the microdroplet levitated. This study has

been conducting in a wide range of solution supersaturations with upper limit approaching the supersaturation of liable region at the given temperature and pressure.

In recent experiments we have studied the aqueous solution of electrolyte solute $(NH_4)_2SO_4$ without and with electrolyte Cr_2SO_4 impurity at different Cr_2SO_4 concentrations: *0.01 ppm, 0.05 ppm, 0.1 ppm, 0.5 ppm* and *1 ppm*. In this study the microdroplets of aqueous solutions containing electrolyte solute $(NH_4)_2SO_4$ and impurity Cr_2SO_4 of known initial concentrations were levitated in the water vapor atmosphere by means of the ELT technique. The following evacuation of water vapor from the levitation chamber was performed in order to measure vapor (solvent) activity versus $(NH_4)_2SO_4$ (solute) concentration. These measurements were carried out until the moment of nucleation onset. Each set of experiments corresponding to the same initial concentrations of $(NH_4)_2SO_4$ and Cr_2SO_4 consisted of at least seven experimental trials executed under the same evacuation rate of water vapor. Results of our study demonstrates that under the following conditions:

1) absolute Cr^{3+} concentration increases;
2) the ratio of $(NH_4)_2SO_4$ and Cr_2SO_4 concentrations remains unchanged;

activity (i.e., the effective supersaturation of $(NH_4)_2SO_4$) goes sharply down, meaning that Cr^{3+} ions can be considered as the nucleation inhibitors since lower supersaturations usually mean longer induction times. Therefore, in this specific case the impact of Cr^{3+} ions on the HPN phenomenon is in its slowing down. Thermodynamically this means that the presence of Cr^{3+} ions in the solution increases the formation energy of solute nuclei. The further study is required to understand the micro-physical nature of nucleation inhibition.

The systematic knowledge gained in this project will be directed to elaborate the ways allowing to control the HPN and by virtue of this the following SN. This includes understanding of regimes where the HPN occurs at a minimum possible rate under given conditions, such as temperature, pressure and gravity. We, thus, come to the conclusion that the ELT technique supported by the additional effective research technique such as Raman Light Scattering opens a way to identify the factors influencing the HPN phenomenon. The following comparison with the HPN observed in bulk experiments will allow elaboration of the regimes of maximum suppression of HPN and by virtue of this of maximum suppression of SN as well. Achievement of this goal will provide the control of SN what will result in a significant increase in the fraction of successful crystallization experiments and, thus, in the efficiency of flight and ground-based experiments.