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Solid-Liquid Equilibrium in the Benzene-Pyridine System

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The complete solid-liquid equilibrium phase diagram has been determined for the benzene-pyridine system by a method of warming curve thermoelectric thermometry. The system is of the eutectic type with large regions of solid solution formation. The solidus curves and the curves representing the limits of mutual solid solubility below the eutectic temperature have been located.

LITERATURE on solid-liquid equilibrium in cyclic organic systems, especially those containing hetero atoms, is relatively rare. Wright (12) and Murray (6) have shown, in their investigation of the benzene-thiophene system, that pairs of organic substances form solid solutions because of fairly close similarity in the sizes, shapes, and electrical force fields of the molecules. The fact that thiophene forms a continuous series of solid solutions with benzene would seem to indicate that pyridine, being more similar to benzene in molecular structure, most certainly would, also. However, Pickering (7), Hatcher and Skirrow (4), and Kravchenko (5) have shown that the benzene-pyridine system is not of the continuous solid solution type but rather of the eutectic type.

This paper extends the work of the above authors and presents the complete solid-liquid phase diagram for the benzene-pyridine system.

EXPERIMENTAL

Materials. Baker's C.P. benzene, thiophene-free, was further purified by two fractional crystallizations followed by a fractional distillation from P₂O₅ through a 15-theoretical plate fractionating column. The center cut, collected over a 0.06° C. range, had a purity of 99.98 mole %, as determined by the warming curve method of Schwab and Wichers (9), and later described in greater detail by Glasgow, Streiff, and Rossini (3).

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Fisher reagent grade pyridine was refluxed over BaO for 2 days and then distilled through the above fractionating column. The center cut, collected over a 0.04° C. range, had a purity of 99.68 mole %.

Apparatus. The apparatus, which combined the features of the melting point calorimeter of Skau (10) and the semimicro heat conduction calorimeters of Andrews (1), Stull (11), and Ziegler and Messer (13), was a radiation-type calorimeter in which the sample was contained in a gold-plated copper can in the center of a hollow copper block which was wound with a heater coil. Thus, the sample was heated by radiation from the copper block. The whole block assembly was supported in an unevacuated, unsilvered Dewar flask immersed in an eutectic mixture of carbon tetrachloride and chloroform maintained at dry ice temperature. Temperatures were measured by a system of calibrated copper-constantan thermocouples.

Procedure. The various benzene-pyridine mixtures, each weighing 7 to 8 grams, were prepared in advance and sealed in glass capsules. The day before a run, the appropriate sample ampoule was broken and its contents were weighed quickly into the sample can to prevent exposure to atmospheric moisture. The can and contents then were placed in the calorimeter, slowly brought to dry ice temperature, and allowed to equilibrate overnight. The next morning the cooling bath was recharged with dry ice and the thermal head (defined as the temperature difference between the sample can and the surrounding copper shield) was slowly brought to approximately 140 μ v. (about 4.2° C.) by adjusting the heaters manually while

using a potentiometer-galvanometer setup for temperature measurement. The head control was then switched to a photoelectric cell, which kept the head constant at $150 \pm 1 \mu\text{v.}$ throughout the run.

Readings were taken at 25- $\mu\text{v.}$ intervals up the first break in the warming curve by setting the potentiometer 25 $\mu\text{v.}$ greater than the temperature of the sample and watching as the galvanometer light beam approached the zero point on the lamp scale as the sample temperature increased. When the light beam crossed the zero point, one stop watch was started and the other stopped, and the time interval and temperature were recorded.

When a flat portion of the curve was reached, the readings were taken approximately every 10 minutes. Thus, the sample was heated slowly, and readings were taken until the final break in the warming curve was passed and normal time intervals returned, indicating complete melting of the sample.

RESULTS

The pertinent data for the mixtures as determined from the time-temperature curves are given in Table I. Breaks in the warming curves were determined by plotting the thermometric data (in microvolts) on 19×24 inch graph paper divided into millimeter divisions, and extrapolating (2).

Typical warming curves showing eutectic and subsolidus solubility limit breaks are given in Figures 1 and 2, respectively. The complete phase diagram is given in Figure 3, where the data of Kravchenko and Pickering also are shown for comparison. In plotting Pickering's data, each point had to be raised by a factor of 7.9 times the mole fraction of pyridine because his "pure" pyridine had a melting point 7.9°C. lower than that used by both Kravchenko and this research, and consequently all of his points were low.

DISCUSSION

The liquidus points of Kravchenko and those of this research are in excellent agreement on the benzene side of the eutectic, while those of Pickering are slightly higher. However, on the pyridine side the reverse is found. The general shape of the liquidus curve is, however, the same in all three cases.

The eutectic point as determined from the phase diagram occurred at -57.7°C. and had a composition of 75.5 mole % pyridine and 24.5 mole % benzene, which is in close agreement with Kravchenko's results. In order to check the accuracy of this eutectic point, a warming curve (Figure 4) was run on a mixture having the determined eutectic composition and a purity determination made by the method of Schwab and Wichers. The close similarity of this warming curve to that of a pure compound, and the fact that the purity calculation showed the eutectic to

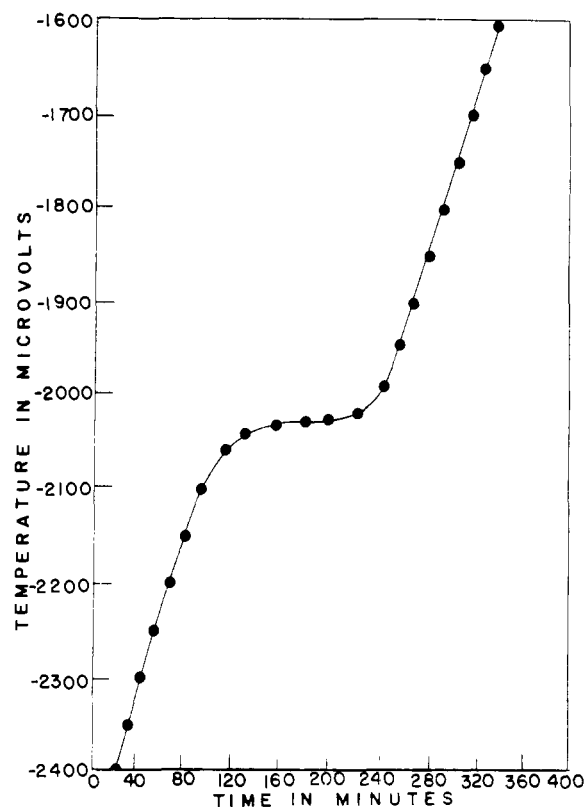


Figure 1. 0.351 mole fraction pyridine
Showing eutectic, solidus, and liquidus breaks
Temperature, microvolts
Time, minutes

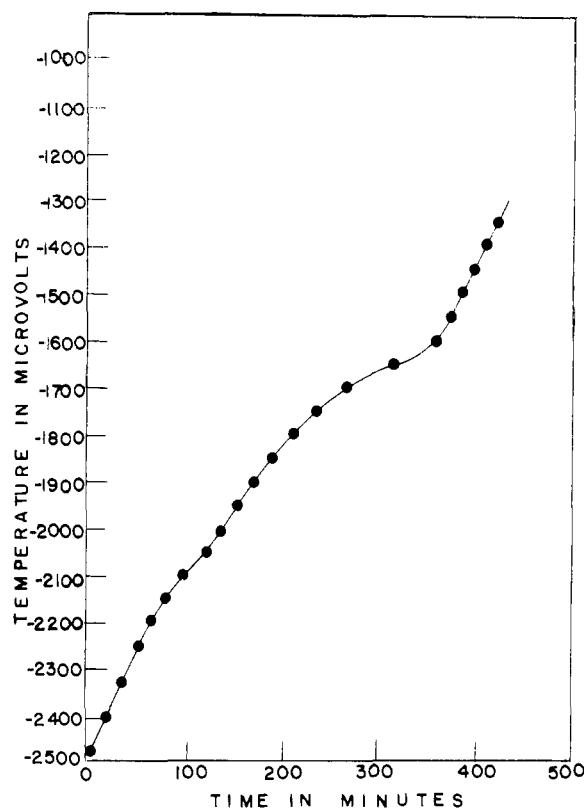


Figure 2. 0.943 mole fraction pyridine
Showing liquidus, solidus, and miscibility gap breaks
Temperature, microvolts
Time, minutes

Table I. Data for the Benzene-Pyridine System

Mole-Fraction, Pyridine	Liquidus, $^\circ\text{C.}$	Solidus, $^\circ\text{C.}$	Eutectic, $^\circ\text{C.}$	Subsolidus Solubility Limit, $^\circ\text{C.}$
0.0000	5.56	5.56
0.1092	-0.35	-32.78	...	-63.49
0.1911	-5.27	...	-58.74	...
0.3508	-16.05	...	-58.13	...
0.5010	-28.88	...	-57.94	...
0.7522	-57.03	...	-57.60	...
0.9154	-47.14	-49.11	...	-59.08
0.9433	-44.93	-48.88	...	-60.12
0.9791	-43.01	-46.41	...	-61.60
1.0000	-42.00	-42.00

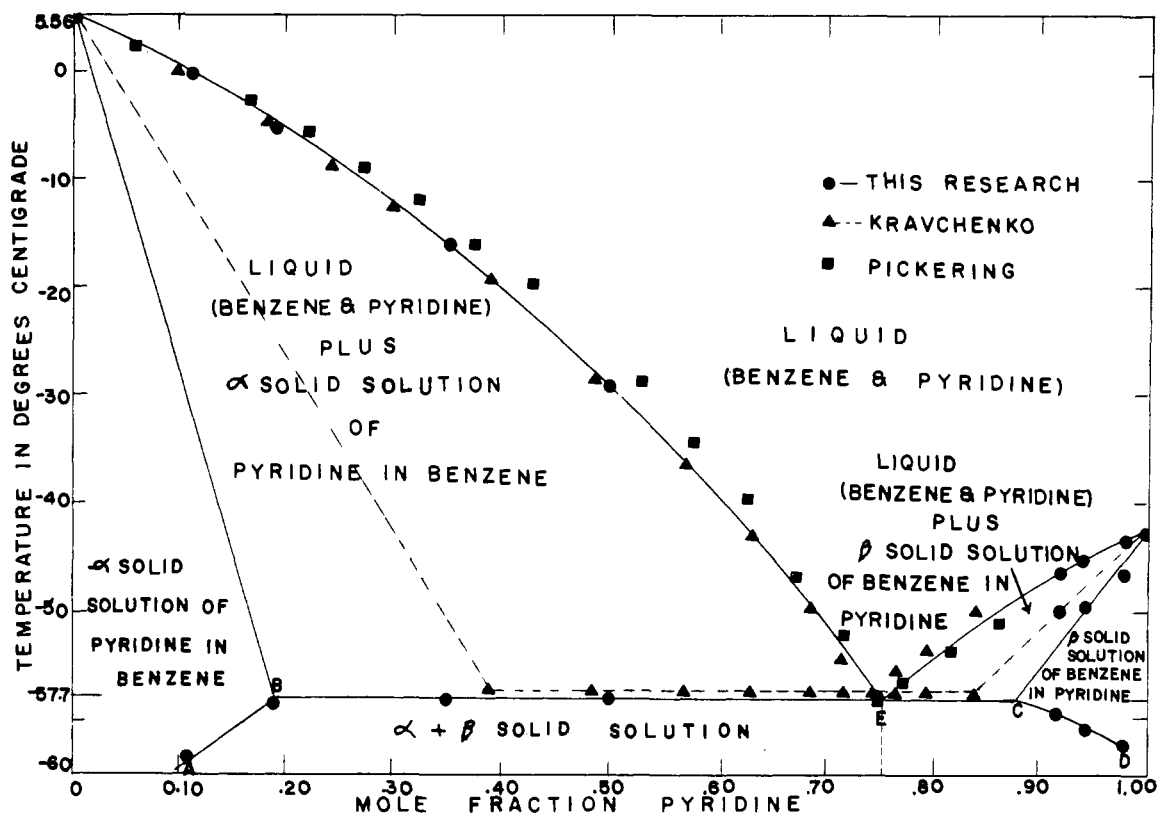


Figure 3. Benzene-pyridine system
Temperature, degrees Centigrade. Mole fraction pyridine

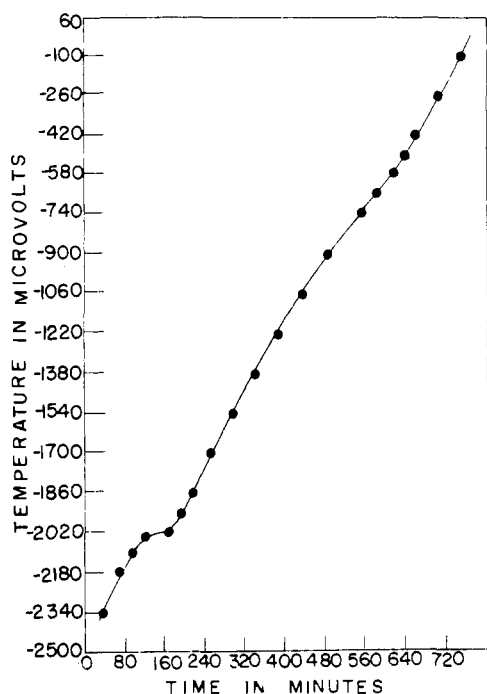


Figure 4. 0.752 mole fraction pyridine
Eutectic composition
Temperature, microvolts
Time, minutes

be 99.81 mole % pure further substantiated the accuracy of the eutectic point.

The eutectic arrest determined by this research extends from 19 to 87.5 mole % pyridine, while Kravchenko gives no solidus or eutectic data from 0 to 40 and from 86 to 100 mole % pyridine.

Mixtures of less than 19 and more than 87.5 mole % pyridine showed three breaks in their warming curves. The lower break in each case was below the determined eutectic temperature. The curves formed by these lower breaks (curves AB and CD in Figure 3) outline the miscibility gap (8)—i.e., they represent the limits of mutual solid solubility below the eutectic temperature.

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