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# Phase Separation Kinetics in Immiscible Liquids

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## Abstract

The kinetics of phase separation in the succinonitrile-water system are being investigated. Experiments involve initial physical mixing of the two immiscible liquids at a temperature above the consolute, decreasing the temperature into the miscibility gap, followed by imaging of the resultant microstructure as it evolves with time. Refractive index differences allow documentation of the changing microstructures by noninvasive optical techniques without the need to quench the liquid structures for analysis.

## Introduction

Miscibility gaps, both stable and metastable, are known to exist in many technologically important systems. Control of phase separation phenomena is essential in achieving microstructures that yield desired properties. In this regard it is imperative that the transformation kinetics be well understood.

In many cases heterogeneous interconnected microstructures result. In early studies investigators were prompted to conclude that the mechanism of transformation is spinodal decomposition.<sup>1</sup> Further work has cast doubt upon some of the conclusions of these investigations and indicated that inference of the mechanism of separation from observations of the final phase morphologies can be completely misleading.<sup>2-7</sup> It is clear that the kinetics of the transformation must be studied as it occurs, especially during its earliest stages when differences in mechanism are best elucidated. The later stages of any transformation are dominated by coarsening kinetics.<sup>2-8</sup>

Reduced gravity offers the opportunity to produce microstructures unattainable on earth. Specifically, it is possible to solidify two-phase liquids as dispersions, thereby yielding exciting properties as a consequence of the metastable microstructure. The generation of dispersed second phase droplets in reduced gravity poses interesting questions in phase transformation kinetics. It is well known from the now classical studies of solid-solid transformations that within the miscibility gap phase transformation occurs not simply by nucleation and growth but, over well defined regions of composition and temperature, by spinodal decomposition instead. The same behavior is expected with liquid-liquid phase transformations. From the standpoint of fundamental studies liquid-liquid phase transformations are interesting because "matrix effects" present during the demixing of solid solutions are not expected to be significant in liquids.

## The Present Study

The present study is an attempt to follow phase separation kinetics in immiscible liquids. The classical studies separation have been done on solid phase system: liquids stratify in a gravity field. Thus, the two principal techniques are electron microscopy and electromagnetic scattering (both light scattering and small angle x-ray). In low-gravity phase separation studies of liquids that are transparent to visible light a variety of optical imaging techniques based upon differences in refractive index become available, for example, laser schlieren imaging.<sup>9</sup> Experiments then involve an initial physical mixing of the two immiscible liquids followed by imaging of the resultant microstructure as it evolves with time.

Reduced gravity studies are important because they allow the observation of phase separation without stratification which occurs when the second phase particles grow beyond the size at which interfacial tension no longer counteracts the force of gravity. In reduced gravity there is no need to alter the relative densities or interfacial energies of the two phases by adding stabilizers, nor is it necessary to quench the liquid structures for analysis. Furthermore, the experiments can be repeated by simply remixing. As part of the present study, laboratory scale equipment is being designed and built such that it can be readily adapted for zero gravity flight.

The results will be compared with theory. For constant volume fractions of the separated phases, the average particle diameter is expected to increase as the cube root of time and the number of particles to decrease as the reciprocal of time.<sup>10</sup> Much work has been done in oxide glass systems and has been exhaustively reviewed by Uhlmann and Kolbeck.<sup>11</sup> While agreement is good for systems undergoing spinodal decomposition, there is no comprehensive analysis for phase separation by the competing nucleation and growth mechanism

It has been suggested that electron microscopy be used to differentiate between nucleation and growth and spinodal decomposition.<sup>12</sup> For nucleation and growth the volume fraction transformed should increase with time (following an incubation period), while for spinodal decomposition the volume fraction should in many cases decrease with time to reflect a transition from compositional waves symmetric about the mean concentration to compositional waves fluctuating between the equilibrium concentrations (seen as relative volume fraction) of the two phases. The experimental technique should be able to observe the decrease in second-phase volume fraction during the period of this transition. Such measurements, however, are not simple because of the difficulties in differentiation between the two phases and in accurately determining their volume fractions. One of the goals of the initial phase of this study is to develop the optical techniques to permit such accurate measurements.

The physical system under investigation is succinonitrile-water which exhibits liquid immiscibility and has a consolute temperature of 56°C.<sup>13</sup> However, the compositional dependence of several important physical properties is not known, specifically, the density and interfacial tension. As a result, density measurements by the direct Archimedean technique are being performed to support the kinetic studies described above.

The results of this study will be of importance in commercially significant systems such as inorganic glasses, biochemicals, semiconductors, colloidal suspensions, and aircraft metal alloys.

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