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DETERMINATION OF THE SUCCINONITRILE-BENZENE AND SUCCINONITRILE-CYCLOHEXANOL PHASE DIAGRAMS BY THERMAL AND UV SPECTROSCOPIC ANALYSIS

By William Kaukler, Donald O. Frazier, and
Barbara Facemire

Space Science Laboratory
Science and Engineering Directorate

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16. ABSTRACT

Equilibrium temperature-composition diagrams were determined for the two organic systems, succinonitrile-benzene and succinonitrile-cyclohexanol. Measurements were made using the common thermal analysis methods and UV spectrophotometry. Succinonitrile-benzene monotectic was chosen for its low affinity for water and because UV analysis would be simplified. Succinonitrile-cyclohexanol was chosen because both components are transparent models for metallic solidification, as opposed to the other known succinonitrile-based monotectics.

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I. INTRODUCTION

The work described here served several purposes. There is a need to compile as many transparent model monotectic systems as possible. Each one offers a subtle difference in behavior. To date, the best model monotectics are based on succinonitrile. Succinonitrile is chosen because it has a convenient melting point, it is chemically stable, it can be readily purified and most importantly, it freezes as a metal does.

While finding new systems to study, it was also desired to generate the phase diagram by using ultraviolet spectroscopic techniques (UVS) rather than the old thermal analysis technique which is based on cooling curves. Of the model binary monotectics known to date, none had as the second component a metal model organic material. The prerequisite is that the material have a low entropy of fusion and a cubic crystal structure in the solid state as succinonitrile has. Cyclohexanol met these requirements.

Benzene was also a good candidate as the second component for two reasons. Composition measurements using quantitative UV spectroscopy would be facilitated when using benzene. Secondly, benzene is less susceptible to water contamination than all of the other candidate systems which, either by design or contamination, would contain some quantity of water. These other systems include: succinonitrile and water, deuterium oxide, ethanol, glycerol and methanol.

II. EXPERIMENTAL

A. Thermal Apparatus

The thermal analysis apparatus for both systems is shown in Figure 1. These organic materials allow use of very simple assemblies because the working temperatures are near room temperature. The device is a cooling-curve type constructed of glass to permit observation of the phase transformations as they occur. A thermocouple as a temperature monitor is sufficient to detect the onset of fusion or crystallization but not the crossing into the dome of the two-phase liquid region. This transition must be marked by direct observation.

The sample, thermocouple, and stirring bar were inserted into a plain, small glass bottle with screw cap. This assembly was placed on a warm stirring hot plate to homogenize the solution. After the solution was homogeneous, the specimen bottle was dropped into the jacketed glass bath. The solution temperature was monitored on a chart recorder. The stir bar kept the solution well mixed to ensure that it was isothermal. The jacketed bath sat on a magnetic stirring device.

FIGURE 1

CROSS SECTION THROUGH THERMAL ANALYSIS APPARATUS

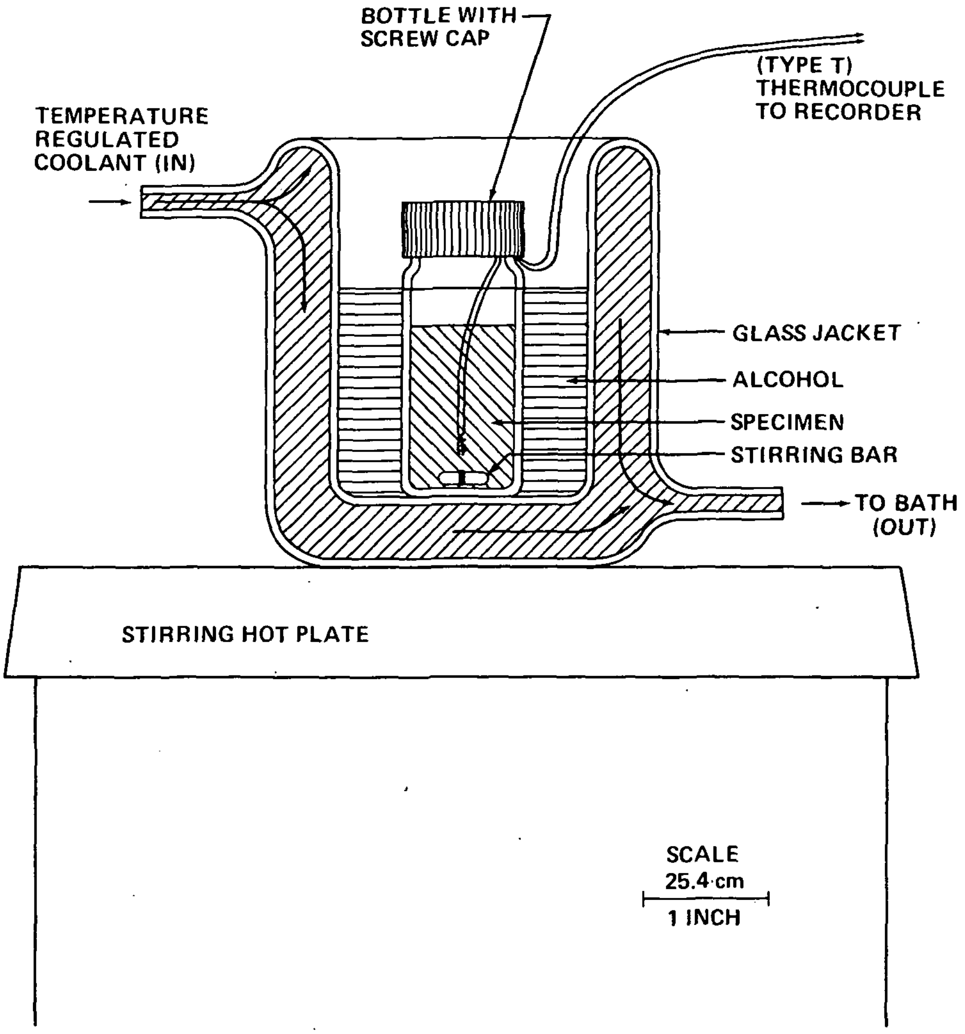

Figure 1. Cross section through thermal analysis apparatus.

The thermocouple junction was simply a twisted pair of wires (type T thermocouple) to ensure that the behavior would not deviate from the published tables. Use of an electronic ice point did not reduce accuracy because the measurements were made near room temperature. More uncertainty was found when interpreting the temperature tracings.

The jacket temperature was set to a point just below the anticipated "cloud point" or consolute temperature. In this way, the cooling rate was reasonably slow and occurred smoothly. A typical run lasted for approximately 20 min resulting in a cooling rate of about 1°C/min. After the cloud point temperature was noted, the bath temperature was reset to force the solution to freeze. The transition temperature was observed from the arrest point on the cooling curve. Again, the cooling rate was smooth and as slow as the water cooling system allowed due to its large thermal capacity. The specimen solution volume was approximately 10 milliliters.

B. UV Spectroscopy Apparatus

Benzene is well known as a calibration standard for UV spectroscopy. Under the best conditions, quantitative measurements of dilute benzene solutions in cyclohexane should be possible with one percent accuracy. It was not possible to measure succinonitrile concentrations with UVS because there were no absorption peaks in the wavelength range covered.

Standard solutions were prepared of benzene and cyclohexane to calibrate the instrument. Several solutions were used to cover the range of concentrations anticipated from making phase diagram measurements. Both high and low concentrations of benzene were anticipated because the system was an immiscible one. Specimens for UVS analysis were prepared by diluting the lower and upper phases of the succinonitrile-benzene system with cyclohexane.

The two phases were sampled from the mixture at a temperature 0.5°C above the observed freezing point of one of the phases. This liquid phase, on the bottom, was identified as liquid 1 having the monotectic composition. Therefore, the top phase became liquid 2. Because of the volatility of the benzene, rapid sampling and specimen transfers were essential. Where high dilutions were needed, a second dilution maintained the precision of the measurements. The concentrations were measured by weight and subsequent calculations made for volumes and molarities. Table 1 summarizes the samplings and dilutions.

A Heath spectrophotometer model 701 instrumented this preliminary evaluation. Fused quartz cuvettes contained the samples to allow analysis in the UV spectral range spanning the benzene spectrum (Fig. 2). This study relied on the indicated UV transitions. A calibration curve yielded the molar extinction coefficient (Section IV, A).

TABLE 1. SAMPLINGS AND DILUTIONS

Standards

ID	Molarity	Series
1	2.426×10^{-2}	2
2	2.154×10^{-3}	2
3	4.829×10^{-3}	2
4	7.617×10^{-4}	2
4	1.339×10^{-2}	1
7	1.233×10^{-3}	1
8	8.89×10^{-5}	1

Unknowns

ID	Dilution (w/o)	Series	Temperature (°C)
Top #5	0.21429	1	12
Top #6	0.02022	1	12
Bot #9	0.22488	1	12
Top	0.51729	2	21.9
Bot	0.45566	2	21.9
Top #2	0.06703	2	21.9
Bot #2	0.06791	2	21.9

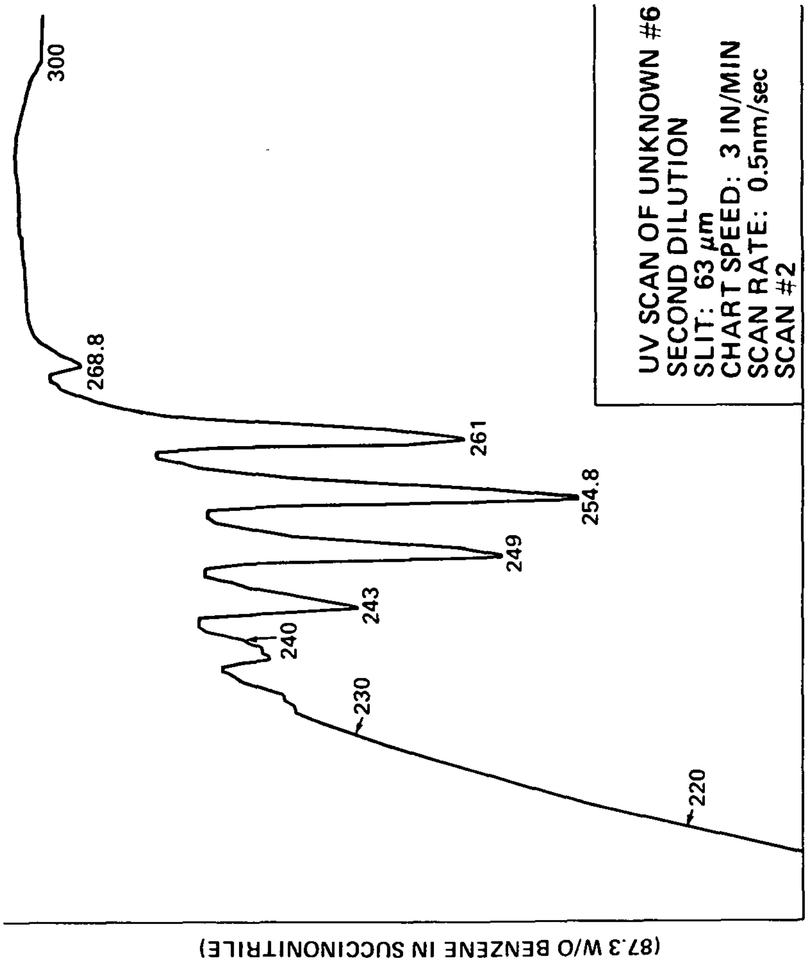

Figure 2. UV scan of unknown No. 6.

C. Material Preparation

The succinonitrile was purified by distilling twice under vacuum. The benzene was reagent grade from the supplier. The cyclohexanol was also reagent grade, but was dried over zeolite to minimize likely contamination by water. The UVS diluent, cyclohexane, was also reagent grade.

Succinonitrile and benzene solution sample preparation involved adding molten succinonitrile to room temperature benzene until there was approximately an equal volume of each phase as solutions. This mixture was cooled to determine which phase was liquid 1 by noting at what temperature it froze. The specimens for the UVS were taken from this mixture.

Each solution for thermal analysis was prepared in the same way. For each new sample, the succinonitrile was poured into the bottle and was weighed after it was capped and cooled. The required amount of the cyclohexanol or benzene was added to this specimen bottle, again to minimize vaporization losses. The weight was measured to the nearest ten thousandth of a gram. This made composition the most accurate parameter of the data.

III. RESULTS

A. Method and Measurements of UV Spectrometry

As mentioned before, a series of dilutions were prepared of both standards and specimens. A series of strong absorption peaks were found for the benzene solutions. Four peaks were selected to perform the quantitative measurements. For all dilutions there was no interference by other materials such as succinonitrile, water nor cyclohexane. Only the raw benzene absorption was seen. No shifting of peak maxima was seen as a function of dilution. The peaks selected to measure were at 254.7, 238.85, 233, and 268 nm (Fig. 2). The scans were performed with a slit width of 66 micrometers, deuterium lamp, scan rate of 1 nm per sec and with the pure cyclohexane control cuvette, the full scale deflection was set to 95 percent of full scale on the chart. Variation between cuvettes was tested with pure cyclohexane and a difference of 1 to 2 percent was found. In order to account for machine error, for each peak-height measurement of a sample or standard, another check was made of the pure cyclohexane standard. Once the peaks were selected, a simple switching of the sample or standard with the pure cyclohexane standard was performed four to six times and the measurements combined into a single reading. Peak height was measured from the shutter closed value to the peak maximum.

The specimen transmission was calculated from the ratio of the specimen peak height to cyclohexane peak height. This was done for each wavelength. The absorbance is calculated from the transmittance by:

$$A = -\log T \tag{1}$$

where

$$T = I/I_o \tag{2}$$

and I_o is the initial intensity of the monocromatic light beam; I is the intensity after the sample has absorbed the light.

Absorption is related to the concentration in molarity, M, and cell path length, b, through the Beer-Lambert laws for light absorption:

$$A = ebM \tag{3}$$

where the cell path length, b, is 1 cm. The Beer-Lambert laws require linearity and the proportionality constant, e, is called the molar extinction coefficient (Section IV.A).

Dilutions were measured by weighing, so calculations were made to determine the specimen molarities. As will be explained in Section IV.A, absorbance (A) versus molarity (M) was graphed first for the standards and then the specimen measurements were situated on the fitted lines from the standard data. This was done by locating the line for the wavelength of interest and then placing the sample value on the line at the corresponding level of absorbance. Reading down to the M axis will give the measured concentration of the specimen. Further back-calculations were made and the original composition determined before dilution by assuming the succinonitrile component did not contribute to the absorption.

Table 2 summarizes the over 200 individual measurements which are plotted as A versus M in Figure 3.

TABLE 2. UVS MEASUREMENTS

Standards			
ID	Wavelength (nm)	Absorbance	Series
Std 4	254.9	3.773	1
7	254.9	0.7174	1
8	254.9	0.0289	1
Std 4	243.2	2.8285	1
7	243.1	0.35905	1
Std 4	254.7	0.4493	2
2	254.7	1.146	2
3	254.7	2.4680	2
Std 1	268.6	0.7083	2
2	268.6	0.0541	2
3	268.6	0.20597	2
4	268.6	0.0573	2
Std 1	238.85	2.8698	2
2	238.85	0.2663	2
3	238.85	0.6900	2
4	238.85	0.13117	2
Std 1	233.85	1.778	2
3	233.85	0.4345	2
4	233.85	0.0948	2
Unknowns			
Top #5	254.9	3.884	1
Top #6	254.9	0.9137	1
Bot #9	254.9	2.9826	1
Bot #5	254.7	2.5314	2
	268.6	0.1538	2
	238.85	0.65225	2
	233.85	0.38714	2
Top #6	254.7	0.94527	2
	268.6	0.074137	2
	238.85	0.27966	2
	233.85	0.20024	2
Top #2	254.7	2.7209	2
	238.85	0.6485	2
Bot #2	254.7	0.9712	2
	238.85	0.2894	2

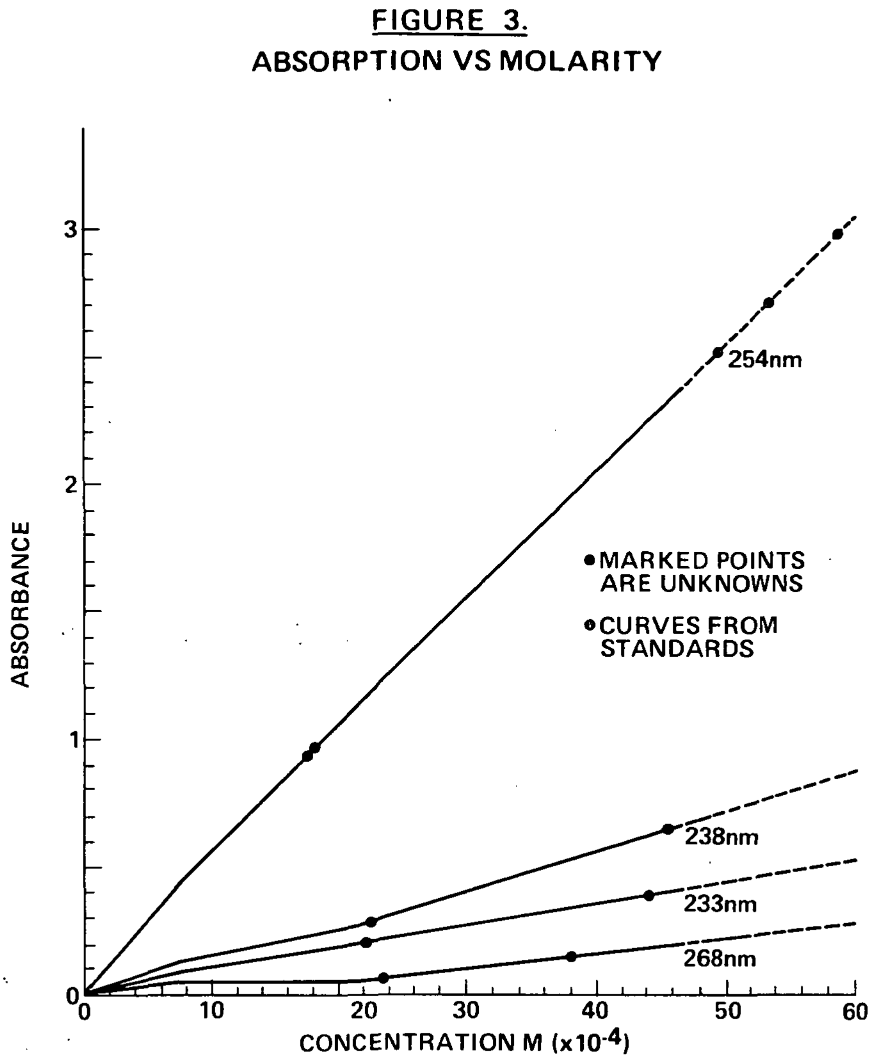

Figure 3. Absorption versus molarity.

B. Thermal Data

Thermal analysis by cooling curves was performed on both systems. Twelve separate samples of cyclohexanol-succinonitrile solutions and ten samples of benzene-succinonitrile solutions were prepared. Generally two cooling curves were made for each specimen. In addition, visual observations were made to track the behavior both on cooling and remelting. During these observations it was found that the eutectic temperature was never approached upon cooling but rather upon recalescence from varied amounts of undercooling (from 1 to 5°C). The eutectic temperature given is the value best representing the plateau portion of the curve. On occasion, as the composition diverged from the invariant point in question (either monotectic or eutectic), the thermal trace would not register the transformation. As a result some data points are not available for the diagrams which are presented as Figures 6, 7, 8, and 9.

The temperatures are summarized in Table 3. Two representative curves are given in Figures 4 and 5.

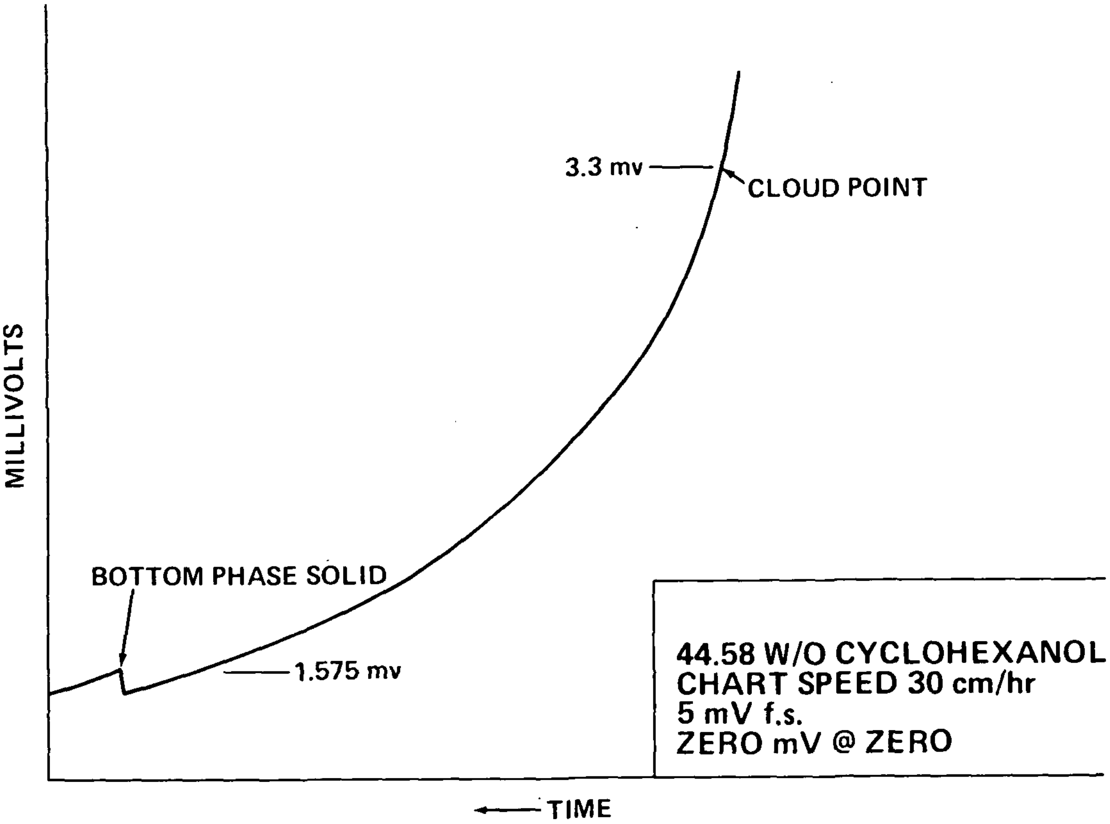

Figure 4. Cooling curve.

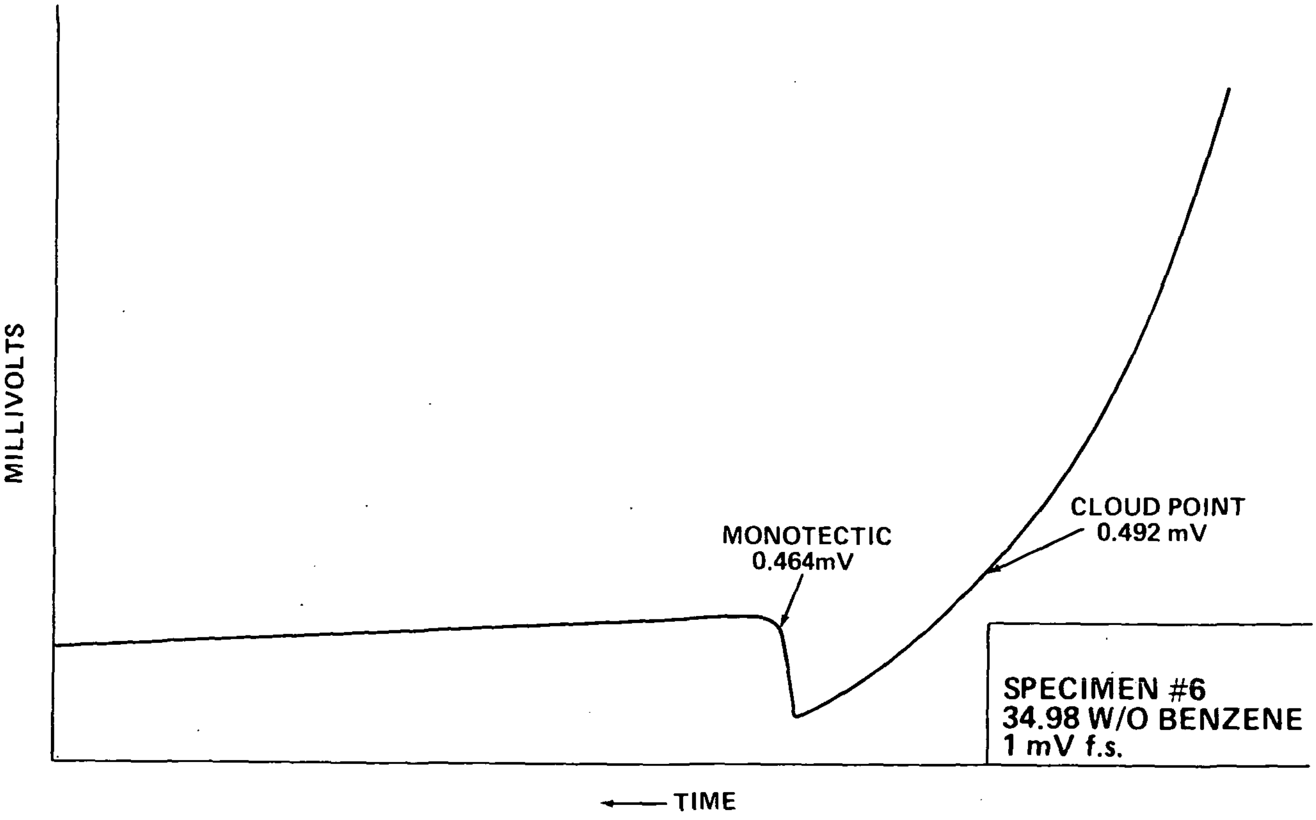

Figure 5. Cooling curve.

TABLE 3. TEMPERATURES

Succinonitrile-Cyclohexanol

Sample No.	Wt.% Cyclo.	Mole% Cyclo.	Temperatures (°C)
6	8.825	7.184	40.5, 43.9
2	14.301	11.773	40.5, 48.0
4	29.570	25.134	38.7, 70.0
7	44.588	39.151	38.8, 79.0
1	57.940	52.415	40.0, 40.1, 79.7
5	69.215	64.258	40.5, 79.0
12	85.017	81.940	68.0, 29.4
10	95.150	94.007	48.0

Succinonitrile-Benzene

Sample No.	Wt.% Benzene	Mole% Benzene	Temperatures (°C)
9	10.0860	10.315	35.41
7	20.0619	20.466	20.87, 21.557
1	29.9600	30.488	13.2
6	34.9800	35.551	13.5, 12.1, 12.05, 11.84
10	45.0420	45.662	29.901, 29.99
3	58.0430	58.651	39.5, 12.0
5	68.4970	69.035	40.0, 3.0
4	80.6000	80.988	33.5, 11.2
8	87.9900	88.252	15.075
2	89.8500	90.076	7.5

UV Measurements

Sample I.D.	λ	Wt.% Benzene	Mol% Benzene	Temperatures (°C)
B2	254	27.068	27.565	21.9
T2	254	79.185	79.595	21.9
T6	254	87.300	87.575	12.0
B5	254	30.290	30.821	12.0

IV. ANALYSIS

A. Extinction Coefficient

The tendency of a substance to absorb light is measured experimentally in terms of the molar extinction coefficient, e, and is defined by the equation:

$$e = -1/(M(2.303)\ I\ (dI/dx) \qquad (4)$$

where M is the molarity of the absorbing substance, I is the light intensity at some point x, and dI is the decrease in intensity that results when the light passes through a layer of substance dx thick. When this equation is integrated, one obtains:

$$I = I_o\ 10^{-eMx} \tag{5}$$

where I_o is the intensity of the light falling on the surface of the absorbing medium, and I is the intensity remaining after the light has traveled a distance x through the medium. These are the Beer-Lambert laws of light absorption.

If a bound electron is exposed to a beam of monochromatic light, of an appropriate energy for absorption, the electron will oscillate depending on the circular frequency, w, of the light wave. Practically, the electron motions will be much faster than that of a molecular vibration, and the positive nucleus in the environment is assumed stationary. The excited electron movements, therefore, set up an induced dipole moment, which when divided by the field strength, defines the polarizability of the atom which may be either in-phase or out-of-phase with the monochromatic light beam. Out-of-phase electron motions will dissipate the initial beam intensity into scattered radiation and heat. The rate of energy dissipation, W, per square centimeter is relatable to the molar extinction coefficient by the following. When a beam of light whose cross section is one square centimeter passes through a thickness dx of a medium containing n absorbing atoms per square centimeter, the energy dissipated in unit time is:

$$dI = -nW\ dx \tag{6}$$

then from equation (4),

$$e = nW/2.303\ MI \tag{7}$$

The absorption behavior of a substance should always be tested by constructing a graph of absorbance versus concentration. A straight line passing through the origin indicates conformity to the Beer-Lambert law. Lack of conformity may be attributed to failure of a chemical system to remain invariant. The extinction coefficient, e, may range from 10^5 liter mol^{-1} cm^{-1} for the strongest bands to 1 or less for very weak absorptions.

It is reasonable to assume that the most loosely held electrons will most easily undergo the electronic transitions necessary to absorb part of the light beam. To anticipate the relative energies of transitions, one should be mindful that sigma (σ) electrons are generally the most bound to nuclei and hence require a great deal of energy to undergo transitions, while pi and ni electrons require less energy (usually n < pi). Thus, $\sigma \rightarrow \sigma^*$ transitions fall in the far ultraviolet (up to 200 nm), pi → pi* and $n \rightarrow \sigma^*$ appear near the borderline separating the near and far ultraviolet (200 to 300 nm), and n → pi* come into the near ultraviolet and visible regions (300 to 700 nm). A strong benzene absorption band at 254 nm is most likely a pi -> pi* transition with no known measured molar extinction coefficient, in cyclohexane solutions previously reported. A linear plot of absorbance versus concentration indicates solution conformity to the Beer-Lambert laws.

Of the four wavelengths selected, the best results were obtained with the 254 nm data. One reason the results were felt to be disappointing was that the calculated values of the specimen compositions based on the four wavelength data were not mutually consistent. While the plots of A versus M were essentially linear as they should be for the standards, the positions of the unknown's compositions were not vertically lined up on each wavelength. In an effort to reduce the error in interpolating the compositions, the lines were fitted by least-squares. Also, because of the way solutions were prepared, a dilute approximation was used to calculate molarities, this however is readily justified with the very dilute solutions used here. The fitted equations for the lines on Figure 3 with the axis as labeled are:

254 nm wavelength, $A = 505.94\ M + 0.0445$

238 nm wavelength, $A = 140.3\ M + 7.8 \times 10^{-5}$

233 nm wavelength, $A = 89.9\ M + 3.8 \times 10^{-3}$

268 nm wavelength, $A = 40.2\ M + 6.8 \times 10^{-4}$

Clearly, the line with the largest slope will give the greatest accuracy when used to determine the concentration of an unknown from absorption data. Unknown concentration determinations, therefore, relied only on the 254 nm absorbance with a calculated extinction coefficient of 505.9 $1\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1}$.

B. Phase Diagrams

Four phase diagrams (Figs. 6, 7, 8, and 9) are presented which represent a compilation of both the thermal and UV analysis. The two sets of diagrams are given in terms of weight percentages and mole percentages. Unlike the succinonitrile and water or ethanol systems, these two methods of graphing the phase diagram do not differ significantly as the densities of the compounds are all similar.

The UV data account for four data points on the succinonitrile-benzene diagrams. From all the measurements made, those based on the largest peak of the four selected gave the best results. In fact, there was considerable variation between the values measured as one compares the different peaks. As a result, the results for the extinction coefficient and quantitative results are from the 254.7 nm curve only.

C. Eutectic Point Calculation

The liquid melt in the eutectic region is a dilute solution of succinonitrile in benzene. Assuming ideal solution behavior, the eutectic point itself should be consistent with the normal freezing point depression expected by solvent vapor pressure lowering (benzene cryoscopic constant, $k_f = 5.12$).

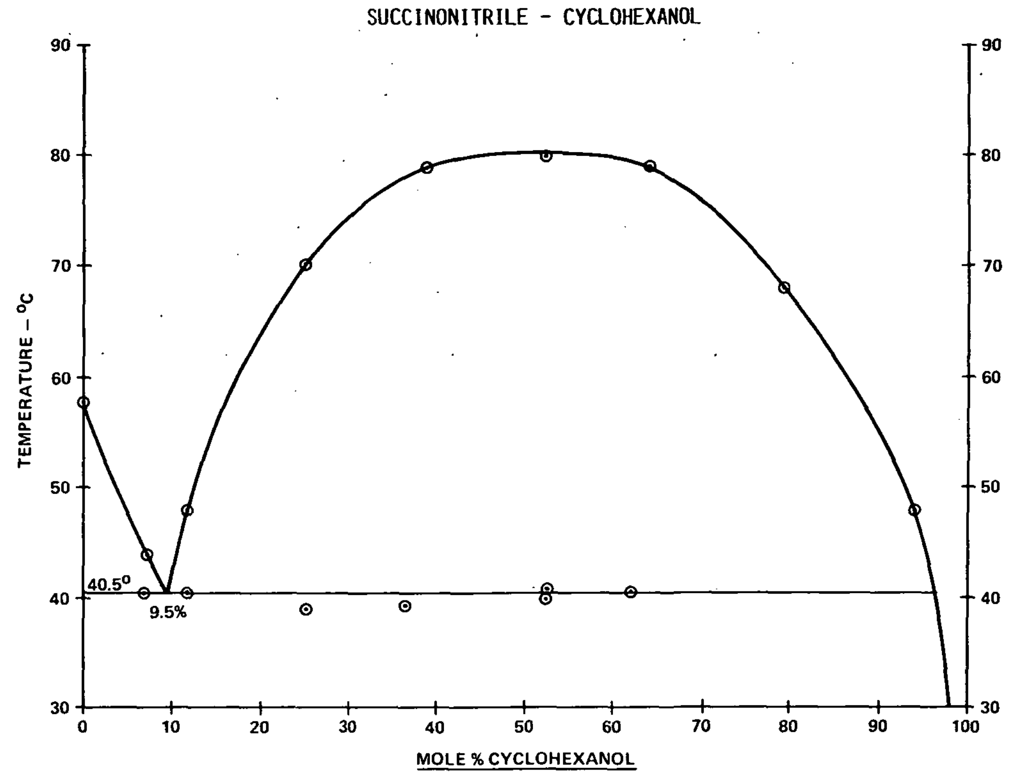

FIGURE 6

Figure 6. Phase diagram.

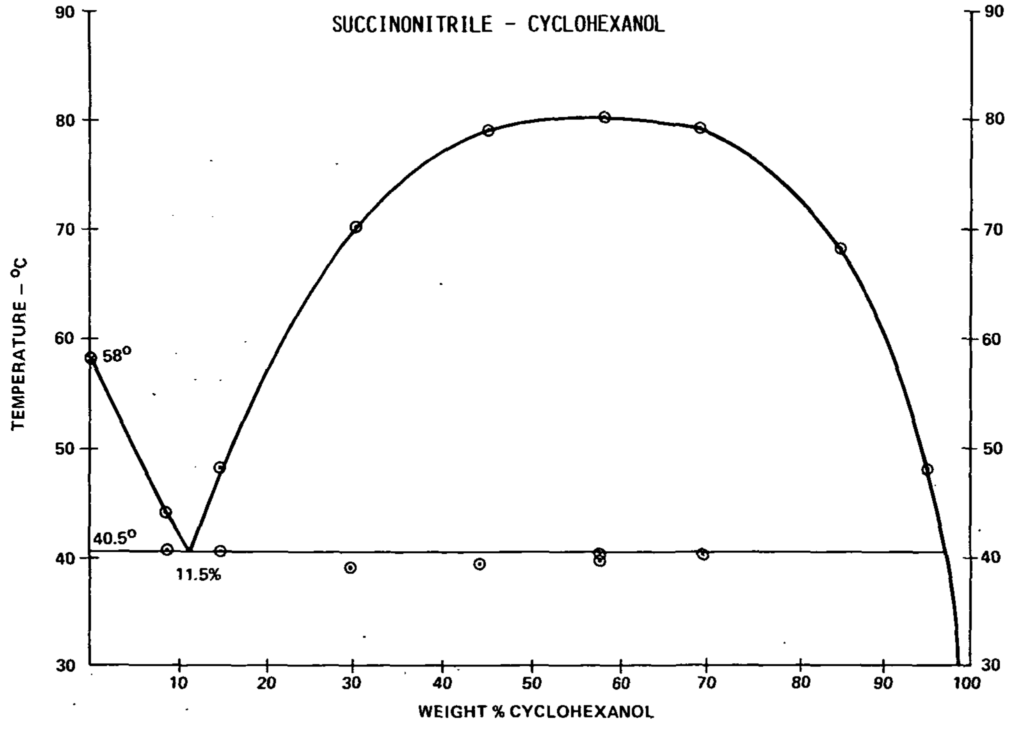

FIGURE 7

Figure 7. Phase diagram.

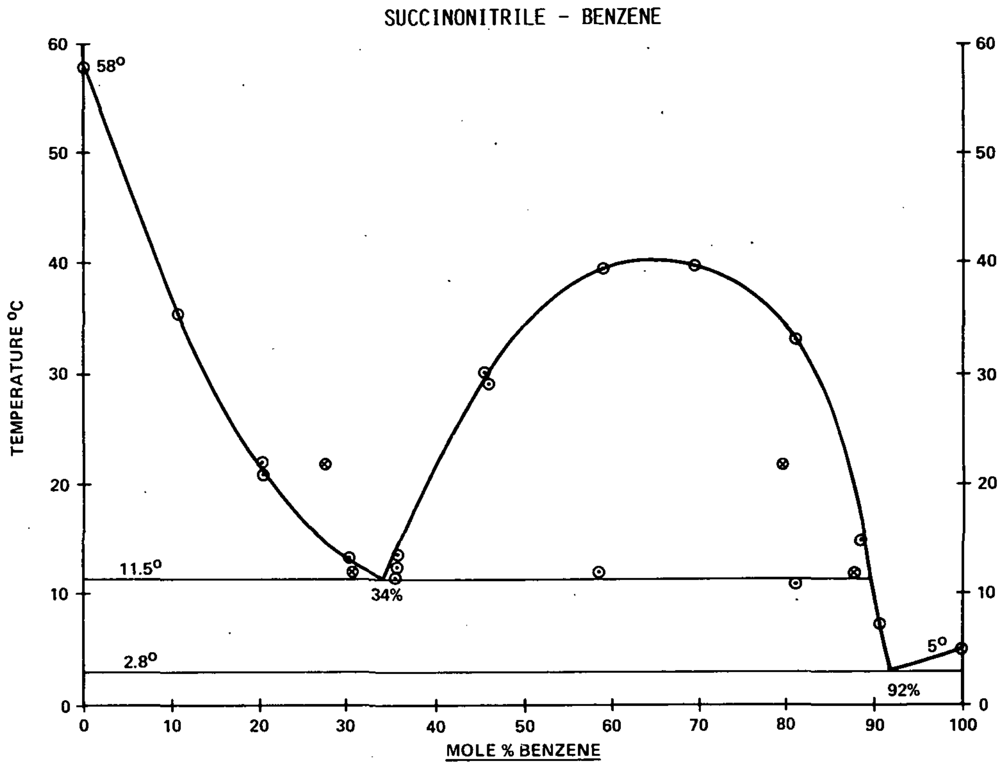

FIGURE 8

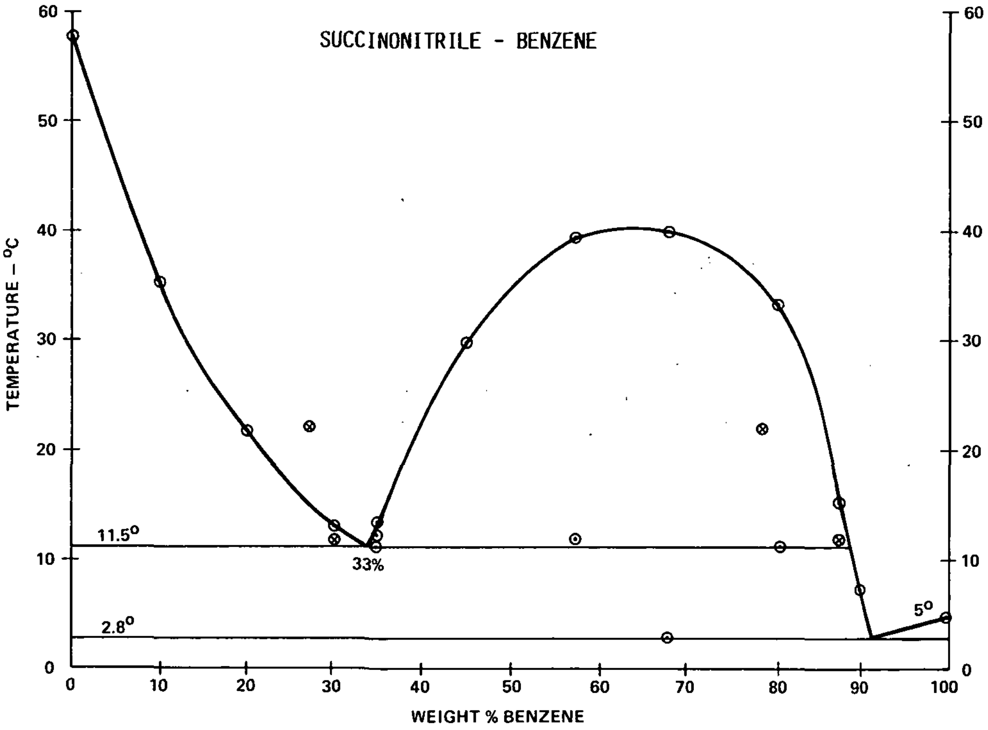

FIGURE 9

Figure 9. Phase diagram.

After determining the intersection of the liquidus and binodal curves, the composition at that point should estimate the corresponding temperature as a colligative effect. The phase diagram developed in this work establishes the eutectic composition at 91.63 wt.% benzene and a temperature of 2.8°C. The calculated temperature in this case is -0.340°C. Differences between experimental and calculated temperatures may be largely due to non-ideal solution behavior of the succinonitrile-benzene liquid phase; however, there are too few experimental points defining the liquidus line and the eutectic temperature to discuss fully the possibilities in the disagreement. Furthermore, impurities may be present in the benzene that would also distort colligative effects.

D. Error Estimate

The reading of the temperature has a confidence of 1°C; however, an accuracy of 2° is given overall because most of the measurements are based upon the relatively subjective determination of cloud point or thermal arrest. This should also account for errors caused by cooling at an accelerated rate. The thermal measurements will be repeated with better care and more objective determinations of temperature using laser-light scattering to determine the cloud point and monotectic temperature.

The UV analysis results were disappointing because the strong benzene absorption peaks should have made it possible to determine concentrations to within 1 percent. The difficulties encountered were vapor loss and equipment problems. If the phase diagram curves as determined by thermal analysis are considered accurate, then by comparison, the UV results differ by as much as 12 percent and as little as 2 percent by weight. Note however, that the compositions to test thermally for the benzene-based system were selected based on the UV measurements.

V. CONCLUSIONS

Very useful phase diagrams were obtained for the succinonitrile-cyclohexanol and succinonitrile-benzene systems. Points were determined using thermal (cooling curve) analysis and UV spectrometry. The two techniques were evaluated and compared for their future use in determining phase diagrams for organic systems. The ease of sample preparation, rapidity of analysis, higher accuracy and the ability to measure solidification transformations make thermal analysis the method of choice in this case. Future refinements would be to improve the approach to the UV spectrometry with emphasis on evaporation control and dilution techniques. Instrumentation capable of direct absorbance readings will eliminate the need to calculate absorbance from relative intensity measurements and reduce the errors.

APPROVAL

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The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

AJ Dessler

A. J DESSLER
Director, Space Science Laboratory

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