

Density measurements in the succinonitrile–water system

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The variation of density with temperature and composition in the succinonitrile–water system was measured by the direct Archimedean method. At fixed composition, density was found to vary linearly with temperature. At constant temperature, density was found to vary linearly with composition. Along the phase boundary there is a density reversal: at temperatures above 45°C the water-rich phase is denser; below 45°C the succinonitrile-rich phase is denser.

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Utilisant la méthode directe d'Archimède, on a mesuré la variation de la densité du système eau–succinonitrile en fonction de la température et de la composition du mélange. On a trouvé que pour une composition déterminée, la densité varie linéairement avec la température, tandis qu'à température constante la densité varie linéairement avec la composition. Il y a une inversion de la densité le long de la frontière des phases : la phase riche en eau est plus dense à une température supérieure à 45°C. En dessous de cette température c'est la phase riche en succinonitrile qui est plus dense.

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1. Introduction

Miscibility gaps are present in many technologically important systems. In order to attain microstructural goals in these systems it is imperative that phase separation phenomena be strictly controlled during materials processing operations. This requires a knowledge of the kinetics of phase transformation.

Classical studies of phase separation were restricted to solids where it is effectively impossible to observe microstructural evolution as it occurs. However, conclusions based on the final morphologies can be misleading (1–6). It is clear that the transformation must be studied in real time.

The novelty of the present work is that for the first time a liquid system was made the subject of a phase transformation study. The succinonitrile–water system was chosen because it is liquid at ambient temperature and transparent to visible light. The latter allows the use of noninvasive optical techniques for real time measurement of microstructure. However, this requires a knowledge of the variation of the index of refraction. Such data have not been reported for the succinonitrile–water system. As the index of refraction is related to density, the purpose of the present study was to measure the dependence of density on temperature and composition in this system.

2. Experimental

Density was measured by the direct Archimedean technique in which one monitors the weight change of a calibrated bob upon immersion in the solution under study (7). The apparatus is shown in Fig. 1. The upper limb is 66 cm long and houses the fused quartz spring; the lower limb is 16 cm long and holds the sample which is heated by circulating water. Water temperature is regulated by a constant temperature circulator.¹ The spring is centered by the ball and socket joint at the top of the upper limb and is raised and lowered by the pulley mechanism. During the experiment the sample is kept under an atmosphere of argon.

The density bob is made of borosilicate glass and weighs about 3 g. The bob is connected to the spring by means of a stainless steel wire, 0.5 mm in diameter. The fused quartz spring² has a sensitivity of 0.05 g cm^{-1} and extremely good linearity. Spring displacement was measured by cathetometer³ which read to the nearest 0.1 mm and can

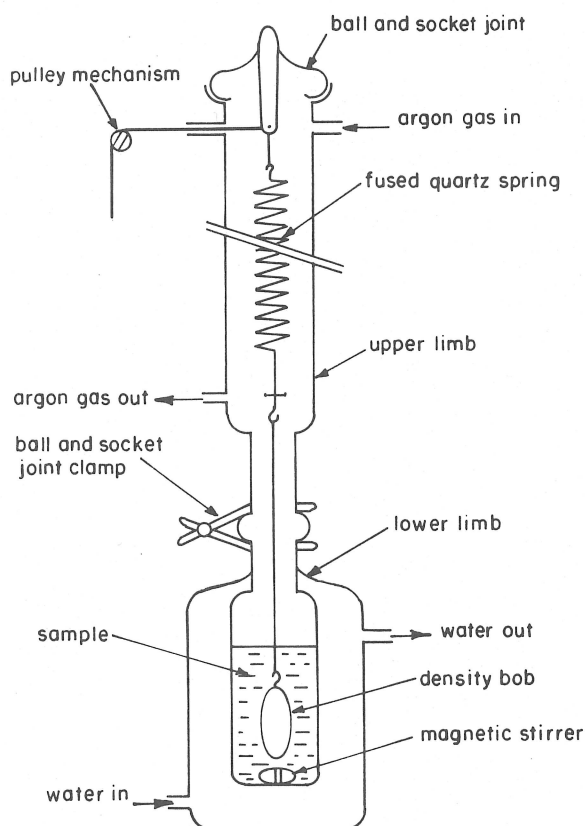


FIG. 1. Apparatus for the measurement of density.

measure a maximum length of 40 cm. In order to minimize calibration errors, an effective "cell constant" which relates spring displacement to the density of the sample was determined by measuring the temperature dependence of the density of water and comparing these results with those in the literature (8).

Reagent grade succinonitrile⁴ was vacuum distilled several times until a clear residue remained. The melting point of the distillate was measured by cryoscopy and taken to be a further indication of purity. Binary solutions of succinonitrile–water were prepared by adding high purity water to succinonitrile and heating the mixture to obtain a

¹Model 800, Allied Fisher Scientific, Pittsburgh PA.

²Ruska Instrument Corporation, Houston TX.

³Model 5100, Eberbach Corporation, Ann Arbor MI.

⁴Eastman Kodak, Rochester NY.

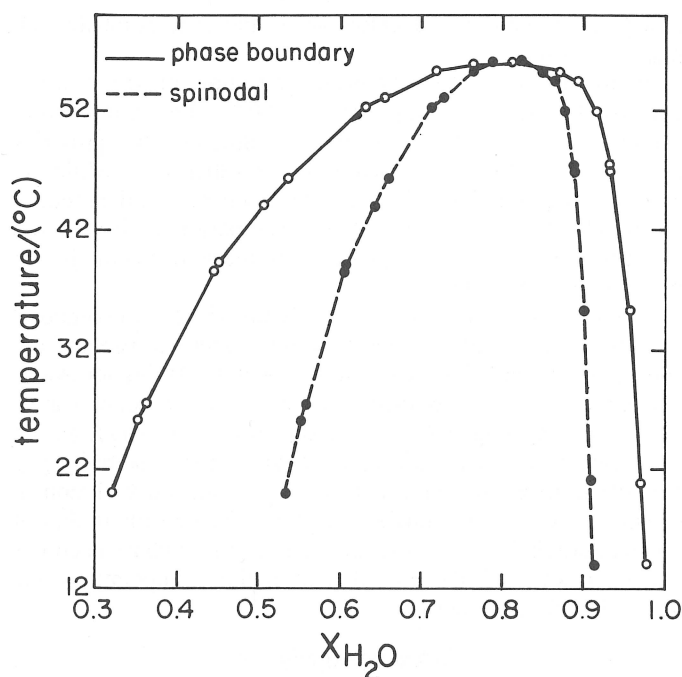


FIG. 2. Phase diagram of the succinonitrile-water system. Spinodal calculated by the "root three" rule.

homogeneous solution which was then transferred to the apparatus. The composition of the sample was then checked once again by comparing the temperature of the phase boundary as reported in the phase diagram (9) to the homogenization temperature as determined by heating the sample and visually inspecting for the presence of any second phase particles. The phase diagram is reproduced for the convenience of the reader in Fig. 2 which also gives the spinodal as calculated by the "root three" rule (10).

In a typical experiment the temperature of the sample, which weighed about 30 g, was varied from approximately 2 K above the solubility limit to a maximum temperature of 80°C. Once the temperature of the sample was set, it was mixed for 10 min by magnetic stirrer. Next, the bob was lowered into the solution, and the extension of the spring was measured by cathetometer. The bob was raised and lowered into the sample again, and another reading was taken. This was repeated at least four times before the temperature was changed. Care was taken to ensure that the immersion depth of the bob was constant in all measurements. The results were checked for reproducibility by performing the experiment on at least two different samples at every composition. The range of composition in this study was 0.3 to 0.97 mole fraction of water. In addition, the density of pure succinonitrile was measured between 60 and 80°C.

3. Results and discussion

At each composition the density measurements were fitted to the following linear function of temperature:

$$[1] \quad \rho/(\text{g cm}^{-3}) = a - bT$$

where T is in Kelvins. Equation [1] is valid only in the single-phase region outside the miscibility gap. The results are shown in Table 1. The fit was extremely good for all compositions, including that of pure succinonitrile. In consideration of the experimental errors associated with this technique, the accuracy of all the density measurements is assessed to be 0.2%.

There are no reports of the density of binary solutions of succinonitrile-water. However, Timmermans and Hennaut-

TABLE 1. Temperature dependence of density in the succinonitrile-water system. $\rho/(\text{g cm}^{-3}) = a - bT$, where T is in Kelvins

$X_{\text{H}_2\text{O}}$	$a/(\text{g cm}^{-3})$	$b/(\text{g cm}^{-3} \text{K}^{-1})$
1.000	1.1421	0.000479
0.970	1.1842	0.000599
0.950	1.2021	0.000653
0.900	1.2302	0.000739
0.827	1.2506	0.000803
0.700	1.2629	0.000847
0.600	1.2672	0.000861
0.500	1.2712	0.000873
0.400	1.2678	0.000861
0.300	1.2618	0.000842
0.000	1.2550	0.000823

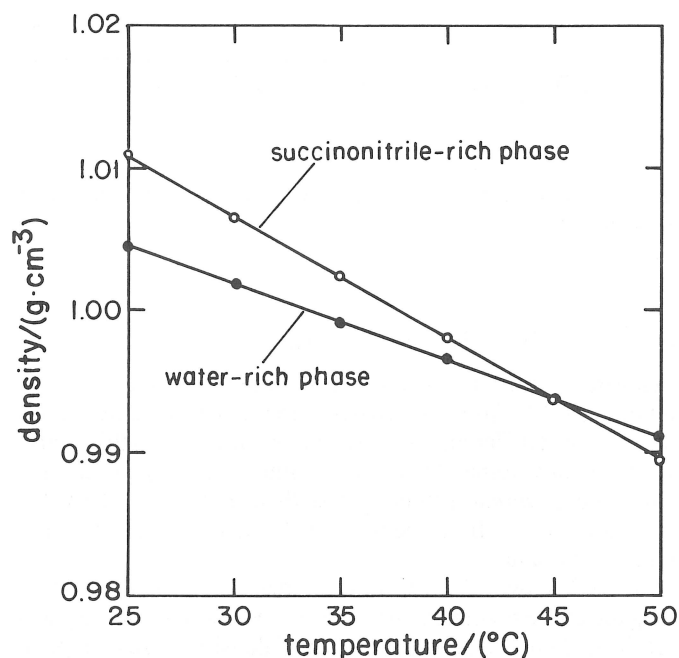


FIG. 3. Variation of density with temperature at compositions along the phase boundary.

Roland have measured the density of pure succinonitrile (11), and their results differ by less than 0.2% from the present work.

The molar volume was calculated from the density data through the use of the equations in Table 1. The molar volume at a given composition is defined as the molar mass of the solution divided by its density. In a binary system the molar mass refers to the mass of one mole of solution and is calculated by adding the molar masses of the pure components weighted by their mole fractions. The molar volume isotherm was found to be a linear function of composition at any given temperature. At temperatures below the consolute the solutions separate into two phases, and the molar volume is undefined in this two-phase region. However, molar volume isotherms of the water-rich solutions and succinonitrile-rich solutions were piecewise linear and appear to lie on the same line when projected across the miscibility gap.

Equation [2] represents the variation in molar volume with composition at a constant temperature of 60°C.

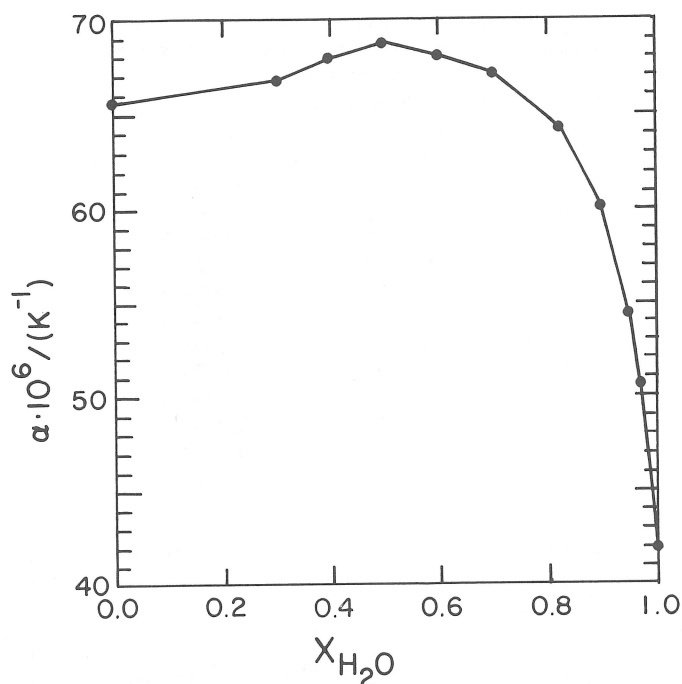


FIG. 4. Variation of thermal expansivity, α , with composition at a temperature of 60°C.

$$[2] \quad V_m / (\text{cm}^3) = 81.70 - 63.42X_{H_2O}$$

Equation [2] was constructed by computing the values of molar volume at 60°C from the least squares fits of density versus temperature at different compositions as measured in this study. For the molar volume of pure succinonitrile eq. [2] gives a value of 81.70 cm³ which differs by less than 0.1% from the value calculated directly from the measured density of succinonitrile at this temperature.

Figure 3 shows the variation in density with temperature along the phase boundary. At each composition the density was calculated from the least-squares fit of density versus temperature evaluated at the corresponding phase boundary. There are two lines, one for the water-rich phase and one for the succinonitrile-rich phase.

This system exhibits density reversal. During the course of experiments the liquid phases were observed to exchange position at temperatures near 45°C. This is consistent with Fig. 3 which shows that at temperatures above 45°C the water-

rich phase is denser and below 45°C the succinonitrile-rich phase is denser.

Figure 4 shows the isothermal variation of the thermal expansivity, α , with composition at 60°C. This temperature was chosen because it is above the consolute and thus provides access to the full compositional range. Furthermore, while the absolute magnitude of α changes with temperature, the relative magnitude of α across an isotherm is comparatively insensitive to temperature, i.e., the shape of the isotherm does not change much with temperature.

Figure 4 shows that α is effectively invariant with composition spanning the interval between pure succinonitrile and the consolute composition, 82.7 mol% water. At higher water contents the value of α drops sharply to that of pure water, which is only about half that of succinonitrile. Thus, as the temperature of a two-phase mixture within the miscibility gap is made to decrease, there is a more pronounced variation in density of the succinonitrile-rich phase. The result is that at temperatures below 45°C the succinonitrile-rich phase becomes denser in spite of the fact that at higher temperatures the water-rich phase is denser.

Acknowledgements

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