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MEASUREMENT OF INTERFACIAL TENSION OF IMMISCIBLE  
LIQUID PAIRS IN MICROGRAVITY

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ABSTRACT

*A discussion is given of a containerless microgravity experiment aimed at measuring the interfacial tension of immiscible liquid pairs using a compound drop rotation method. The reasons for the failure to execute such experiments in microgravity are described. Also, the results of post-flight analyses used to confirm our arguments are presented.*

INTRODUCTION

The primary objective of this flight experiment was the measurement of the liquid-liquid interfacial tension between immiscible liquid pairs. A secondary goal was the detection and measurement of certain instability points associated with a rotating, compound drop.

The surface tensions were to be measured by a contactless, drop rotation method. A triple-axis acoustic positioning chamber was to be utilized for both maintaining the position and inducing controlled rotation of compound liquid drops. The shape distortions of the inner and outer droplets caused by the induced rotation were to be analyzed quantitatively through the analysis of cine film and video records. From accurate measurements of the major and minor axes of the inner droplet (and correction for optical distortion due to the lens effect from the outer liquid), the liquid-liquid interfacial tensions were to be determined using the theory developed by Bauer and Siekmann (1). This theory was developed to predict the equilibrium shapes of a liquid sphere which contains a concentrically positioned gas bubble or immiscible liquid droplet of lower density. The equilibrium shapes which are formed at a given rotation rate are functions of the densities and volumes of each phase, the interfacial tension between the phases, and the surface tension of the outer phase. Thus, knowledge of the pertinent droplet volumes and densities and liquid-air surface tension of the outer droplets, used in conjunction with the measured values of the lengths of the minor and major axes of the prolate spheroid shaped inner droplet (produced by rotation), allows for the determination of the liquid-liquid interfacial tension.

Several nearly immiscible organic liquid pairs were selected for the flight experiment, and the interfacial tension determinations were to have been performed at room temperature. Since several simpler techniques are available for making such measurements on Earth (2-5), one might question the motivation for this flight experiment. In response, however, one should note that the use of conventional methods for measurement of liquid-liquid surface tension at high temperatures are fraught with difficulties (6) and in some instances not possible. Thus, the use of a contactless, low-gravity technique for making such measurements is highly desirable. The low gravity requirement stems from the fact that there can be significant density differences between the droplets, and this feature precludes the execution of such experiments in a 1-g levitator.

Hence, the room-temperature liquid-liquid flight experiment was viewed as a logical prelude to a more difficult high temperature glass experiment which would have been conducted on a future flight. The interfacial tension data which were to have been generated from the microgravity study were to have been compared with values obtained from ground-based measurements (7) employing methods which are standard for measuring liquid-liquid interfacial tensions at room temperature and under 1-g conditions. Thus, the flight experiment was to have demonstrated the feasibility of the method.

The reason that the measurement of the liquid-liquid interfacial tension between immiscible solutions at high temperature is important relates to the problem of liquid-liquid phase separation in glass forming systems. There have been theories developed to predict the kinetics of the different types and various stages of phase separation processes. An initial nucleation process, intermediate growth processes, and a final coarsening process can be distinguished. There have been many experimental investigations conducted to test these various theoretical mechanisms. However, there have been only a few attempts to quantitatively compare theory and experiment. For the simpler binary glass compositions which should be most amenable to theoretical treatment, a major stumbling block has been the unavailability of sufficiently accurate values of some of the needed thermodynamic parameters, in particular, those for the interfacial tensions between co-existing phases. The accurate determination of the interfacial tension for the separating phase in a single simple glass system should allow, for the first time, a critical test of the essential correctness of some of these important kinetic theories.

In summary, the specific goals of the flight experiment were: (1) to determine the liquid-liquid interfacial tension between immiscible liquid pairs via the rotation of a compound droplet, (2) to determine the rotation rates at which bifurcation of compound droplets occur, and (3) to ascertain if "burst through" (i.e. penetration of inner droplet through the outer) could be evoked under appropriate conditions.

## I. BACKGROUND

Three sets of partially immiscible organic liquid pairs were chosen for employment on USML-1. These were (1) ethylhexyl acetate (EHA) / 1,2-propanediol (P); (2) 2-octanol (O) / formamide (F); and (3) 1-nonanol (N) / formamide. The first liquid given for each of these sets is the liquid of lower density, which becomes the inner droplet of the compound drop. In addition, the denser liquids contained trace concentrations of 55  $\mu\text{m}$  cross-section aluminum particles, which were introduced to allow accurate determination of the angular velocities of the compound drops. Four experimental runs were planned using the EHA/P pair in the first and fourth runs, the O/F pair in the second run, and the N/F pair in the third run.

The above liquid pairs were selected from more than one hundred totally or partially immiscible organic liquid pairs which were considered based upon the following criteria:

1. Density differences between pair liquids should be as large as possible.
2. Interfacial tensions should be as small as possible (and less than 5 dynes/cm).
3. All of the flight liquids must be non-explosive, of low combustibility, and of low toxicity.
4. All liquids must have relatively low vapor pressures, and the denser liquids should have very low vapor pressures to avoid appreciable evaporation in the DPM chamber.
5. The refractive index differences between inner and outer liquids should be sufficiently large as to allow their interfaces to be readily optically visible.

The five liquids and their respective pairs listed above were found to be acceptable according to these requirements. The interfacial tensions of these pairs, which were measured in our laboratory, ranged from 1.5 dynes/cm for the EHA/P pair to 3.4 dynes/cm for the N/F pair. Also, the density of each liquid when saturated with its pair liquid was determined in our laboratory by two independent methods, and the density differences found to be satisfactory. Information concerning the other parameters was obtained from the literature for the pure components. These data are summarized in Table 1.

The saturated liquids for the flight samples were prepared by the following procedure. Three 250 ml separatory funnels (one for each liquid pair) were cleaned by washing with distilled water followed by washing with spectroscopic grade acetone. The contents from bottles (100 ml each) of octanol, nonanol and propanediol were then poured, respectively, into the three funnels. To each of the first two sep funnels 100 ml of formamide was added, and to the third sep funnel 100 ml of ethylhexyl acetate. Then each sep funnel was closed with its glass stopper and shaken vigorously for about one minute until the liquid pair contained within formed a single homogeneous emulsion. The sep funnels were placed upright in ring stands and the liquids allowed to re-separate (a process which required less than one minute for the O/F pair and nearly 30 minutes for the EHA/P pair). The emulsifying and re-separating procedure was repeated an additional five times over a two day period. After the final agitation, the

heavy and light liquid fractions were allowed to segregate over a two day period. The room temperature during this time was 25-26 °C. The heavier bottom fractions were drained through the bottom glass stopcocks of the sep funnels into Erlenmeyer bottles (having screw-on lined plastic caps). These heavier liquids were drained to about 1 cm from the horizontal interface layer which indicated the separation of the heavy and light fractions. About 10 ml of the middle fraction about the interface (which contained both heavy and light liquids) was drained off from each sep funnel. Finally, the remainders of the lighter upper liquids were drained into bottles. All bottles were appropriately labeled, with each bottle containing about 95 ml of saturated liquid. Each bottle was visibly inspected and its contents noted to be clear and single phase. About 25 mg of 55 µm aluminum powder was then weighed out and introduced into each of the three bottles containing the formamide and propanediol. Each bottle was then capped and sealed. The manufacturer label information concerning the chemicals and aluminum powder used is shown in Table 2.

## II. FLIGHT RESULTS

The procedure which was specified for the execution of the flight experiments is described below. Each compound drop was to have been prepared in the DPM chamber as follows: A precise measured volume of the liquid pair member of greater density containing the dispersed aluminum tracer particles (with a density of about 1.1 g/cm<sup>3</sup>) was to have been deployed first. Next a precisely measured volume of the less dense liquid was to have been injected into the denser drop. For each drop rotation experiment, an incremental increasing acoustic torque was to have been applied to produce equilibrium drop angular velocities from a minimum of about 2 radians/sec to a maximum of from about 8 to 12 radians/sec, depending upon the characteristics of the particular sample. The particular rotation rates were chosen to produce axial ratios of the distorted inner drop of about 1.1, 1.2, and 1.3, after the shape had equilibrated at a given constant velocity.

After a drop shape and rotation rate had equilibrated, high speed filming was to have been conducted. Filming at frame rates of 100-400 frames/sec for 3 sec per measurement or 12 sec per sample was required. For the short time periods indicated above, two orthogonal high resolution cine or video pictures of the sample were to have been taken, with one of the cameras having its axis coinciding with the rotation axis of the drop. Single frame fields of view were required to be 2.7 x 2.7 cm with a linear resolution of 20 µm. Also, combinations of lens aperture/film rate/lighting to obtain sharpest focus of entire compound drops and view of inner droplets were to have been tested pre-flight under simulated Spacelab conditions to verify the adequacy of the resolution in the film data, and to set the employment conditions for these parameters for the Spacelab experiments. Finally, a dedicated real-time video downlink between the experiment operator and the PI team was requested to be available during the

critical times of the experiment, such as during the creation and deployment of the compound drops and at each step just prior to recording the high speed film data.

In the first flight experiment the P and EHA immiscible pairs were to have been used. After a long delay, due to experiment set-up time and incorrect specification of injector tips, the outer droplet was deployed successfully. However, there was great difficulty in injecting the inner droplet, and the first several attempts failed. Eventually the inner drop was deployed, but with several unwanted consequences. In addition to the major inner droplet, several satellite droplets formed and a very large air bubble was introduced between the two fluids. The air bubble obscured the visibility of the inner droplet. Also, the lighting arrangement was so poor that the liquid-liquid interface was not detectable. Shortly after the formation of the compound drop, the time allotted for this experiment expired. Therefore, it is unlikely that any useful results will be obtained from this experiment although the video tapes are being analyzed currently.

The second flight experiment was an even greater disaster. The saturated octanol and nonanol solutions were observed to contain colored droplets. Since we couldn't explain their origin, NASA would not permit us to deploy these flight samples.

### **III. POST FLIGHT ANALYSIS (PFA)**

#### **A. PFA Goals**

The goals of the post flight analysis are: (1) to attempt to find causes for the problems encountered with the flight experiment fluids, and (2) to analyze the flight data for the first experiment. In order to pursue the first objective the sensitivity of the equilibrium compositions to temperature changes has been studied. In addition, potential contamination of the flight samples by water and/or a colored dye solution has been investigated. The analysis of the flight data is being performed at Clarkson University.

#### **B. Temperature Effects**

Since the equilibrium concentrations are functions of temperature, we measured the octanol-formamide and nonanol formamide binodals in order to gauge the sensitivity of the saturated formamide, octanol, and nonanol solutions to temperature excursions.

The experiment was conducted using a system consisting of a viewing cell partially submerged in an isothermal temperature bath (see Fig.(1)). Specifics of the bath varied with the experimental temperature range. A 16 liter transparent acrylic tank filled with water was used to collect all data below 90°C. To obtain data between 90°C and 150°C a 15 liter cylindrical glass tank filled with an ethylene glycol/water mixture was used. For temperatures above 150°C the heating bath consisted of a 2 liter

pyrex dish with mineral oil. The isothermal heater/circulator was capable of attaining a maximum temperature of 150°C, and thus for those points above 150°C a simple stirring hot plate was used to heat the oil bath. Regardless of the bath arrangement used, the heating solutions were stirred continually and the temperature was monitored with thermometers at several locations in the bath to ensure a constant and uniform temperature

The liquids used were used as received from the manufacturer (Aldrich) with no further purification. A complete list of liquids and properties can be found in Tables 2 and 1, respectively. These solutions were placed in a 25 ml cylindrical viewing cell with a magnetic stir bar spinning at approximately 700 rpm and partially submerged in the bath. Care was taken to keep the total solution volume between 5 and 10 ml so the stir bar was capable of stirring through the entire volume of liquid and not just the bottom fraction. The viewing cell was sealed with a septum at all times while in the heating bath to prevent moisture from entering. A small gauge needle was placed through the septum to prevent the pressure from building up at higher temperatures.

Data points were obtained by heating a solution of predetermined composition until it cleared and there was no visual evidence of a second phase. The clear solution was then cooled slightly until it clouded or a second phase appeared. This procedure was repeated three times or until a consistent clearing temperature was observed. These temperatures were recorded and used as data to construct the binodal curves. The composition was then altered by adding a small known amount of one of the liquids and the heating/cooling procedure was repeated for that composition. At temperatures above 150 °C new liquids were used for each repeated measurement since there was some concern about reaction and/or decomposition of the solutions.

The results of these measurements are shown in Figs. (2) and (3), which are the binodal curves for the octanol-formamide and nonanol-formamide pairs, respectively. These two curves are nearly identical, both exhibiting steep slopes on the formamide rich side and much smaller slopes on the formamide poor side. This feature indicates that at room temperature the saturated octanol and nonanol solutions should be much more sensitive to temperature deviations than the saturated formamide solutions.

This result explains why the saturated octanol and nonanol solutions showed a much greater tendency to phase separate than the saturated formamide flight samples. In particular, a simple calculation employing the lever rule shows that 3.2 ml and 3.8 ml of liquid will phase separate when 100 ml of saturated nonanol and octanol solutions are cooled from room temperature to 0°C. Since we were not informed of the thermal history experienced by our flight samples, we are unable to compute the anticipated degree of phase separation. However, we can conclude that it is highly probable that the

small extent of phase separation experienced by several of our flight samples was due to unwanted temperature excursions.

### C. Water

As was mentioned, the saturated octanol and nonanol in the returned flight syringes were both contaminated with several or more ml of bluish-green foreign droplets. A further objective of the first PFA goal was to determine the chemical identity of these colored droplets and to ascertain how they might have gotten there. Since water is largely insoluble in either octanol or nonanol, we sought to determine if they might have been contaminated by the green-colored aqueous dye solution used in other of the DPM experiments.

However, IR analysis of small droplets extracted from the foreign colored liquids in the octanol and nonanol showed them to be mostly or almost entirely formamide and not mostly water. Since the saturated octanol and nonanol solutions contain about 24 mol % formamide each, and since formamide is completely soluble in water, the following experiments were conducted to determine if water might somehow have been introduced into the syringes and caused the formation of the colored formamide drops.

- 1) The solubility of water in pure octanol and nonanol was measured and determined to be about 5 wt % in each.
- 2) The effect of adding 1% and 10% water to pure formamide and to formamide saturated with octanol and nonanol was observed, and the IR spectra of these solutions obtained. It was noted that these additions of water caused no visual change to the formamide liquids and no new liquid phase to form. However, the most intense IR band of formamide at  $3350\text{ cm}^{-1}$  was found to broaden somewhat with the addition of water (due to the overlap of the fundamental OH stretch band in this same region).
- 3) The effects of adding several drops of water to saturated solutions of O/F and N/F were observed. In these experiments the solutions + water were shaken and then allowed to stand for a total of four days. Immiscible droplets settled from each solution. The N/F droplet increased in size with time, but the O/F droplet appeared to remain a constant size. The immiscible droplets were extracted and their IR spectra were obtained. The IR spectrum from the (O/F + water) droplet was found to be essentially identical to the F/O + 1% water spectrum. The IR spectrum of the (N/F + water) droplet was also found to be very similar to the F/N + 1% water spectrum, but even more similar to the spectrum of pure F/N.

The IR spectra of the foreign colored droplets in the O/F and N/F flight syringes were compared with the spectra of the prepared solutions described above. As was mentioned earlier, it is clear from

these comparisons that the colored syringe droplets are mostly formamide. However, it is inconclusive as to whether or not the colored droplet in the octanol also contain water, due to the similarity of the spectra. The spectrum of the droplet from the nonanol syringe is most similar to that of pure formamide without added water.

#### **D. Contamination**

The returned flight syringes showed three separate signs of contamination: (1) the octanol in the syringe was yellow instead of being colorless as sent, (2) the octanol syringe contained blue-green droplets of a second immiscible liquid, and the nonanol syringe contained a blue foreign drop, and (3) most of the syringes contained varying amounts of blue flakes around their metal tips. A further goal was to investigate the source of this contamination.

The blue flakes in the tips of the octanol and nonanol syringes were extracted for experimentation. They were found to be completely insoluble in pure octanol, nonanol and formamide. They also appeared to be completely insoluble in water, acetone and alcohol. It was thus not possible to obtain their IR absorption spectrum. It was conjectured that the flakes might be the remnants of some lubricant (possibly silicone grease) that was employed. At any rate, they were apparently not related to the green dye, since they were not water soluble.

The dried McCormick green food color dissolved readily in pure formamide and in the F/O and F/N solutions to form greenish solutions. The IR spectra of these colored solutions were all identical to that of pure formamide. Thus, it was not possible to determine the source of the color of the droplets in the octanol and nonanol syringes by the use of IR spectroscopy.

The dried McCormick green dye would only partially dissolve in the N/F solution to form a blue solution. The dye would not dissolve at all nor color the O/F solution. Hence, this dye does not appear to be the source of the yellow color of the octanol in the returned flight syringe.

#### **CONCLUSIONS**

Our tentative conclusions regarding the flight experiment are as follows:

- (1) The small degree of phase separation exhibited by several of the flight samples was probably due to temperature variation experienced by these fluids prior to flight, although
- (2) Small quantities of water (less than 1%) will cause perceptible phase separation in the octanol and nonanol solutions.
- (3) Several of the flight samples were contaminated either during loading into the syringes or some time thereafter.



(4) Although we have not excluded the possibility that the food dye was the source of the colored droplets, this possibility seems unlikely since the dye did not dissolve in the saturated octanol solution.

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Table 1

## PROPERTIES OF LIQUID PAIRS

Property	Pair 1 <u>EHA/P</u>	Pair 2 <u>O/F</u>	Pair 3 <u>N/F</u>
interfacial tension* (dyne/cm)	1.5	3.3	3.4
surface tension* (dyne/cm)	<u>25.3</u> 28.0	<u>25.1</u> 29.4	<u>27.0</u> 29.1
density* (g/cm <sup>3</sup> )	<u>0.8774</u> 1.0376	<u>0.8422</u> 1.1171	<u>0.8490</u> 1.1279
refractive index** (n <sub>D</sub> <sup>20</sup> )	<u>1.4204</u> 1.4331	<u>1.4203</u> 1.4475	<u>1.4338</u> 1.4475
viscosity** (cm <sup>2</sup> /sec)	<u>0.017</u> 0.541	<u>0.095</u> 0.034	<u>0.135</u> 0.034
boiling point** (deg C)	<u>198.6</u> 188.2	<u>179</u> 210.5	<u>215</u> 210.5
flash point** (deg C)	<u>82</u> 107	<u>71</u> 154	<u>75</u> 154
vapor pressure** (mm at 25°C)	<u>&lt;0.1</u> 0.08	<u>0.158</u> 0.08	<u>0.024</u> 0.08

\*mutually saturated liquids

\*\*pure liquids

**Table 2**

**CHEMICAL INFORMATION SHEET**

Formamide  
Sigma Chemical Co.  
Lot #11H 1015  
Toxic

2-Octanol, 98%  
Aldrich Chemical Company  
Lot #04720LX  
Severe eye irritant

2-Ethylhexyl Acetate  
Kodak Eastman Fine Chemicals  
Lot #8091531240  
Causes skin and eye irritation

Propylene Glycol  
(1,2-Propanediol)  
Sigma Chemical Co.  
Lot #51H 0752  
Harmful by inhalation  
and if swallowed

1-Nonanol, 99%  
Aldrich Chemical Company  
Lot #05631MV  
Toxic

Aluminum Powder  
Grade: 5240  
Alcan-Toyo America, Inc.  
Lot #S071051  
Sieved: 53-75 micron range

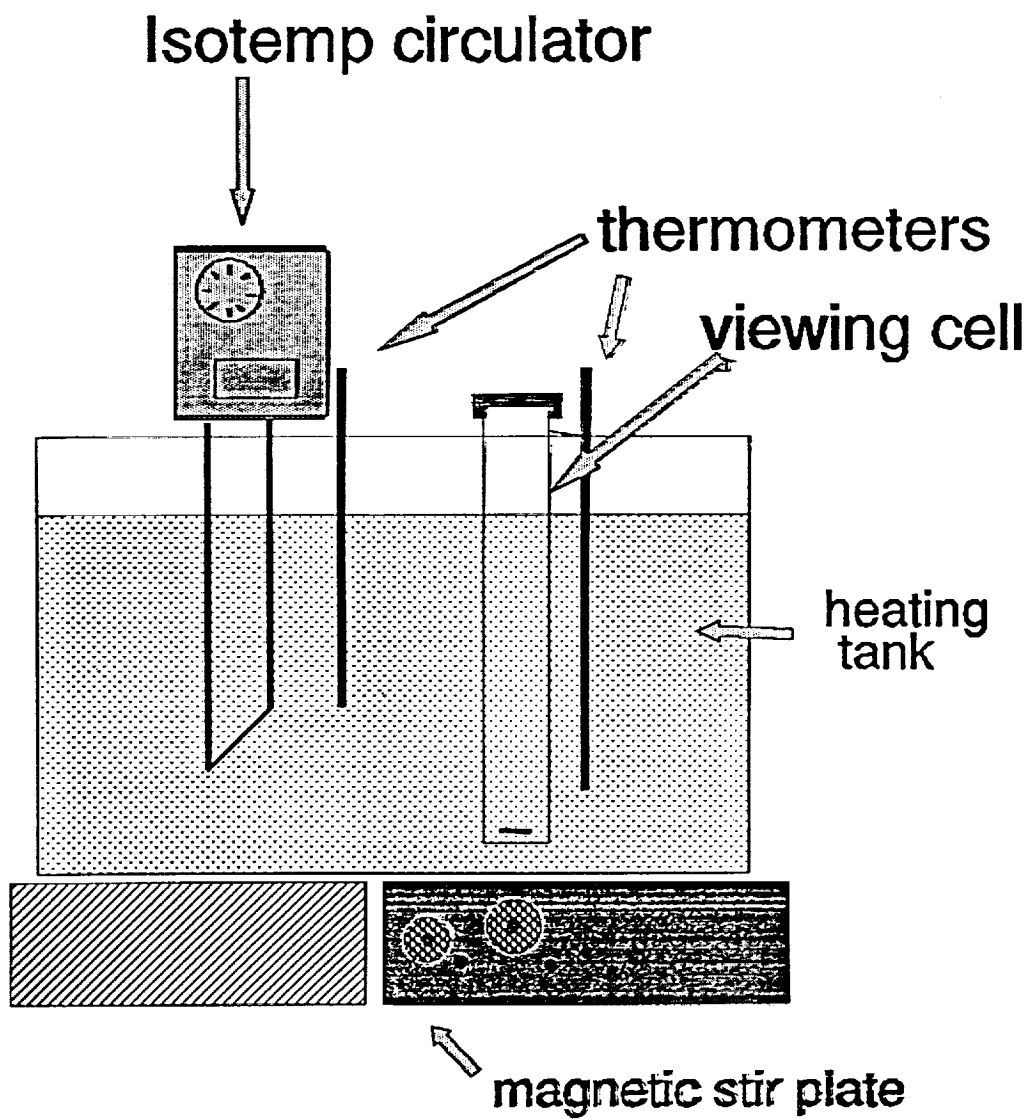


Figure 1 Schematic of experimental arrangement for measuring binodal curves.

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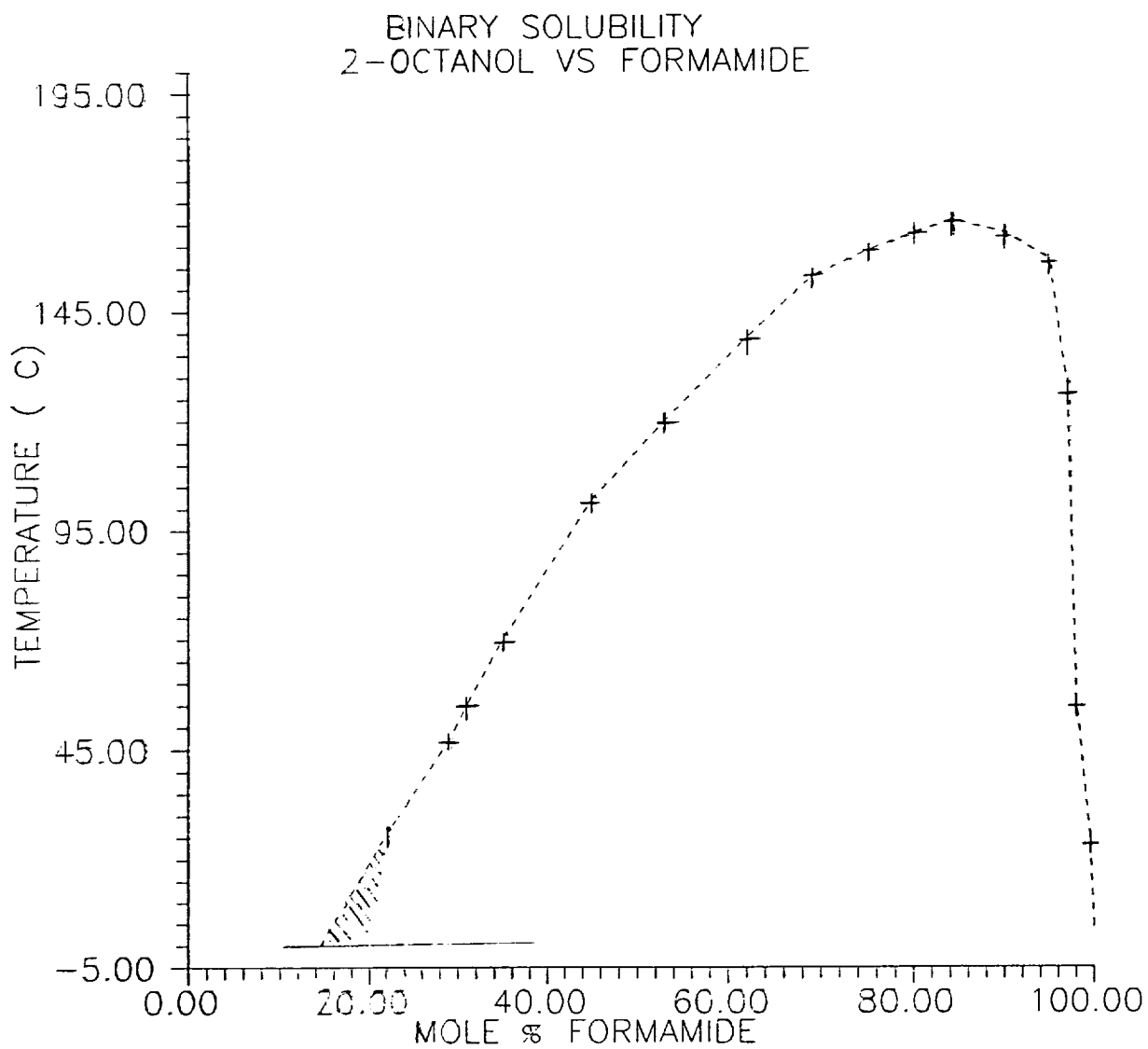


Figure 2 Temperature at which two liquid phases are at equilibrium vs. composition for the octanol-formamide system.

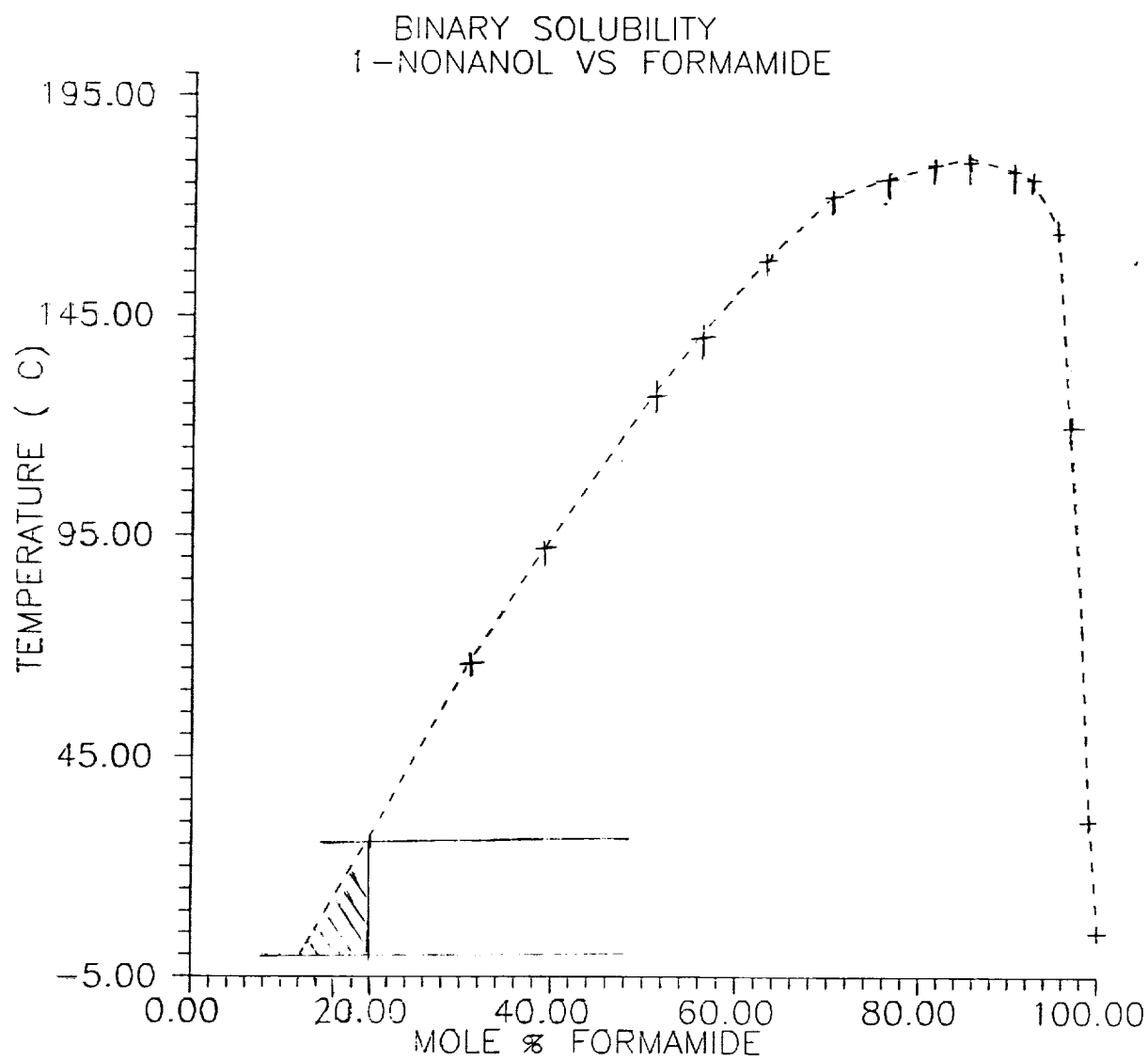


Figure 3 Temperature at which two liquid phases are at equilibrium vs. composition for the nonanol-formamide system.