1982

NASA/ASEE SUMMER FACULTY RESEARCH FELLOWSHIP PROGRAM

MARSHALL SPACE FLIGHT CENTER
THE UNIVERSITY OF ALABAMA

SOLIDIFICATION STUDIES
OF MONOTECTIC SYSTEMS

Prepared by: Kichoon Chang, Ph.D.

Academic Rank: Associate Professor

University and Department: Alabama A&M University
                                    Department of Chemistry

NASA/MSFC
    Laboratory: Space Science Laboratory
    Division: Space Processing
    Branch: Solid State

MSFC Counterpart: Donald O. Frazier, Ph.D.

Date: August 13, 1982

Contract No.:   NGT-01-002-099
                                    University of Alabama

SOLIDIFICATION STUDIES OF MONOTECTIC SYSTEMS

By

Kichoon Chang

Associate Professor of Chemistry
Alabama A&M University
Normal, Alabama   35762

ABSTRACT

It has been suggested that at low or zero gravity critical point wetting and thermal migration of second-phase droplets due to interfacial tension gradient play major roles in phase separation and solidification of a monotectic system.

Understanding of these roles requires estimation of interfacial tensions. However, solid-liquid interfacial tensions are very difficult to measure. Ellipsometric techniques are being investigated to measure liquid film thickness as a means of determining the solid-liquid interfacial tensions at var-temperatures and pressures.

INTRODUCTION

Investigation of monotectic and related systems has been of considerable interest in recent years. However, one of the first relatively detailed studies of a monotectic system[1], succinonitrile - water, was reported in 1897.

In the last decade metallic monotectic systems have been of renewed concern within NASA in view of recent space processing experiment.[2] Currently a number of immiscible organic binary mixtures are under investigation as models for metallic pseudo binary systems.

In a monotectic system two component liquids are miscible in any composition above an upper critical solution temperature. Below the critical temperature and between certain composition limits two immiscible liquid phases are produced, creating a miscibility gap. All such miscibility gaps are two-phase regions. The two liquid phases generally differ in density and separate by Stokes settling in a gravity field.

At the monotectic temperature one of the liquid phases decomposes into a solid phase and the other liquid phase. In all known monotectic phase diagrams the amount of the solid phase produced is always greater than that of the liquid phase produced.[3] This liquid phase solidifies at the lower eutectic temperature.

A number of theories have been developed for explaining the separation and solidification phenomena of binary systems.

The motion of bubbles in a temperature gradient in pure liquids and binary liquids and Marangoni convection have been studied by a number of workers. The velocity[4] of the bubble was related to both the thermal variation of the surface tension and the temperature gradient along which the bubbles moved.

It was shown[5] that near the critical point one of the critical phases completely wets the third phase and that at some temperature below this point perfect wetting terminates in a first-order transition of the surface.

If the third phase is a container wall which is wetted preferentially by the minority phase, the phase separation by the spreading minority phase, as the temperature is lowered, may be avoided if a crucible which is primarily wetted by the majority phase is chosen. On the other hand, if the majority phase begins to form solid at the monotectic temperature, it will be preferentially wetted by the liquid of the phase because of their closeness in composition.

Cahn[6] reports that perfect wetting of the monotectic solid by the monotectic liquid occurs whenever the monotectic temperature is close to the critical temperature.

In a study of monotectic systems including Al-In, Cu-Pb, Cd-Ga and succinonitrile-water, Grugel and Hellawell[7] showed that the solidification behavior of systems containing a

liquid miscibility gap appeared to be related to the height of the gap. They even modified the microstructure of the solids by changing the height of the miscibility gap.

In certain binary solutions the lower of the two liquid phases forms a layer which intrudes between the upper liquid phase and the vapor.[8] The thickness of the intruding wetting layer was ellipsometrically measured and reported.

Pohl and Goldburg[9] verified experimentally a predicted transition[5] from complete to partial wetting at a temperature away from the consolute temperature.

The Gibbs surface excess measurement for two miscibility gap systems, ethyl salicylate - diethylene glycol and hexane-aniline, was reported by NASA workers.[10] Their measurement of the surface excess by use of the Gibbs adsorption equation led to the conclusion that the surface excess increases as the binary solutions approach the conditions of the consolute point. They also observed that near the consolute temperature the surface-active components are switched if the two pure components have a small surface tension difference. The component switching will apparently affect the thickness of the intruding layer and the liquid film thickness on the container wall because of different molecular size and different vapor pressure.

RECENT WORK WITH MODEL MATERIALS

Succinonitrile is a plastic crystal with a small entropy of fusion and freezes like metals, crystallizing with its molecules in random orientations. The crystal grows dendritically into undercooled melt like metals which have small entropies of fusion.[11,12]

A monotectic system of succinonitrile and water mixture has a convenient temperature range to work with for its solution and solidification. Some of the properties including the phase diagram have been relatively well established.[1,11,13]

The density difference between the two phases in the miscibility gap is small and can be further minimized by adjusting the amount of H_2O and D_2O to reduce the gravity effect on the phase separation and solidification. Thus the system continues to draw interest within NASA as a model for pseudo metallic systems for investigating composite growth.

Diethylene glycol - ethyl salicylate system has also been studied for excess quantities measurement by NASA workers.[10] The same workers further investigated the miscibility gap system for particle growth and thermal migration by means of holographic techniques.[14]

A number of other systems with miscibility gap and metal-like transparent organic compounds have been studied.[2,7,12,14]

In solidification of monotectic systems in the absence of gravitation the critical-point wetting[5] and thermal migration of droplets[4] appear to play major roles.

Generally, the surface free energy of the system is described by Young's equation

$$\gamma_{SL_2} = \gamma_{SL_1} + \gamma_{L_1L_2} \cos \theta$$

for two immiscible liquids L_1 and L_2 in contact with a non-deforming solid surface of the container. The contact angle θ is between the liquid-liquid interface and the solid surface. For all values of θ

$$\gamma_{L_1L_2} \geq \gamma_{SL_2} - \gamma_{SL_1}$$

In a temperature region below the critical temperature the contact angle vanishes as the critical temperature is reached.[5] One of the liquid phases, say, L_1 intrudes as a wetting phase between the solid phase S and liquid phase L_2. At the critical temperature, $\theta = 0°$ and a perfect wetting of the solid by liquid L_1 occurs. This perfect wetting may be expressed in terms of the spreading coefficient of liquid L_1 over solid S

$$\text{spreading coefficient} = \gamma_{SL_2} - \gamma_{SL_1} - \gamma_{L_1L_2}$$

which is greater than zero for a spontaneous spreading. Thus, for the perfect wetting

$$\gamma_{L_1 L_2} < \gamma_{S L_2} - \gamma_{S L_1}$$

and Young's equation no longer holds and the contact angle becomes indeterminate. The inequality sign has reversed.

As solidification occurs at the monotectic temperature

$$L_1 \longrightarrow S_1 + L_2$$

the solid S_1 will be preferentially wetted by liquid L_1, resulting in a perfect wetting. For this situation, again

$$\gamma_{L_1 L_2} < \gamma_{S_1 L_2} - \gamma_{S_1 L_1}$$

Under these conditions liquid L_2 is a nonwetting phase and monotectic composite can not be grown unless the growth velocity is large enough to overcome the disjoining pressure.[6]

However, Grugel and Hellawell[7] suggested that if the critical wetting temperature T_w is above the monotectic temperature T_m it may be possible to have steady-state composite growth with solid S_1 being wetted also by liquid L_2. On the other hand, with T_w lower than T_m for low miscibility gap systems, liquid L_2 is separated due to the preferential wetting of solid S_1 by liquid L_1 and high growth velocities become necessary for composite growth.

OBJECTIVE

As previously discussed, Cahn's theory[5] predicts that when two fluid phases are near a critical point one of them must completely wet any third phase, excluding the other fluid from contact with the third phase. If the majority phase wets the container preferentially the system is in stable condition. Phase separation could then primarily result from droplet migration due to temperature gradient effect on surface tension.

On the other hand, if the minority phase wets the third phase, the system is unstable and the minority phase droplets will spread over the entire surface. In either case, phase separation follows. Whether or not preferential or perfect wetting of the monotectic solid phase S_1 occurs when a monotectic reaction takes place is to be determined by the location of the critical wetting temperature.[7]

Thus, an attempt is being made to determine critical wetting temperatures in monotectic systems and to investigate the wetting phase on the container walls and the phase preferentially wetting the monotectic solid. This will eventually lead to an examination of Young's equation in these critical wetting regions.

PROCEDURES

Critical wetting occurs when the surface energies of the three phases, two fluids and a solid, are balanced by the equation,

$$\gamma_{L_1 L_2} = \gamma_{S L_2} - \gamma_{S L_1}$$

for which the contact angle θ of Young's equation has approached zero.

Measurement of $\gamma_{L_1 L_2}$ may be made by using a ring method but the surface energies of the solid, $\gamma_{S L_1}$ and $\gamma_{S L_2}$, can not be measured directly.

An alternative is to estimate the surface energies from liquid film thickness X on the surface in question.

If the surface excess of the vapor adsorbed from liquid L_1 or L_2 at a given temperature is substituted in the form of an ideal gas in the Gibbs adsorption equation and integrated over the vapor pressure range, the film pressure π is obtained:

$$\pi = \gamma_S - \gamma_{SV} = \frac{RT}{v^o \Sigma} \int_o^P X(P) \, d \ln P$$

where γ_S is the surface free energy of the solid, v^o the molar volume of the vapor adsorbed at the standard temperature and pressure and Σ the toal surface area of the adsorbing solid.

Integration of $X(p)$ over the vapor pressure range gives $\gamma_S - \gamma_{SV}$. By repeating this process at a given temperature

for both liquid phases L_1 and L_2 of the miscibility gap and subtracting one film pressure from the other, the surface tension of the solid (γ_s) is eliminated but the desired quantity, $\gamma_{SL_2} - \gamma_{SL_1}$, which is indeed $\gamma_{SV_2} - \gamma_{SV_1}$ in the experiment because of the equilibrium between the liquid and its vapor, is obtained. With this value together with the measured quantity $\gamma_{L_1 L_2}$, the contact angle θ of Young's equation can be calculated at the given temperature.

The entire process can be repeated at different temperatures and the results are extrapolated to estimate the critical-point wetting temperature at which

$$\gamma_{L_1 L_2} = \left| \gamma_{SL_2} - \gamma_{SL_1} \right|$$

The main task for integrating the equation to obtain the film pressure is in determination of the liquid film thickness as a function of vapor pressure at different temperatures.

Surface Viscosity Method

Migration of gas bubbles or liquid droplets in a liquid phase is retarded by the viscosity of the liquid.[4] On the other hand, the film pressure π was shown to be related to the surface viscosity η^S by the equation[15]

$$\log \eta^S = \log \eta_0^S + c\,\pi$$

where η_0^S is the surface viscosity with the activation energy for flow at zero pressure and c is a constant. The accuracy of this equation was confirmed by the experimental

work on surface films.[16] Thus a well established relationship of the film pressure with the surface viscosity in terms of experimental data will be useful in predicting one quantity from the other.

More recently[17] it was shown for polymers that the thickness adsorbed on the liquid-solid interface is proportional to the intrinsic viscosity over a wide range of thickness in theta solvents such as benzene, cyclohexane and methylethyl ketone.

If the surface viscosity η^S is known, the film thickness X may be calculated from the bulk viscosity η by the equation

$$X = \frac{\eta^S}{\eta}$$

which is a convenient relationship for experimental purposes if surface viscosity can be measured without difficulty.

The measurement of surface viscosity is subject to substantial sensitivity limit. The surface canal method, though more sensitive ($\sim 10^{-5}$ surface poise) than others such as oscillating pendulum and rotational methods, is also limited to surface concentrations which give appreciable film pressures. Furthermore, the method, when applied to soluble adsorbed films, suffers from the disadvantage that the film pressure causes desorption and adsorption as well as subphase drag.

Davies and Mayers[18] developed a circular viscous traction

viscometer which can be used for interfacial viscosity measurement with two circular rings held concentrically in the interface. They were able to measure the surface viscosity to an accuracy of 1 x 10^{-4} surface poise.

Ellipsometric Method

Ellipsometry is sensitive and can detect film thickness as thin as 0.1 Å and up to tens of thousands of Å. The technique has been used for measuring oxide films and adsorption of gases and liquids.[19,20]

The basis of ellipsometry is the fact that the state of polarization of a light beam is altered upon reflection from a bare or film-covered surface. When the light reflects from the specimen, the polarization of the light changes in accordance with the specimen film thickness, the optical characteristics of the film and the surface it is deposited on.

In actual use of the ellipsometer, the compensator (a quarter wave plate) is set at a fixed angle and the polarizer and analyzer circles are rotated until the reflected beam from the specimen is extinguished.

From the angular settings of the polarizer and analyzer at this condition two ellipsometric parameters required to determine the state of polarization are obtained: The amplitude ratio and the phase difference. These parameters are then used to determine the film thickness and refractive index of the film by using graphs, tables or computer programs

provided the optical constants of the substrate are known. The refractive index is independent of the film thickness.

The computer programs are available at the Marshall Space Center for calculating the optical constants (real and imaginary values of the refractive index) and the film thickness.

Kwon et al.[8] used ellipsometry to measure the thickness of the intruding layer of liquid with He-Ne laser at several temperatures for certain solutions. The result was as predicted by de Gennes' long-range intermolecular potential.[21]

In our preliminary investigation a cell of pyrex glass was designed. Cells with specific angles[22] will be designed and tested for maximum sensitivity in the thickness measurement for monotectic systems.

CURRENT INVESTIGATION

A pyrex glass cell was built and is being tested for ellipsometric measurement. Several cells will be designed with specific angles for maximum sensitivity and the investigation will be continued.

On the other hand, each layer of succinonitrile-water miscibility gap is being analyzed for vapor composition by slow distillation and condensation in a specially designed cell below the critical temperature.

The result of this investigation and subsequent experiments with monotectic systems will be reported when significant amount of data are obtained and analyzed.

REFERENCES

1. Schreinemakers, F. H. A., _Zeitschr. f. Physik. Chemie_, Leipzig, _23_, 417(1897).

2. Ang, C. Y. and Lacy, L. L., "Monotectic and Synthetic Alloys, Experiment MA-044," _ASTP Preliminary Technical Report_, NASA TMX-64956, Sept., 1975; ibid, _AIAA Progress in Astronautics and Aeronautics_, _52_, 523(1977); Lacy, L. L. and Ang, C. Y., "_Apollo-Soyuz Test Project Summary Science Report_," _I_, NASA SP-412, 403(1977); Gelles, S. H. and Markworth, A. J., "_Space Processing Applications Rocket Project_, SPAR II Final Report," NASA TM78125, Nov., 1977.

3. Chadwick, G. A., "Metallography of Phase Transformations," Crane, Russak & Co., Inc., New York. Chapter 4.

4. Young, N. O., Goldstein, J. S. and Block, M., "The Motion of Bubbles in a Veritcal Temperature Gradient," _J. Fluid Mech._, _6_, 350(1959).

5. Cahn, J. W., "Critical Point Wetting," _J. Chem. Phys._, _66_, 3667(1977).

6. Cahn, J. W., "Monotectic Composite Growth," _Met. Trans. A_, _10 A_, 119(1979).

7. Grugel, R. N. and Hellawell, A., "Alloy Solidification in Systems Containing a Liquid Miscibility Gap," _Met. Trans. A_, _12A_, 669(1981).

8. Kwon, O'D. et al, "Thickness of the Liquid-Vapor Wetting Layer," _Phys. Rev. Lett._, _48_, 185(1982).

9. Pohl, D. W. and Goldburg, W. I., "Wetting Transition in Lutidine - Water Mixtures," _Phys. Rev. Lett._, 48, 1111 (1982).

10. Nishioka, G. M., Lacy, L. L. and Facemire, B. R., "The Gibbs Surface Excess in Binary Miscibility Gap Systems," J. Colloid and Interface Sci., 80, 197(1981).

11. Glickman, M. E., Schaefer, R. J. and Ayers, J. D., "Dendritic Growth - A Test of Theory," Met. Trans. A, 7A, 1747(1976).

12. Jackson, K. A. and Hunt, J. D., "Transparent Compounds That Freeze Like Metals," ACTA METALLURGICA, 13, 1212 (1965), and references cited therein.

13. Glickman, M. E. and Huang, S. C., "Convective Heat Transfer During Dendritic Solidification," AIAA 16th Aerospace Sciences Meeting, Huntsville, Ala., Jan., 1978, AIAA Paper 78-220.

14. Lacy, L. L., Witherow, W. K., Facemire, B. R., and Nishioka, G. M., "Optical Studies of Model Binary Miscibility Gap Systems," to be published.

15. Glasstone, S., Laidler, K. J. and Eyring, H., Theory of Rate Processes, McGraw-Hill Book Co., Inc. 1941. p. 512.

16. Boyd, E. and Harkins, W. D., "Molecular Interactions in Monolayers: Viscosity of Two-Dimensional Liquids and Plastic Solids," J. Am. Chem. Soc., 61, 1188(1939).

17. Chemistry and Physics of Interfaces, based on the Symposium on Interfaces, June, 1964, American Chemical Society Publications, "Structure of Macromolecules as Liquid-Solid Interfaces."

18. Davies, J. T. and Mayers, G. R. A., "Studies on the Interfacial Viscosities of Monolayers," Trans. Faraday Soc., 56, 691(1960).

19. Archer, R. J., "Determination of the Properties of Films on Silicon by the Method of Ellipsometry," J. Opt. Soc. Am., 52, 970(1962).

20. ibid, "Measurement of the Physical Adsorption of Vapors and the Chemisorption of Oxygen on Silicon by the Method of Ellipsometry," Nat. Bur. Std., Misc. Publ. No. 256, 1964. p. 255.

21. De Gennes, P. G., "Some Effects of Long range Forces on Interfacial Phenomena," J. Phys.-Lett. (Paris), 42, L-377(1981).

22. McCrackin, F. L. et al., "Measurement of the Thickness and Refractive Index of Very Thin Films and Optical Properties of Surface by Ellipsometry," J. Res. Nat. Bur. Std., 67A, 363(1963).