FINAL REPORT

NASA Research Grant NAG8-960

for research study entitled

"DIFFUSION, VISCOSITY AND CRYSTAL GROWTH IN MICROGRAVITY"

Principle Investigator: *Dr. Allan S. Myerson*

The period covered by the report: *June 01, 1993 - May 31, 1996*

The name and address of the Grantee's institution: *Department of Chemical Engineering*
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The following objectives of the proposed research have been achieved.

1. **Experimental study of the diffusivity and viscosity of triglycine sulfate (TGS), KDP, ADP and other compounds of interest to microgravity crystal growth, in supersaturated solutions as a function of solution concentration, "age" and "history".**

Results of this study have been published in the following journals and conference proceedings:

1.A. *Ph.D.(Chemical Engineering) Dissertation at the Polytechnic University, 1996*

"DIFFUSION, VISCOSITY AND ACTIVITY OF SUPERSATURATED SOLUTIONS OF POTASSIUM DIHYDROGEN PHOSPHATE, AMMONIUM DIHYDROGEN PHOSPHATE AND TRIGLYCINE SULFATE AND THE GROWTH OF CRYSTALS IN MICROGRAVITY"

by M. Bohenek

The factors that affect the growth of crystals from water solutions in microgravity have been examined. Three non-linear optical materials have been studied, potassium dihydrogen phosphate (KDP), ammonium dihydrogen phosphate (ADP) and triglycine sulfate (TGC). The diffusion coefficient of the solutions in the supersaturated region was measured using Gouy interferometry. The viscosity of the solutions in the supersaturated region was measured using a capillary viscometer. At low supersaturations the diffusion coefficient is changing rather slowly, while the viscosity is rising more rapidly. The activity of the solution was measured in a levitated microdroplet experiment. The width of the metastable region has to be much wider than originally obtained in bulk solutions. Theories of cluster formation have been used to estimate values for the extent of solute clustering and the critical cluster size using these data. Column gradient experiments showed no sign of clustering at low supersaturations and there was no measurable time change of the viscosity. The crystal growth rate is strongly affected by the change of the diffusion coefficient with concentration.

1.B. *CRYSTAL GROWTH OF ORGANIC MATERIALS, edited by A.S. MYERSON, D. GREEN and P. MEENAN (ACS, WASHINGTON D.C., 1996)*

"DIFFUSION, VISCOSITY AND CRYSTAL GROWTH IN MICROGRAVITY"

by M. Bohenek and A.S. Myerson

The diffusion coefficient and viscosity of supersaturated water solutions of three crystalline substances were measured. The diffusion coefficient data were used to model the concentration gradients near the crystal of one of the substances.

1.C. *IND.ENG.CHEM.RES., 35, pp. 1078-1084, 1996*

"METASTABLE SOLUTION THERMODYNAMIC PROPERTIES AND CRYSTAL GROWTH KINETICS"

by S. Kim and A.S. Myerson

The crystal growth rates of $NH_4H_2PO_4$, KH_2PO_4 , $(NH_4)_2SO_4$, $KAl(SO_4)_2 \cdot 12H_2O$, NaCl, and glycine and the nucleation rates of KBr, KCl, $NaBr \cdot 2H_2O$, and $(NH_4)_2SO_4$ were expressed in terms of the fundamental driving force of crystallization calculated from the activity of supersaturated solutions. The kinetic parameters were compared with those from the commonly used kinetic expressions based on the concentration difference. From the viewpoint of thermodynamics, rate expressions based on the chemical potential difference provide accurate kinetic representation over a broad range of supersaturation. The rates estimated using the expression based on the concentration difference coincide with the true rates of crystallization only in the concentration range of low supersaturation and deviate from the true kinetics as the supersaturation increases.

1.D. *J.PHYS.D: APPL.PHYS., 26, pp.B123-B127, 1993*

"STATISTICS OF EXPERIMENTS ON CLUSTER FORMATION AND TRANSPORT IN A GRAVITATIONAL FIELD"

by A.S. Myerson and A.F. Izmailov

Metastable state relaxation in a gravitational field is investigated in the case of non-critical binary solutions. A relaxation description is presented in terms of the time-dependent Ginzburg-Landau formalism for a non-conserved order parameter. A new Ansatz for solution of the corresponding partial non-linear stochastic differential equation is discussed. It is proved that , for the supersaturated solution under consideration, the metastable state relaxation in a gravitational field leads to formation of the solute concentration gradients due to the sedimentation of subcritical solute clusters. The pure discussion of the possible methods to compare theoretical results and experimental data related to the solute sedimentation in a gravitational field is presented. It is shown that in order to describe these experiments it is necessary to deal both with the value of the solute concentration gradient and with its formation rate. The stochastic nature of the sedimentation process is shown.

2. Development of a theoretical model of diffusivity and viscosity in a metastable state.

Results of this study have been published in the following journals and conference proceedings:

2.A. *PHYSICA, A224, pp.503-532, 1996*

"GRAVITY INDUCED FORMATION OF CONCENTRATION GRADIENT OF SUBCRITICAL SOLUTE CLUSTERS IN SUPERSATURATED BINARY SOLUTIONS"
by A.F. Izmailov and A.S. Myerson

Experimental and theoretical studies of the anomalously rapid formation of the Concentration Gradient of Subcritical Solute Clusters (CGSSC) in supersaturated binary solutions in a gravitational field were carried out. The CGSSC formation was associated with heterogeneous birth process of the subcritical solute clusters in a gravitational field. It was suggested to describe the birth-death process of the new solute-rich phase domains (subcritical solute clusters) in terms of the time-dependent Ginzburg-Landau formalism developed for the metastable state relaxation in binary (solute+solvent) non-critical solutions in presence of a gravitational field. A new mathematical Ansatz was developed for solution of such kind of the time-dependent Ginzburg-Landau equations. It has been demonstrated analytically that solute distribution inside of the subcritical solute clusters is heterogeneous: it has spatially periodic structure. The critical radius of solute clusters (radius of nucleation) and induction time in these systems are found to be gravity-dependent. It is concluded that the subcritical solute clusters are themselves distributed heterogeneously in a gravitational field. This kind of heterogeneity, which appears due to the heterogeneous birth-death process of the subcritical solute clusters in a gravitational field, initiates the noticeable CGSSC along vertical columns of supersaturated binary solutions. An analysis and comparison of theoretical results and experimental data related to the CGSSC formation in a gravitational field are presented.

2.B. *J.CRYSTAL GROWTH, 166, pp.981-988, 1996*

"THERMODYNAMIC STUDIES OF LEVITATED MICRODROPLETS OF HIGHLY SUPERSATURATED ELECTROLYTE SOLUTIONS"

by A.S. Myerson, A.F. Izmailov and H.S. Na

Highly supersaturated electrolyte solutions are studied by employing an Electrodynamic Levitator Trap (ELT) technique. The ELT technique involves containerless suspension of a microdroplet thus eliminating dust, dirt, and container walls which normally cause heterogeneous nucleation. This allows very high supersaturations to be achieved. A theoretical study of the experimental results obtained for the water activity in microdroplets of various electrolyte solutions is based on the development of the Cahn-Hilliard formalism for electrolyte solutions. A correspondence of *96%-99%* between the theory and experiment for the all solutions studied was achieved and allowed the determination of an analytical expression for the spinodal concentration n_{spin} and its calculation for various electrolyte solutions at *298 K*.

2.C. *CRYSTAL GROWTH OF ORGANIC MATERIALS, edited by A.S. MYERSON, D. GREEN and P. MEENAN (ACS, WASHINGTON D.C., 1996)*

"STUDY OF ORGANIC SUPERSATURATED SOLUTIONS. THEORY AND EXPERIMENT"

by A.S. Myerson and A.F. Izmailov

Hydrodynamic equations describing crystal growth from solutions are supplemented by the thermodynamics of metastability. The main reason for accounting of thermodynamics of metastability is due to the non-trivial dependences of solution density, shear viscosity and solute mass diffusivity on solute concentration in supersaturated solutions. Combination of hydrodynamic and thermodynamic equations allows understanding of conditions which determine effectiveness of crystal growth. The containerless electrodynamic levitation of supersaturated solution microdroplets is suggested and discussed as the main experiment for the study of thermodynamics of metastability.

2.D. *PHYS.REV., E52, pp.3923-3935, 1995*

"SUPERSATURATED ELECTROLYTE SOLUTIONS: THEORY AND EXPERIMENT"

by A.F. Izmailov, A.S. Myerson and H.S. Na

Highly supersaturated electrolyte solutions can be prepared and studied employing an Electrodynamic Levitator Trap (ELT) technique. The ELT technique involves containerless suspension of a microdroplet thus eliminating dust, dirt and container walls which normally cause heterogeneous nucleation. This allows very high supersaturations to be achieved. Theoretical study of the experimental results obtained for the water activity in microdroplets of various electrolyte solutions is based on the development of the Cahn-Hilliard formalism for electrolyte solutions. In the approach suggested the metastable state for electrolyte solutions is described in terms of the conserved order parameter $\omega(\mathbf{r},t)$ associated with fluctuations of the mean solute concentration n_0. Parameters of the corresponding Ginzburg-Landau free energy functional which defines the dynamics of metastable state relaxation are determined and expressed through the experimentally measured quantities. A correspondence of *96%-99%* between theory and experiment for the all solutions studied was achieved and allowed the determination of an analytical expression for the spinodal concentration n_{spin} and its calculation for various electrolyte solutions at *298K*. The assumption that subcritical solute clusters consist of the electrically neutral Bjerrum pairs has allowed both analytical and numerical investigation of the number-size N_c of nucleation monomers (aggregates of the Bjerrum pairs) which are elementary units of the solute critical clusters. This has also allowed estimations for the surface tension α, and equilibrium bulk energy β per solute molecule in the nucleation monomers. The dependence of these properties on the temperature T and on the solute concentration n_0 through the entire metastable zone (from saturation concentration n_{sat} to spinodal n_{spin}) is examined. It has been demonstrated that there are the following asymptotics: $N_c = 1$ at spinodal concentration and $N_c = \infty$ at saturation.

2.E. *J.PHYS.A: MATH.GEN., 26, pp.2709-2725, 1993*

"THEORY OF METASTABLE STATE RELAXATION IN A GRAVITATIONAL FIELD FOR NON-CRITICAL BINARY SYSTEMS WITH NON-CONSERVED ORDER PARAMETER"

by A.F. Izmailov and A.S. Myerson

A new mathematical Ansatz is developed for solution of the time-dependent Ginzburg-Landau non-linear partial differential equation describing metastable state relaxation in binary (solute+solvent) non-critical solutions with non-conserved scalar order parameter in the presence of a gravitational field. It has been demonstrated analytically that in such systems metastability initiates heterogeneous solute redistribution which results in the formation of a non-equilibrium singly-periodic spatial solute structure in the new solute-rich phase. The critical radius of nucleation and the induction time in these systems are gravity dependent. It has also been proved that metastable state relaxation in vertical columns of supersaturated non-critical binary solutions leads to the formation of solute concentration gradient. Analytical expression for this gradient is found and analyzed. It is concluded that gravity can initiate phase separation (nucleation or spinodal decomposition).

2.F. *PHYSICA, A192, pp.85-106, 1993*

"THEORY OF METASTABLE STATE RELAXATION FOR NON-CRITICAL BINARY SYSTEMS WITH NON-CONSERVED ORDER PARAMETER"

by A.F. Izmailov'and A.S. Myerson

A new mathematical Ansatz for A solution of the time-dependent Ginzburg-Landau non-linear partial differential equation is developed for non-critical systems such as non-critical binary solutions (solute+solvent) described by the non-conserved scalar order parameter. It is demonstrated that in such systems metastability initiates heterogeneous solute redistribution which results in the formation of a non-equilibrium singly-periodic spatial solute structure. It is found how the time-dependent period of this structure evolves in time. In addition, the critical radius r_c for solute embryo of the new solute rich phase together with the metastable state lifetime t_c are determined analytically and analyzed.

3. Development of a model of crystal growth from solution including non-linear time dependent diffusivity and viscosity effects.

Results of this study have been published in the following journals and conference proceedings:

3.A. *PHYS.REV., E52, pp.805-812, 1995*

"CONCENTRATION DEPENDENCE OF SOLUTION SHEAR VISCOSITY AND SOLUTE MASS DIFFUSIVITY IN CRYSTAL GROWTH FROM SOLUTIONS" by A.F. Izmailov and A.S. Myerson

The physical properties of supersaturated binary solutions such as its density ρ, shear viscosity η and solute mass diffusivity D are dependent on the solute concentration c: $\rho = \rho(c)$, $\eta = \eta(c)$ and $D = D(c)$. The diffusion boundary layer equations related to crystal growth from solution are derived for the case of natural convection with solution density, shear viscosity and solute diffusivity dependent on solute concentration. Solution of these equations has demonstrated the following:

A) At the vicinity of the saturation concentration c_s the solution shear viscosity η depends on its density ρ as: $\eta_s = \eta(\rho_s) \propto \rho^{1/2}(c_s)$. This theoretically derived result has been verified in experiments with several aqueous solutions of inorganic and organic salts.

B) The maximum solute mass transfer towards the growing crystal surface can be achieved in regions of the solute concentration c where the ratio of $dln[D(c)/dc]$ to $dln[\eta(c)/dc]$ is a maximum.

4. Employment of the model with and without buoyancy driven convective flows to predict the results of earth and microgravity crystal growth and to compare these predictions with experimental results. Development of a computer simulation of the crystal growth process which allows simulation of the microgravity crystal growth including the effects mentioned in the previous achievements.

Results of this study have been published in the following journals and conference proceedings:

4.A. *J. CRYSTAL GROWTH, 166, pp.261-265, 1996*

"MOMENTUM AND MASS TRANSFER IN SUPERSATURATED SOLUTIONS AND CRYSTAL GROWTH FROM SOLUTION"

by A.F. Izmailov and A.S. Myerson

The physical properties of supersaturated solutions such as solution density ρ, shear viscosity η and solute diffusivity D are strongly dependent on solute concentration c_∞: $\rho = \rho(c_\infty)$, $\eta = \eta(c_\infty)$ and $D = D(c_\infty)$. The concentration dependence of the properties has been taken into account in the rederivation of the generalized momentum and mass transport equations governing crystal growth from solutions. The non-linear ordinary differential equations obtained for the steady regime of isothermal crystal growth were analyzed. The exact simultaneous solutions obtained for the rederived transport equations resulted in the following conclusions:

A) there exists a restriction imposed on the Schmidt number for supersaturated solutions: $Sc_\infty >> 4/9$. Only under this restriction the generalized momentum and mass transfer equations have simultaneous consistent solutions.

B) the solution-crystal interface profile "thickness" $\delta_{int}(x_l)$ is proportional to the Diffusion Boundary Layer (DBL) thickness: $\delta_{int}(x_l) \approx 0.24\delta_{diff}(x_l)$.

C) the ratio of solute flux along the solution-crystal interface to the flux along the DBL edge is the increasing function of and is dependent only on Sc_∞.

ES74/Roger L. Kroes
The NASA Technical Officer
George C Marshall Space Flight Center
Marshall Space Flight Center
AL, 35812

Dear Mr. Kroes:

Enclosed is the Final Report for the NASA Research Grant NAG8-960 for research study entitled

"DIFFUSION, VISCOSITY AND CRYSTAL GROWTH IN MICROGRAVITY"

carried out under the directorship of Principle Investigator Dr. Allan S. Myerson. The period covered by the report is June 01, 1993 - May 31, 1996.

Please find enclosed three copies of all manuscripts published and directly related to the research.

Sincerely

A.Myerson