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# Solidification Behavior of the Addition Compound and Eutectics between Picric Acid and Cinnamic Acid

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**The picric acid–cinnamic acid system shows a congruent-type phase diagram with two eutectics and one 1:1 addition compound. The linear velocity of crystallization and microstructures of the eutectics, addition complex, and components have been investigated. Stress–strain measurements of the eutectics and components have also been made. Attempts were made to determine the nature of interaction, present in the 1:1 addition complex.**

## Introduction

In recent years (*1*, *2*) there has been considerable interest in eutectic solidification. Studies indicate that there are organic compounds which solidify in the same way as metals do. These organic compounds and their mixtures have been used as analogues to study the solidification behavior of metals and metallic alloys. Most of the studies have been performed on simple eutectic systems, and only a few studies (*3–5*) on crystallization of eutectics of pure components and addition compounds have been reported. These types of systems are of great technical importance since they are common to many metallurgical systems.

In the present paper we have discussed the congruent-type phase diagram between picric acid and cinnamic acid. The solidification behavior and microstructures of eutectics and the addition complex have been discussed.

## Experimental Section

***Materials and Purification.*** Picric acid (BDH) was purified by successive recrystallization from absolute alcohol. Cinnamic acid (BDH) was purified by recrystallization from hot water. The melting points of pure samples of picric acid and cinnamic acid were 122.0 and 133.0 °C, respectively. The reported values of melting points are 122–3 and 134 °C, respectively (*6*).

***Phase Diagram Study.*** The phase diagram of the picric acid–cinnamic acid system has been studied by the thaw melt method (*7*). Mixtures of various compositions were prepared in glass test tubes by repeated heating, chilling, and grinding in a glass mortar. the melting points and thaw points (start of melting temperature) were determined with a mercury thermometer correct to ±0.1 °C.

***Undercooling Study.*** The undercooling study was made in a manner as described by Rastogi and Bassi (*8*). About 5 g of the mixture or pure components was taken in the test tube. The mouths of the test tubes were sealed and immersed in a bath of paraffin liquid maintained at a temperature of 20 °C above its melting point to destroy any germ nuclei. The bath liquid was stirred by an electric stirrer. When the mixture was completely melted, the heater was stopped. The bath was cooled down with a constant rate and the stirrer was regulated slowly so that there were no jerks due to stirring on the test tube containing the mixture. The difference between the melting temperature and the temperature for the formation of the first nuclei (observable) gave the undercooling value.

***Linear Velocity of Crystallization.*** The linear velocity of crystallization was determined by the technique described by Rastogi and Chatterji (*9*). A glass U-tube (internal diameter = 0.6 cm) with a 15-cm-long flat portion was used for the crystallization study. The tube was filled with the material, which was then melted at a temperature slightly above the melting points to remove any air bubbles. The tube was then kept at a temperature of desired undercooling and a seed crystal was introduced from one end of the tube. The crystallization velocity was measured as a function of time.

***Study of Microstructures.*** The microscopic method was used for the study of microstructures of eutectics, components, and the addition complex. A glass slide was placed in an oven maintained at a temperature slightly higher than the melting points of the material. A very small amount of the substance was kept on the slide. As the sample melted completely, the cover slip was slid onto it. The slide was allowed to cool, and care was taken to provide unidirectional solidification. The photographs were taken under a microscope.

***Dipole Moment Measurement.*** The dipole moment of the 1:1 addition compound of cinnamic acid–picric acid in benzene was measured with the help of a Dekameter (Type DK 03, Wissenschaftlich-Technische Werkstatten, Weilhiem, Germany) at 25 °C. The temperature was maintained by circulating water around the cell from a thermostat. The instrument was calibrated with liquids of known dielectric constants. The refractive index of solutions in benzene was measured with a Carl Zeiss refractometer. The dipole moment was estimated by the method followed by Richards and Walker (*10*).

***Stress–Strain Measurement.*** Stress and strain measurements of components, 1:1 addition compound, and eutectic in the form of pellets were determined by an universal testing machine. The pellets were prepared by solidifying the molten materials in glass test tubes of uniform diameter, and the surfaces were smoothed by rubbing on a emery paper. The data are given in Table VI.

***UV and Visible Spectral Studies.*** Absorption spectra of picric acid, cinnamic acid, and their complex in methanol and benzene in the ultraviolet and visible regions were obtained with a (Spectronic 2000, Bausch & Lomb) spectrophotometer. The spectra are given in Figures 2 and 3.

***DSC Studies.*** Heat of fusion measurements of components, the 1:1 addition compound, and eutectics were made by a differential scanning calorimeter (instrument Model 910 differential scanning calorimeter supplied by Du Pont Instruments U.S.A.). The heating rate was 5 °C/min.

## Results and Discussion

Phase diagram studies show that picric acid forms a 1:1 addition complex with cinnamic acid (Figure 1; Table I). The undercooling values are also given in the same table. In order to decide the nature of interaction present in the addition complex UV and visible spectroscopic measurements were made in methanol and benzene (Figures 2 and 3). The results indicate that the absorption curve for the complex is simply a summation of the absorptions of the individual components indicating that either the complex is dissociated in solution or there is no interaction. The heat of fusion measurements of the components, the 1:1 complex, and the eutectics are given in Table II. The heat of fusion of 1:1 complex is lower than

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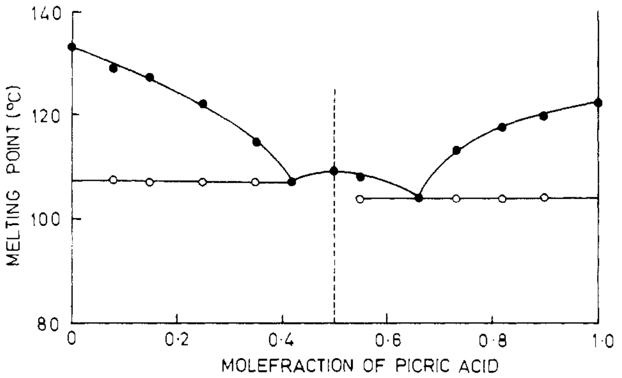

**Figure 1.** Phase diagram for picric acid-cinnamic acid eutectic system. (●) melting temperature; (O) start of melting temperature.

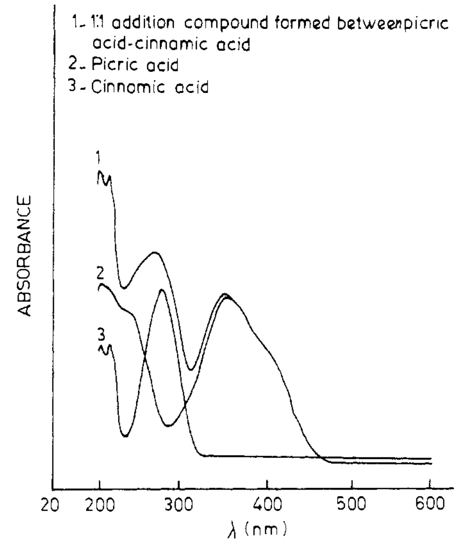

**Figure 2.** UV and visible spectra of 1:1 addition compound of picric acid-cinnamic acid, picric acid, and cinnamic acid, in methanol.

**Table I. Solid-Liquid Equilibrium Data**

| mole fraction of picric acid | start of the mp, °C | mp, °C | $\Delta T$, °C |
|---|---|---|---|
| 1.0000 | | 133.0 ± 0.1 | 5.0 |
| 0.0778 | 107.5 | 129.0 ± 0.2 | 6.5 |
| 0.1501 | 107.0 | 127.0 ± 0.1 | 5.8 |
| 0.2521 | 107.0 | 122.0 ± 0.1 | 6.0 |
| 0.3530 | 107.0 | 114.5 ± 0.2 | 6.2 |
| 0.4200 | 107.0 | 107.0 ± 0.1 | 5.5 |
| 0.5000 | | 109.0 ± 0.2 | 5.8 |
| 0.5501 | 104.0 | 108.0 ± 0.1 | 5.0 |
| 0.6600 | 104.0 | 104.0 ± 0.2 | 5.5 |
| 0.7312 | 104.0 | 113.0 ± 0.1 | 5.8 |
| 0.8171 | 104.0 | 117.5 ± 0.2 | 5.2 |
| 0.9001 | 104.0 | 119.5 ± 0.1 | 5.4 |
| 0.0000 | | 122.0 ± 0.1 | 6.5 |

**Table II. Heat of Fusion**

| system | heat of fusion, J/g |
|---|---|
| picric acid | 147.9 |
| cinnamic acid | 232.0 |
| 1:1 addition compound | 151.4 |
| eutectic containing 0.4200 mole fraction of picric acid | 191.3 |
| eutectic containing 0.6600 mole fraction of picric acid | 160.4 |

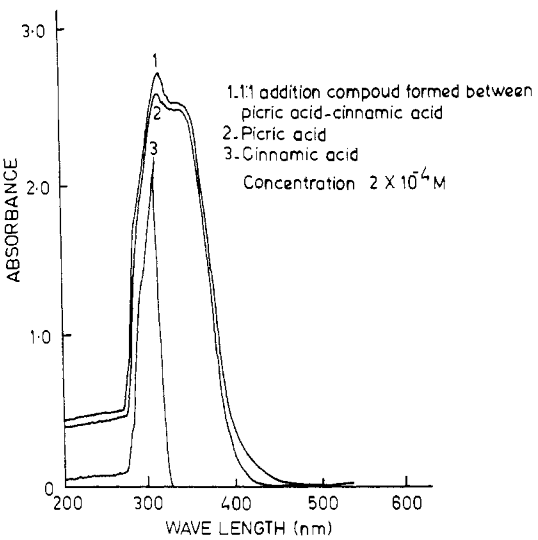

**Figure 3.** UV and visible spectra of 1:1 addition compound of picric acid-cinnamic acid, picric acid, and cinnamic acid in benzene.

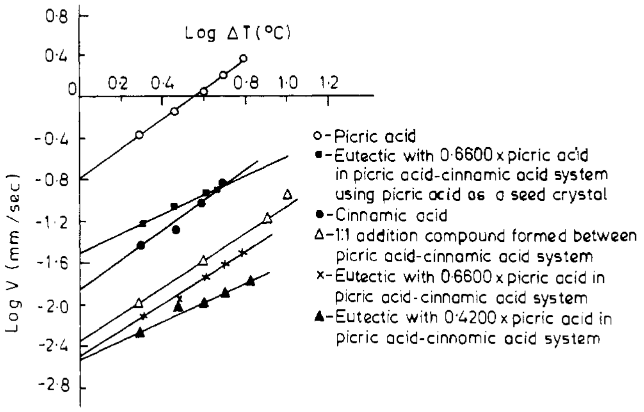

**Figure 4.** Linear velocity of crystallization at various degrees of undercooling for picric acid-cinnamic acid eutectic system.

**Table III. Parameters of Eq 1**

| system | $kn$[a] | $n$ |
|---|---|---|
| picric acid | 0.1585 | 1.5 |
| cinnamic acid | 0.0138 | 1.5 |
| 1:1 addition compound | 0.0045 | 1.3 |
| eutectic containing 0.6600 mole fraction of picric acid | 0.0032 | 1.3 |
| eutectic containing 0.4200 mole fraction of picric acid | 0.0029 | 0.9 |
| eutectic containing 0.6600 mole fraction of picric acid[b] | 0.0283 | 0.9 |

[a] $k$ in units of mm/(s·deg). [b] Seed crystal of picric acid.

the sum of the heat of fusions of the components, indicating that very weak interaction is involved. Dipole moment measurements show that the dipole moment of the complex (4.08 D) is much higher than the sum of the dipole moments of picric acid (2.13 D) and cinnamic acid (1.13 D). This shows that probably dipole-dipole-type interaction is involved in the formation of the complex.

Phase diagram studies indicate that in the system there are two eutectic mixtures and one 1:1 addition complex. Now, the phase diagram can be divided into two parts as shown in Figure 1 by dotted line. On both sides of the dotted line there are two simple eutectic systems. One eutectic at 0.42 mole fraction of picric acid is formed between cinnamic acid and the addition complex whereas another eutectic at 0.66 mole fraction of picric acid is formed between the addition complex and picric acid.

The linear velocity of crystallization of eutectics, components, and addition complex is related to undercooling by

$$V = k(\Delta T)^n \quad (1)$$

where $V$ is the linear velocity of crystallization, $\Delta T$ is the undercooling temperature, and $k$ and $n$ are constants. When log $V$ is plotted against log $\Delta T$, straight lines (Figure 4), showing

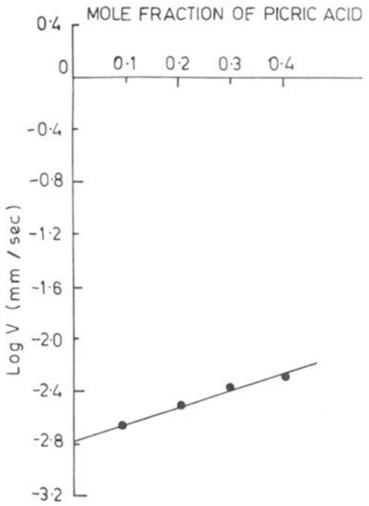

**Figure 5.** Crystallization velocity at same degree of undercooling for picric acid–cinnamic acid system.

**Table IV. Velocity of Crystallization ($V$) with Increasing Amount of Picric Acid**

| system | $\Delta T$, °C | $V$, mm/s |
|---|---|---|
| mixture containing 0.1000 mole fraction of picric acid | 2 | 0.0023 |
| mixture containing 0.2000 mole fraction of picric acid | 2 | 0.0033 |
| mixture containing 0.3000 mole fraction of picric acid | 2 | 0.0046 |
| mixture containing 0.4000 mole fraction of picric acid | 2 | 0.0055 |

**Table V. Test of Eq 2**

| | | $V$, mm/s | |
|---|---|---|---|
| system | $\Delta T$, °C | exptl | mixture law |
| eutectic containing 0.4200 mole fraction of picric acid | 2 | 0.0056 | 0.3497 |
| | 3 | 0.0081 | 0.6457 |
| | 4 | 0.0107 | 0.9679 |
| | 5 | 0.0127 | 1.3978 |
| eutectic containing 0.6600 mole fraction of picric acid | 2 | 0.0073 | 0.1569 |
| | 3 | 0.0104 | 0.2786 |
| | 4 | 0.0165 | 0.4250 |
| | 5 | 0.0318 | 0.6234 |

the validity of eq 1, are obtained. The values of $k$ and $n$ are given in Table III. The linear velocities of crystallization of the eutectics are much lower as compared to that of the components and the addition complex. Further, the linear velocity of crystallization at the same undercooling is increased as the mole fraction of picric acid is increased (Figure 5 and Table IV). Also when for a mixture containing 0.66 mole fraction of picric acid a seed crystal of picric acid was used, the linear velocity of crystallization was found to be much higher than when the mixture itself was used as a seed crystal (Figure 5 and Table III). The results show that picric acid crystal is a better nucleant for the mixtures containing higher amounts of picric acid. Further, if one assumes that the eutectic is simply a mechanical mixture of the two components, the data on the linear velocity of crystallization should obey the mixture law

$$V = x_1v_1 + x_2v_2 \tag{2}$$

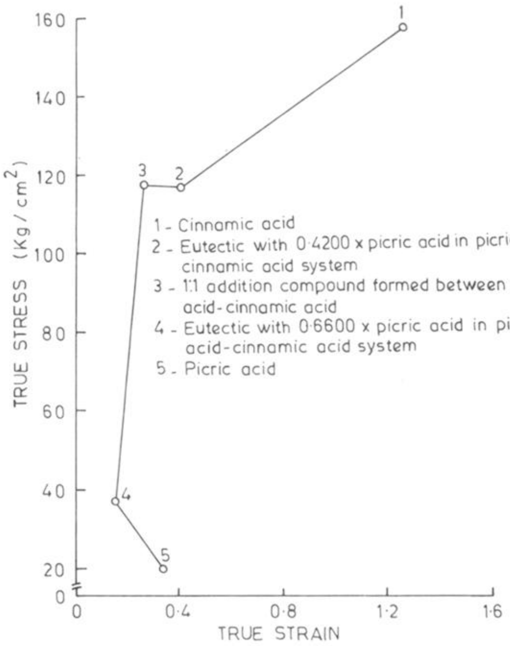

**Figure 6.** Stress–strain variation.

**Figure 7.** Microphotograph of directionally solidified picric acid × 100.

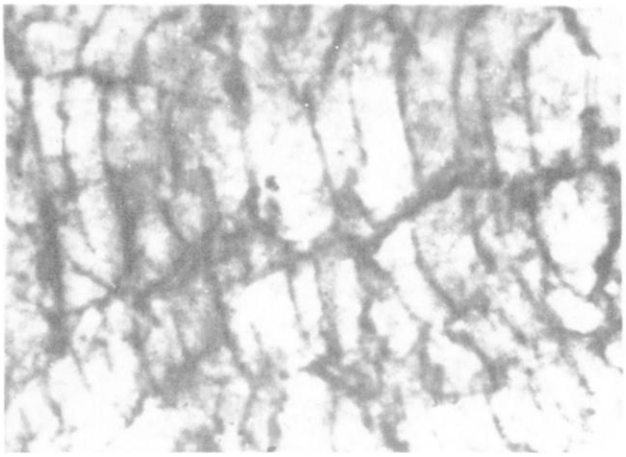

**Figure 8.** Microphotograph of directionally solidified cinnamic acid × 100.

where $x_1$ and $x_2$ are the mole fractions and $v_1$ and $v_2$ are the linear velocity of crystallization of components 1 and 2. The values of $V$ calculated from eq 2 and determined experimentally are given in Table V. From the table it is quite clear that the calculated values of $V$ are much higher than the experimental values. The heat of fusion data also do not follow the rule of additivity. The results simply show that the eutectic is not simply a mechanical mixture. There may be a certain type of loose interaction between the molecules or some type of molecular association is involved. This may be one of the reasons why the linear velocity of crystallization of different mixtures is lower than that of the pure components.

The variation of stress with strain of the components, eutectics and the addition complex are given in Table VI and Figure 6. From the figure it is quite clear that the compressive strength of cinnamic acid is the maximum and that of picric acid is the lowest. Eutectic with 0.42 mole fraction of picric acid and the addition complex have nearly the same value of com-

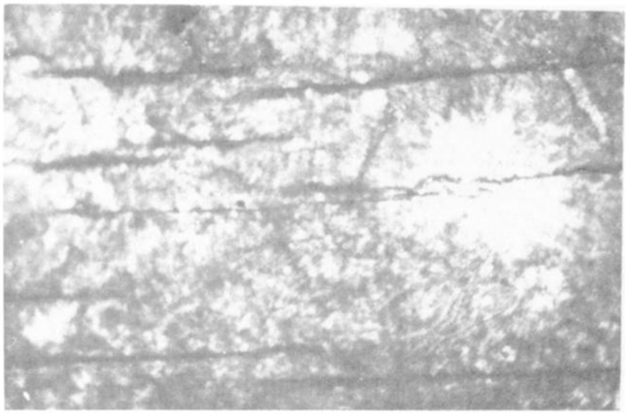

**Figure 9.** Microphotograph of directionally solidified picric acid–cinnamic acid eutectic containing 0.6600 mole fraction of picric acid × 100.

**Figure 10.** Microphotograph of directionally solidified picric acid–cinnamic acid eutectic containing 0.4200 mole fraction of picric acid × 100.

**Figure 11.** Microphotograph of directionally solidified picric acid–cinnamic acid 1:1 addition compound × 100.

pressive strength. The lower values of compressive strength indicate that neither the eutectics nor the addition complex crystallizes in a regular fashion.

The microstructures of the components, the eutectics, and the addition complex are given in Figures 7–11. The microstructures of the addition complex (Figure 11) and the eutectic with 0.66 mole fraction of picric acid (Figure 9) are irregular whereas the eutectic with 0.42 mole fraction of picric acid (Figure 10) appears to have a broken lamellar structure. Microstructures of mixtures of different compositions (Figures 12 and 13) were also examined, but the changes were observed only in two cases.

**Table VI. Stress–Strain Values**

| system | true strain | true stress, kg/cm$^2$ |
|---|---|---|
| cinnamic acid | 1.25 | 158.0 |
| eutectic with 0.4200 mole fraction of picric acid in picric acid–cinnamic acid | 0.42 | 117.4 |
| 1:1 addition compound | 0.27 | 117.5 |
| eutectic with 0.6600 mole fraction acid in picric acid–cinnamic acid | 0.17 | 36.91 |
| picric acid | 0.35 | 19.6 |

**Figure 12.** Microphotograph of directionally solidified picric acid–cinnamic acid system containing 0.1000 mole fraction of picric acid × 100.

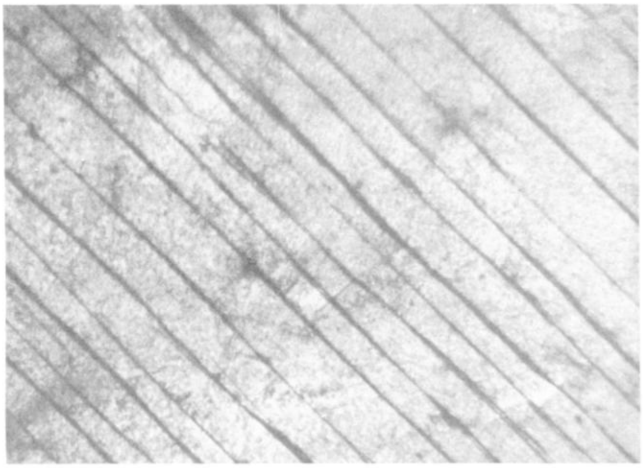

**Figure 13.** Microphotograph of directionally solidified picric acid–cinnamic acid system containing 0.8000 mole fraction of picric acid × 100.

## Acknowledgment

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**Registry No.** Picric acid, 88-89-1; cinnamic acid, 621-82-9; picric acid–cinnamic acid 1:1 compound, 118336-13-3.

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# Vapor Pressure of *n*-Alkanes Revisited. New High-Precision Vapor Pressure Data on *n*-Decane, *n*-Eicosane, and *n*-Octacosane[†]

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**New vapor pressure measurements on *n*-decane (268–490 K), *n*-eicosane (388–626 K), and *n*-octacosane (453–575 K) have been made with a modified ebulliometer and an inclined piston gauge. Benzene and water were the standards in the ebulliometric measurements on *n*-decane and *n*-eicosane, while *n*-decane was the standard for the measurements on *n*-octacosane. The high-quality data for *n*-decane, which were confirmed by a "third-law" analysis, suggest that reported literature data are in error. Similar concerns are raised about reported *n*-eicosane data. The vapor pressure data were regressed with the Cox equation, using as reference the normal boiling point.**

## Introduction

The thermodynamic and thermophysical properties of high molecular weight organic compounds are of increasing importance in the utilization of fossil fuels. The continued fall in demand for residual fuels, the rise in the specific gravity of petroleum crudes, and the eventual shift to fuels derived from oil shale, tar sands, and the liquefaction of coal all contribute to this increasing importance. Information on high molecular weight organic compounds will form the basis for characterization of both heavy petroleum and synthetic liquids.

In the areas of thermophysical property measurement and correlation, the most extensively studied group of organic compounds is the normal alkanes. Because of the availability of extensive experimental information for *n*-alkanes, most property correlations are initially tested using those data. However, tables of thermodynamic and thermophysical properties of *n*-alkanes (or any other class of compounds) often contain values derived by correlation. For example, the TRC tables (*1*) contain vapor pressure values for the *n*-alkanes methane through hectane ($C_{100}$); however, the reported values for $C_{21}$ through $C_{100}$ were obtained from the correlation derived by Kudchadker and Zwolinski (*2*).

In this paper we report new experimental vapor pressures for *n*-decane, *n*-eicosane, and *n*-octacosane. The *n*-decane data were obtained to confirm those of Willingham et al. (*3*), test the low-pressure data of Carruth and Kobayashi (*4*), which have been questioned by Scott and Osborn (*5*), and establish *n*-decane as a secondary standard for ebulliometric vapor pressure measurements. Data for *n*-eicosane and *n*-octacosane are presented as representative examples of high molecular weight compounds whose vapor pressures can be measured with high precision in our laboratory. Measurements on both compounds illustrate the range of our present apparatus. The results are compared with literature data [API 42 (*6*), Macknick and Prausnitz (*7*), and Myers and Fenske (*8*)] and the correlation used in the derivation of the values reported in the current TRC tables (*1*, *2*).

## Experimental Section

***Materials.*** All three *n*-alkane samples were obtained from commercial sources and subjected to stringent purification by Professor E. J. Eisenbraun's group at Oklahoma State University. Gas–liquid chromatographic (GLC) analyses performed on the *n*-alkane samples prior to the experimental measurements confirmed their high purities: *n*-decane had less than 0.002% impurities, *n*-eicosane had 0.05% impurities, and *n*-octacosane had 0.016% impurities.

The water, used as a reference material in the ebulliometric vapor pressure measurements, was deionized and distilled over potassium permanganate. The benzene, used as the other reference material for the ebulliometric measurements, was obtained from the American Petroleum Institute (API) as Standard Reference Material No. 210X-5s. Prior to its use, it was dried by vacuum transfer through Linde 3A molecular sieves.

***Physical Constants and Standards.*** Molar values are reported in terms of the Atomic Weights of 1969 (*9*, *10*), and the gas constant, $R = 8.31441\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, adopted by CODATA (*11*). The platinum resistance thermometers used in these measurements were calibrated with a thermometer previously standardized at the National Bureau of Standards. All temperatures are in terms of the International Practical Temperature Scale of 1968, IPTS-1968 (*12*). Measurements of mass, time, electrical resistance, and potential difference were made in terms of standards traceable to calibrations at the National Bureau of Standards.

***Apparatus and Procedures. Ebulliometric Vapor Pressure Measurements.*** The essential features of the ebulliometric equipment and procedures are extensively described in the literature (*13*, *14*). The ebulliometers were used to reflux the substance under study with a standard of known vapor pressure

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[†] Contribution No. 288 from the Thermodynamics Research Laboratory at the National Institute for Petroleum and Energy Research.

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