

INVESTIGATIONS ON TRANSPARENT LIQUID-MISCIBILITY GAP SYSTEMS

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ABSTRACT

Sedimentation and phase separation is a well known occurrence in monotectic or miscibility gap alloys. Previous investigations indicate that it may be possible to prepare such alloys in a low-gravity space environment but recent experiments indicate that there may be non-gravity dependent phase separation processes which can hinder the formation of such alloys. We are studying such phase separation processes using transparent liquid systems and holography. Holography has advantages over conventional microscopy since large numbers ($10^3 - 10^4 \text{ cm}^{-3}$) of particles can be accurately recorded in a single exposure. By reconstructing such holograms into a commercial-particle-analysis system, real time computer analysis can be performed on emulsions with diameters in the range of $5\mu\text{m}$ or greater. Thus dynamic effects associated with particle migration and coalescence can be studied. Characterization studies on two selected immiscible systems including an accurate determination of phase diagrams, surface and interfacial tension measurements, surface excess and wetting behavior near critical solution temperatures have also been completed. It was found that surface activity of the component of lower surface tension increases as solutions approach the consolute point. These findings agree well with predictions based on the two surface layer model of Defay and Prigogine. Experiments that measure the influence of large values of surface excess on surface tension driven flow are underway.

Values of contact angle against glass in the heterogeneous region of two systems are also reported. The behavior is opposite to that predicted by Cahn. The influence of this behavior on heterogeneous nucleation is now being studied.

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INTRODUCTION

The low-gravity environment of space has prompted interest in the formation of unique monotectic or miscibility gap alloys. Previous experiments using the MSFC drop tower [1,2] have demonstrated that fine dispersions of a Ga-rich phase could be achieved in a Bi-rich matrix. The elimination of buoyancy driven separation has been demonstrated on a Skylab experiment [3] using isothermal dispersions of krytox oil and water. The Skylab dispersions were completely stable for all compositions and for a long period of time (10 hours) even though the spacecraft experienced transient accelerations in the range of 10^{-3} to 10^{-2} g. More recent experiments on metallic systems have, however, provided confusing results.

An experiment [4] performed on the Apollo-Soyuz Test Project in 1975 dealt with an alloy of Pb-Zn slowly (cooling rate $\approx 0.03^\circ \text{C/s}$) and isothermally (thermal gradient $< 2^\circ \text{C/cm}$) cooled through the consolute temperature and then solidified at the monotectic temperature. The Pb-Zn samples consisted of fine dispersions of a Pb-rich phase in a Zn-rich matrix with the Pb-particles showing an aligned structure in much of the sample. The occurrence of major macroscopic regions of Pb-rich and Zn-rich regions in the sample, which corresponded to

the initial location of the pure metals, and the appearance of a diffusion-type gradient away from the interface led to the conclusion that the samples were not homogeneous at the beginning of the cooling period. The appearance of a relatively large Zn-rich particle on the Pb-rich side of the sample provided evidence that major coalescence was probably taking place within the material.

Similar results have also been obtained on Al-In alloys flown on a suborbital rocker flight [5]. In this case, the alloys were cooled at a faster rate ($\approx 15^\circ \text{C/s}$) and contained compositions on both sides of the consolute temperature. The Al-In samples showed almost complete separation of the phases into a lower-surface-tension In-rich phase surrounding a higher-surface-tension Al-rich phase. Unlike the Pb-Zn samples, there was a distribution of particle sizes from micron size to millimeter size. A later analysis of the experiment indicated that this experiment may have been influenced by the lack of a homogeneous starting liquid and a subsequent experiment was reflowed on SPAR V. Since the results of the second flight are similar to the first flight, this provides strong experimental evidence of massive non-gravity dependent phase-separation processes.

The processes in low-gravity which may affect the ultimate structure of miscibility gap alloys include:

1. Nucleation of a dispersed phase or spinodal decomposition of congruent phases.
2. Rapid diffusional growth and Brownian coalescence of the phases during the early stages of phase separation.
3. Coalescence processes of the dispersed phase which are influenced by surface and interfacial forces or by residual spacecraft accelerations.
4. Thermocapillary particle motion due to thermal gradients as has been observed for bubbles in liquids (ref 6).
5. Non-gravity dependent convective fluid motion caused by volume changes occurring during phase changes or differential surface tension gradients.
6. Coalescence processes caused by the interaction of the dispersed phase with the solidification interface.

These processes involve complex kinetic mechanisms which are often interrelated in a given experiment and which are worthy of detailed study.

We have chosen to study these processes in transparent model organic systems because of their obvious advantages. We have proposed the study of growth kinetics in model systems in space because these processes are strongly affected by convection and buoyancy. It should be noted that although three component neutrally buoyant emulsions can be formed at a given temperature, there exists no two component partially miscible system that is neutrally buoyant over range of temperatures [7]. To study the phase separation processes in model materials, we have proposed [8,9] to use holography since it has advantages over conventional microscopy in maintaining good resolution and superior depth of field that allow the recording of 10^3 to 10^5 particles in a single exposure.

EXPERIMENTAL TECHNIQUES AND CHARACTERIZATION STUDIES

Holography has been previously used to measure small particles in meteorology [10] and crystal growth experiments [11]. We have experimentally investigated an in-line system for use with dispersions and emulsions [8,9,12].

Figure 1 is a schematic of the holographic construction system and Figure 2 is a schematic of the reconstruction system. This holographic arrangement allows overall system magnification in the range of 800 to 1200 X. Typical reconstructed holograms of calibrated test squares can be seen in Figure 3 which demonstrates the overall system capability to accurately measure particle diameters for particle sizes $5\mu\text{m}$ or greater. The measured particle size in Figure 3 are shown by the display in the upper left hand corner of each picture. This system is capable of accurately recording up to 10^4 particles/cm³ on a single hologram for later analysis.

In order to determine the system capability to measure particle distributions, holograms were taken of a known distribution of glass

beads dispersed in a clear oil. The holograms were then reconstructed and the particle size measured using the Omnicon computer system. The results are shown in Figure 4 which compares the particle distribution in the dispersed system to the distribution as measured by the Omnicon system using conventional microscopy.

Two binary systems were chosen for ground based characterization study. Both the ethyl salicylate-diethylene glycol system and the cyclohexane-methanol system are relatively nontoxic and have a large miscibility gap region. These systems are almost completely characterized with respect to many important properties, such as the phase diagram, surface and interfacial tensions, density, viscosity, and refractive index.

Because many important processes in space are influenced by surface activity, the quantitative measurement of surface activity (the Gibbs excess) in our miscibility gap systems was undertaken. Figure 5 describes some results, the solid line is the binodal curve and the dotted lines represent lines of equal surface activity, called cosorption lines. The cosorption lines are calculated from surface tension and activity coefficient measurements. Figure 5 reads as a contour map and shows a rise in surface activity of solutions whose temperature and composition approach a point near the active component. In this system ethyl salicylate is the surface active component. Solutions near the critical solution point have high surface activity and display all the phenomena of a soap solution, i.e.: they foam [13,14], they contain micelles [15], and they are probably less responsive to surface tension driven flows than a non-surface active solution, or pure liquid. The last conclusion is a hypothesis we are currently testing.

Figure 6 shows similar behavior in the hexane-aniline system. This plot is derived from data published by Campbell and coworkers [16,17]. Figure 7 shows reduced surface activity for a regular solution using the two layer surface model of Defay and Prigogine [18,19]. Component 1 was assumed to have the higher surface tension, in all three diagrams the maximum in surface activity is shifted towards the component of

higher surface tension.

Heterogeneous nucleation is an important effect as solutions are cooled into the two phase region. The contact angle between the two conjugate phases on a solid substrate is a parameter we have studied since it greatly influences heterogeneous nucleation. Figure 8 summarizes measurements we have made of the cyclohexane-methanol system on glass. Curve b represents behavior for a system of reagent grade methanol-cyclohexane; the methanol contains 0.20% water by weight. Curve a shows behavior of a highly purified system; the methanol contains less than 0.02% water by weight. Although small amounts of water can drastically affect the consolute temperature, the wetting behavior remains essentially the same. One conjugate solution preferentially wets the glass within five degrees of the critical solution point. The contact angle rises very rapidly with rising temperature and becomes 90° close to the critical solution temperature. As temperature then rises to the critical temperature, the meniscus thickens and finally disappears. Similar behavior was observed with the ethyl salicylate-diethylene glycol system.

It is interesting that our observations show that $\cos \theta$ is proportional to $(T_c - T)^{-1}$, in agreement with Cahn's prediction [20]. However, the contact angle approaches 90° near the critical solution point, rather than 0° as predicted by Cahn. This should not be surprising, since as the consolute point is approached, the conjugate phases approach each other in chemical composition and the contact angle should approach the symmetric angle of 90° . Therefore, the two phase region near the critical solution point is better described by the term "critical point dewetting" rather than "perfect wetting" as formerly suggested [20]. We are now examining the influence of different contact angles on heterogeneous nucleation in both of our systems.

Legends for Figures

- Figure 1. In-line holographic construction system for studying emulsions and dispersions.
- Figure 2. Holographic reconstruction and Omnicon particle analysis system.
- Figure 3. Calibration squares measured by Omnicon. The true particle sizes are (a) 100 μ m, (b) 37.5 μ m, and (c) 5 μ m. The measured particle sizes are displayed in the upper left hand corner.
- Figure 4. Comparison of measured particle distribution using ordinary microscopy of the particles placed on glass slides and holograms of the particles dispersed in clear oil.
- Figure 5. Phase diagram and surface activity in the ethyl salicylate-diethylene glycol system. Cosorption lines represent surface excess $\Gamma^{(G)}$ of ethyl salicylate ($\times 10^{10}$ moles/cm²).
- Figure 6. Phase diagram and surface activity in the hexane-aniline system. Cosorption lines represent surface excess $\Gamma^{(G)}$ of hexane ($\times 10^{10}$ moles/cm²).
- Figure 7. Phase diagram and surface activity for a two layer regular solution. Component 1 has the higher surface tension.
- Figure 8. Contact angle vs. temperature in the cyclohexane-methanol system. Curve a represents a system containing less than 0.02% water. Curve b represents a system containing less than 0.20% water.

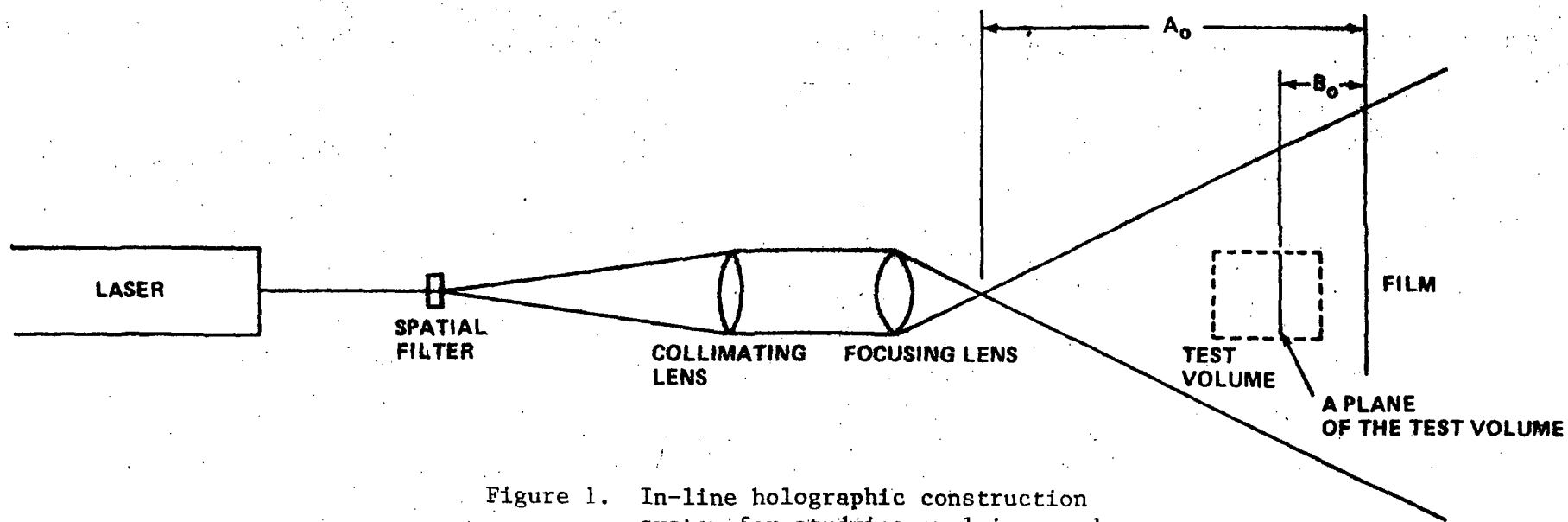


Figure 1. In-line holographic construction system for studying emulsions and dispersions.

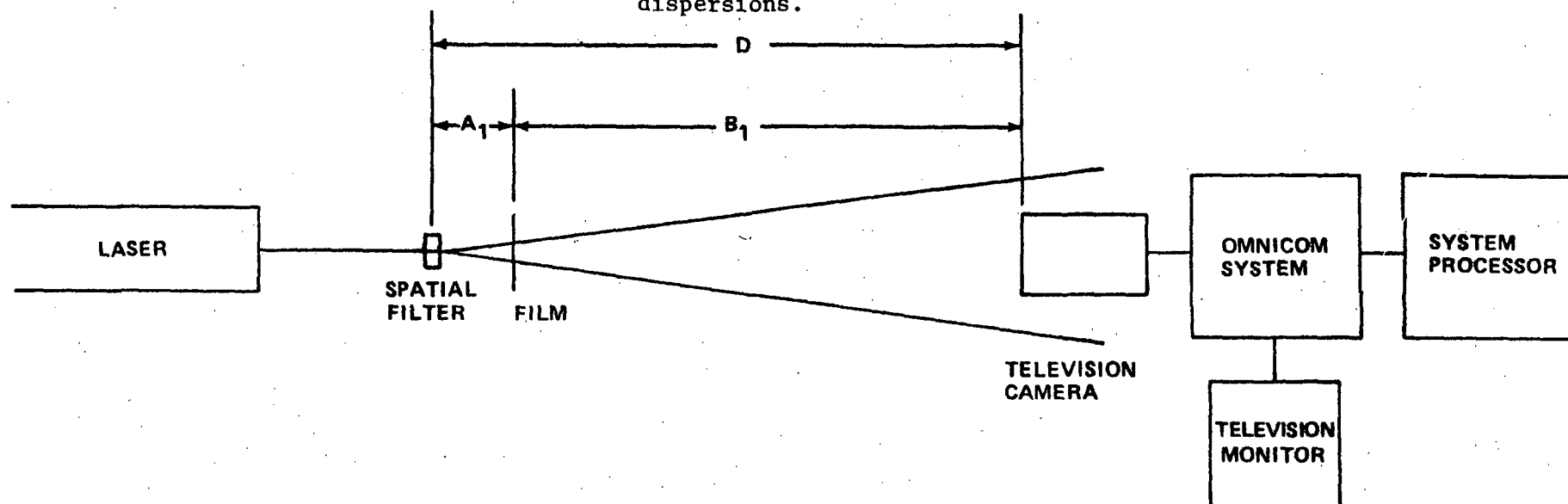


Figure 2. Holographic reconstruction and Omnicon particle analysis system.

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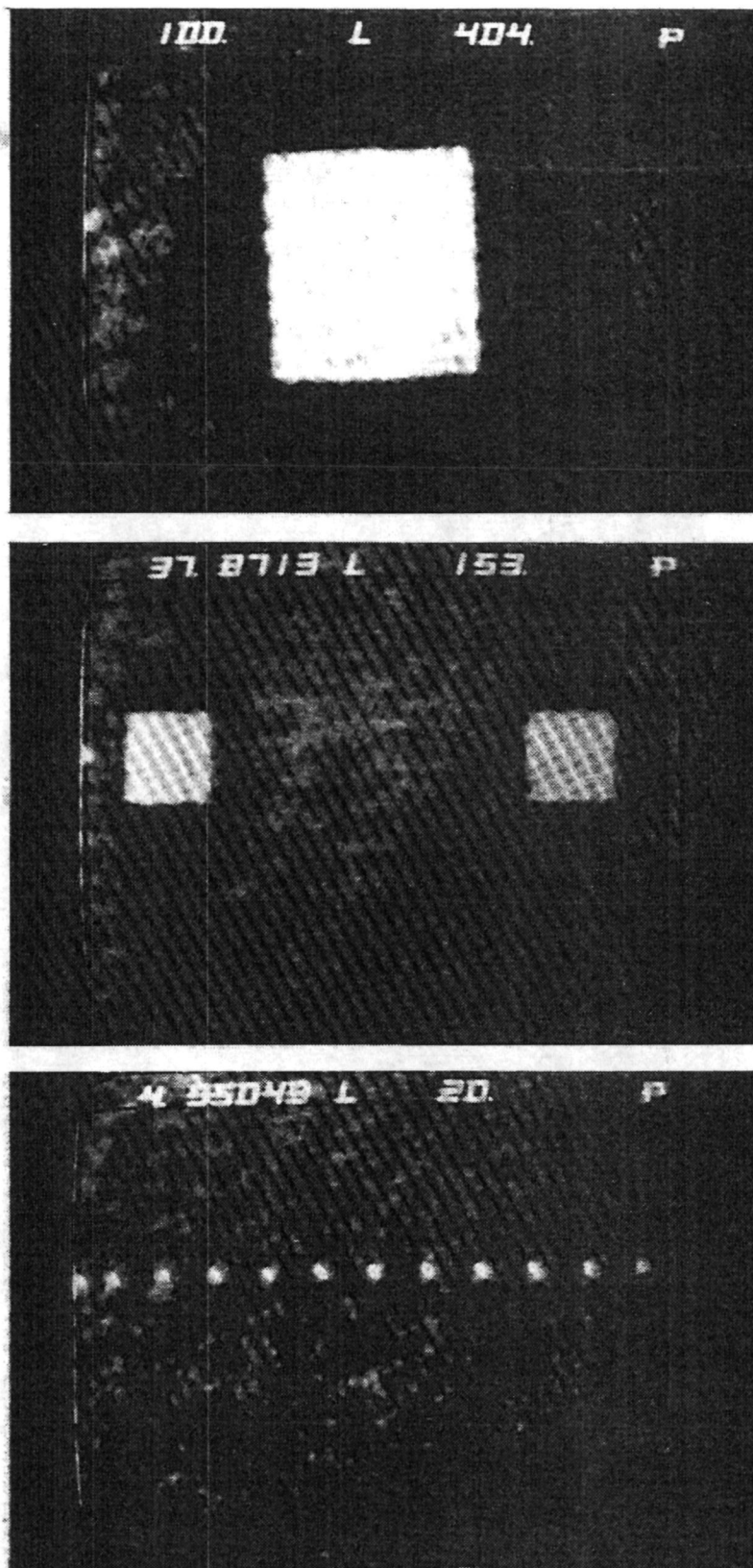


Figure 3. Calibration squares measured by Omnicon. The true particle sizes are (a) $100\mu\text{m}$, (b) $37.5\mu\text{m}$, (c) $5\mu\text{m}$. The measured particle sizes are displayed in the upper left hand corner.

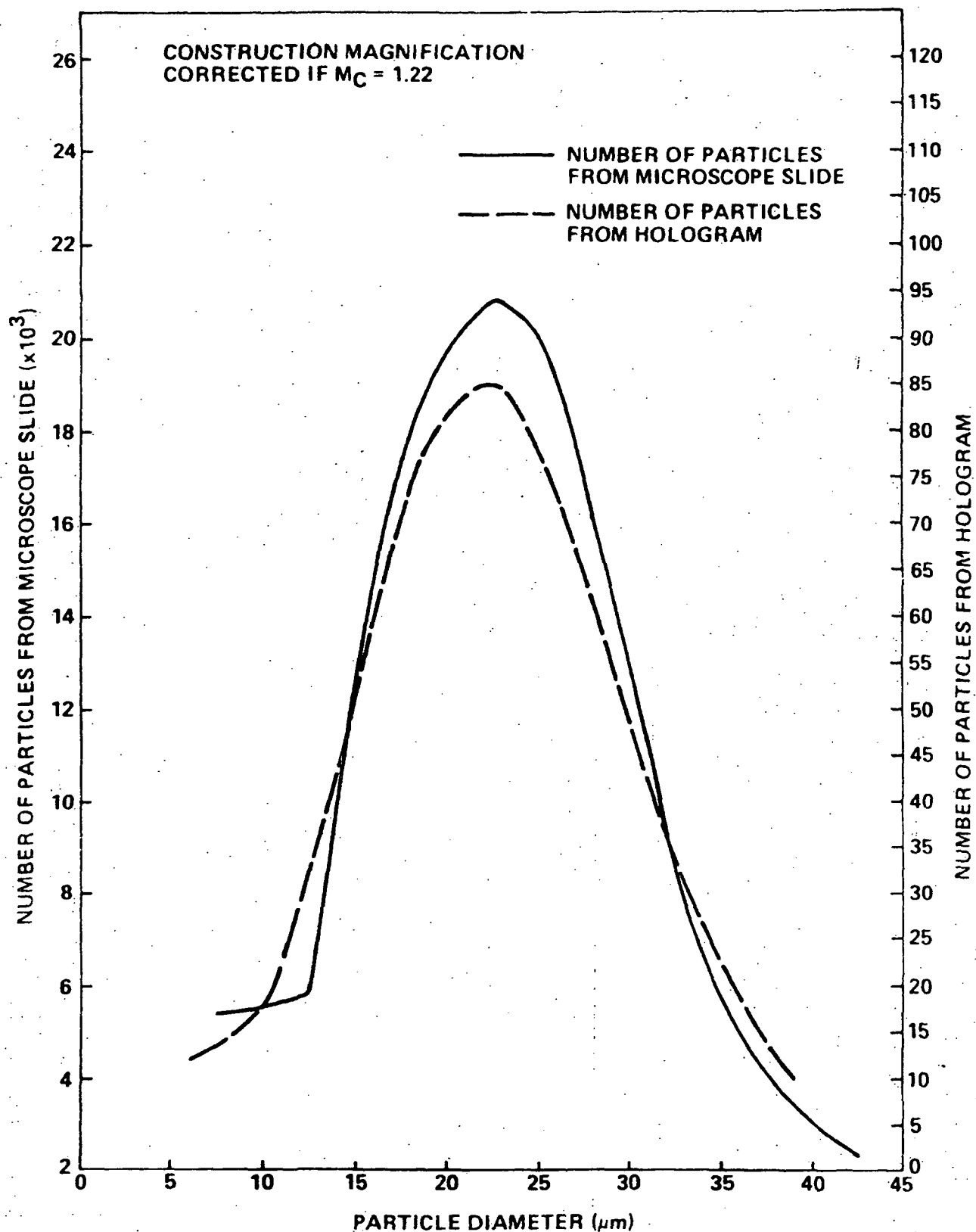


Figure 4. Comparison of measured particle distribution using ordinary microscopy of the particles placed on glass slides and holograms of the particles dispersed in clear oil.

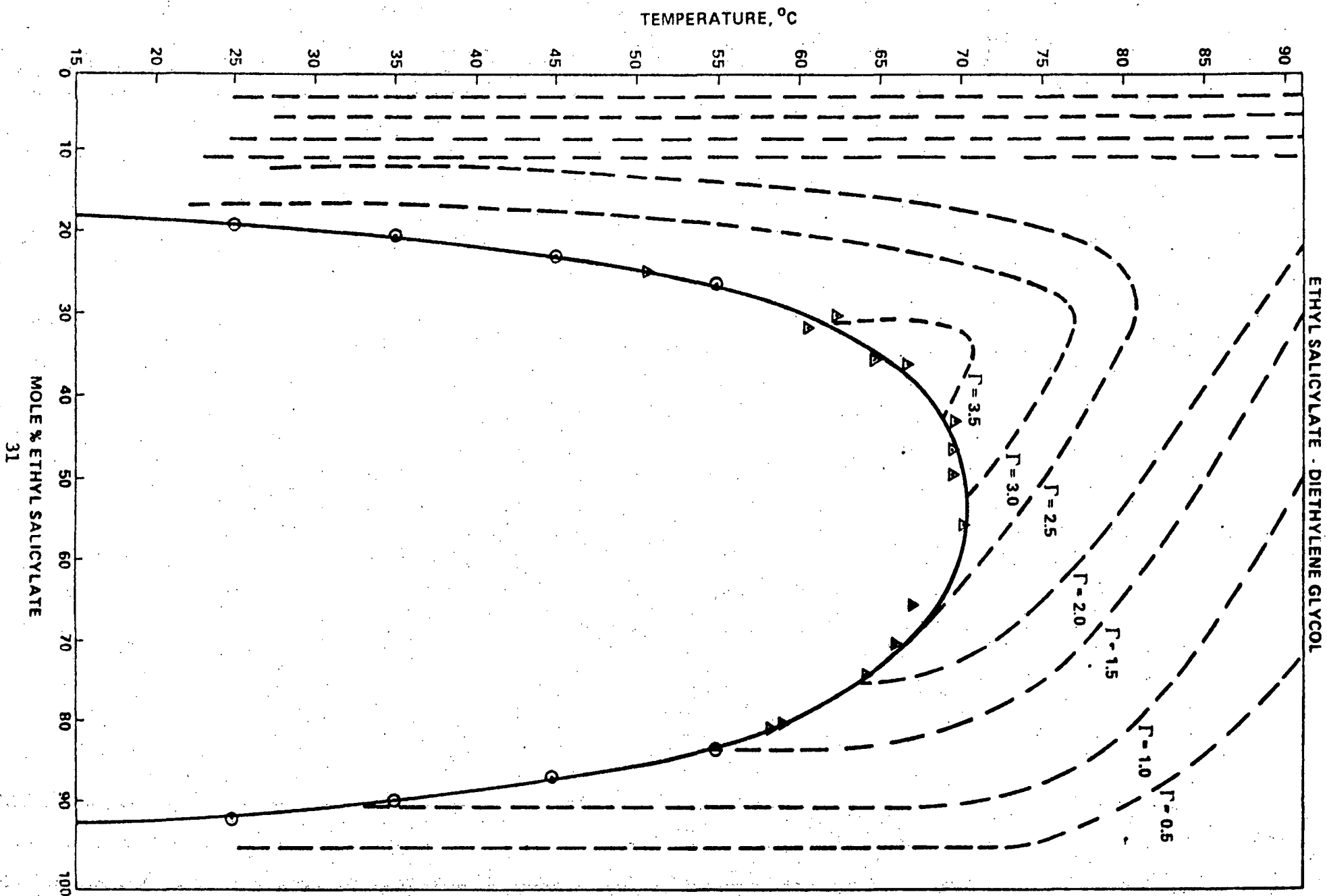


Figure 5. Phase diagram and surface activity in the ethyl salicylate-diethylene glycol system. Cosorption lines represent surface excess $\Gamma(G)$ OF ethyl salicylate ($\times 10^{10}$ moles/cm²).

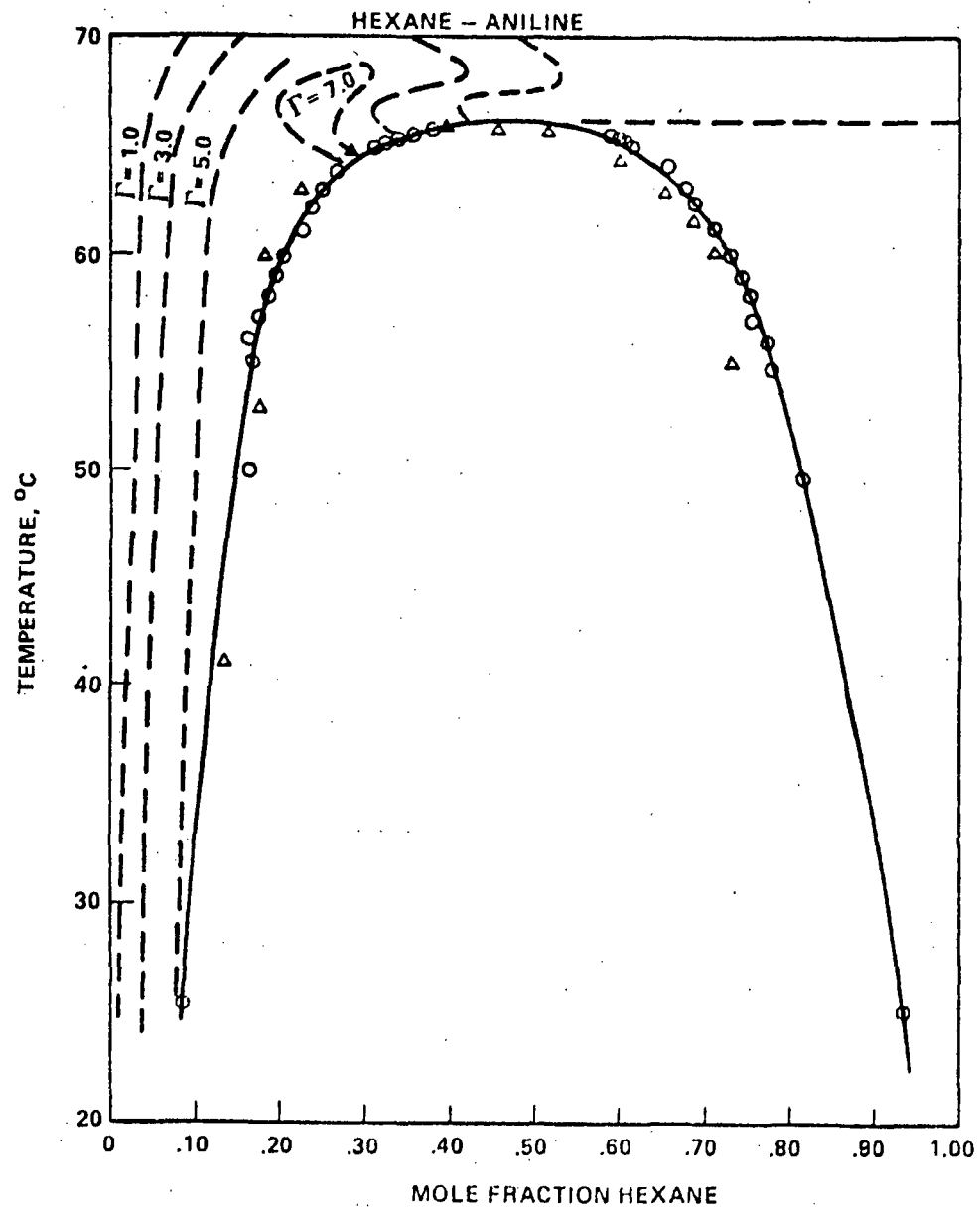


Figure 6

Phase diagram and surface activity in the hexane-aniline system. Cosorption lines represent surface excess $\Gamma(G)$ of hexane ($\times 10^{10}$ moles/cm²).

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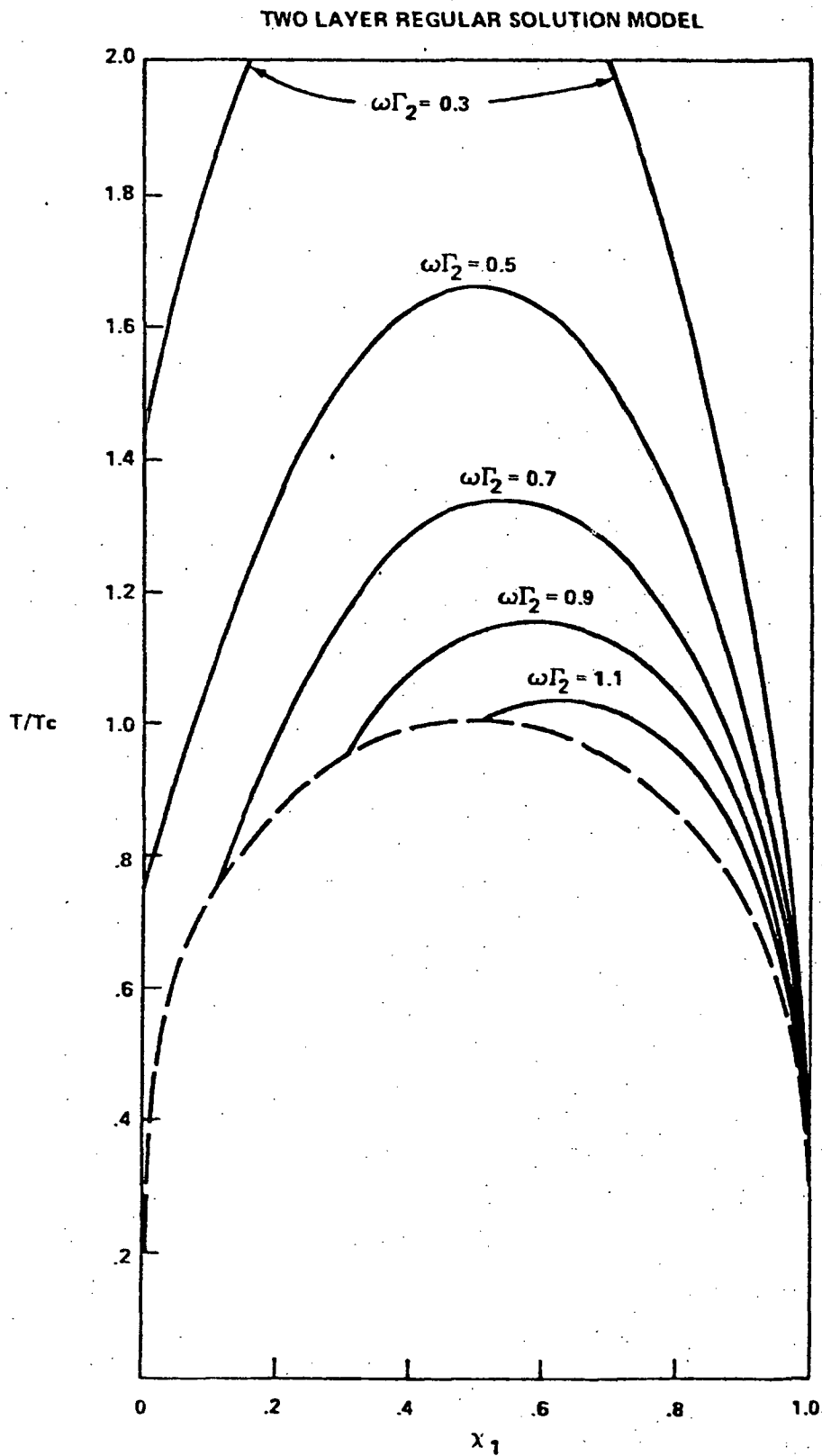


Figure 7. Phase diagram and surface activity
for a two layer regular solution.
Component 1 has the higher surface tension.

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