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## Allotropy of Liquid Nitrobenzene

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New measurements have been made of the surface tension and density of nitrobenzene between 6°C and 20°C. No evidence of allotropy was found. Neither intensive drying with phosphorus pentoxide nor the addition

of moisture produced any anomalous density changes, although some samples, cooled from higher temperatures, were kept for twenty-four hours at 6°C.

RECENT work suggests that certain organic liquids may exist in two or more allotropic forms. Mazur,<sup>1</sup> and Wolfke and Mazur<sup>2</sup> report that the density, rate of cooling and dielectric constant of carbon disulfide, ethyl ether and nitrobenzene exhibit anomalous changes at various characteristic temperatures.

Menzies and Lacoss,<sup>3</sup> studying temperature plots of the specific volume, refractive index, pressure for melting, dielectric constant and specific heat of benzene, show that the smooth curves drawn by the various experimenters to represent their data might better be replaced by broken lines. These discontinuities are at about 40°C except in the pressure for melting. The vapor pressure and viscosity of benzene were found to exhibit similar irregularities.

Probably because of the magnitude and the convenient temperature (about 9.6°C) of the reported change for nitrobenzene, a number of workers have investigated this substance since Mazur's first notes appeared, and much contradictory evidence has resulted. Wolfke and Ziemecki<sup>4</sup> found that their plotted values of the index of refraction of nitrobenzene between the temperatures of 6.6°C and 14.6°C fell on a straight line. The discontinuity in their curve for molecular refraction arises from their use of

Mazur's density data in their calculations. Friend<sup>5</sup> likewise failed to find evidence of a discontinuity in the index of refraction. Repeating Mazur's density work, he obtained a smooth curve, whereas there is a difference of more than 3 percent between Mazur's density measurement at 5.5°C and the value extrapolated from the high temperature portion of his curve. Friend's data of course led to a continuous function for molecular refraction. The density data of Tyrer<sup>6</sup> and of Massy, Warren and Wolfenden<sup>7</sup> are in agreement with those given by Friend.

Piekara,<sup>8</sup> in an investigation of the dielectric constant of carefully dried nitrobenzene, found no evidence of any transition above the freezing point, and further found that values for the super-cooled liquid fell on a curve continuous with that representing the data for temperatures above the freezing point.

Van Itterbeek,<sup>9</sup> using nitrobenzene furnished by the Bureau Internationale d'Etalons physico-chimique of Brussels, investigated the viscosity. His results are very interesting, since he reports no break in the temperature curve of intensively dried nitrobenzene, whereas he does find one at about 9.6°C for material not so dry. Massy, Warren and Wolfenden<sup>7</sup> found no discontinuity either in viscosity or in rate of cooling.

In investigations of the Raman spectrum for evidence of allotropy, neither Wolfke and

<sup>1</sup> J. Mazur, *Nature* **126**, 993 (1930); **127**, 741 (1931); **127**, 893 (1931); *Comptes Rendus des Seances de la Soc. Pol. de Phys.* **V**, 349 (1931); *Acta Phys. Pol.* **1**, 53 (1932).

<sup>2</sup> M. Wolfke and J. Mazur, *Nature* **128**, 584 (1931); *Acta Phys. Pol.* **1**, 71 (1932); *Zeits. f. Physik* **74**, 110 (1932).

<sup>3</sup> Menzies and Lacoss, *Proc. Nat. Acad. Sci.* **18**, 145 (1932).

<sup>4</sup> M. Wolfke and S. Ziemecki, *Acta Phys. Pol.* **1**, 271 (1932).

<sup>5</sup> J. N. Friend, *Nature* **129**, 471 (1932).

<sup>6</sup> D. Tyrer, *J. Chem. Soc.* **105**, 2534 (1914).

<sup>7</sup> N. B. Massy, F. L. Warren and J. H. Wolfenden, *J. Chem. Soc.* 1932, p. 91.

<sup>8</sup> A. Piekara, *Nature* **130**, 93 (1932).

<sup>9</sup> A. Van Itterbeek, *Nature* **130**, 399 (1932).

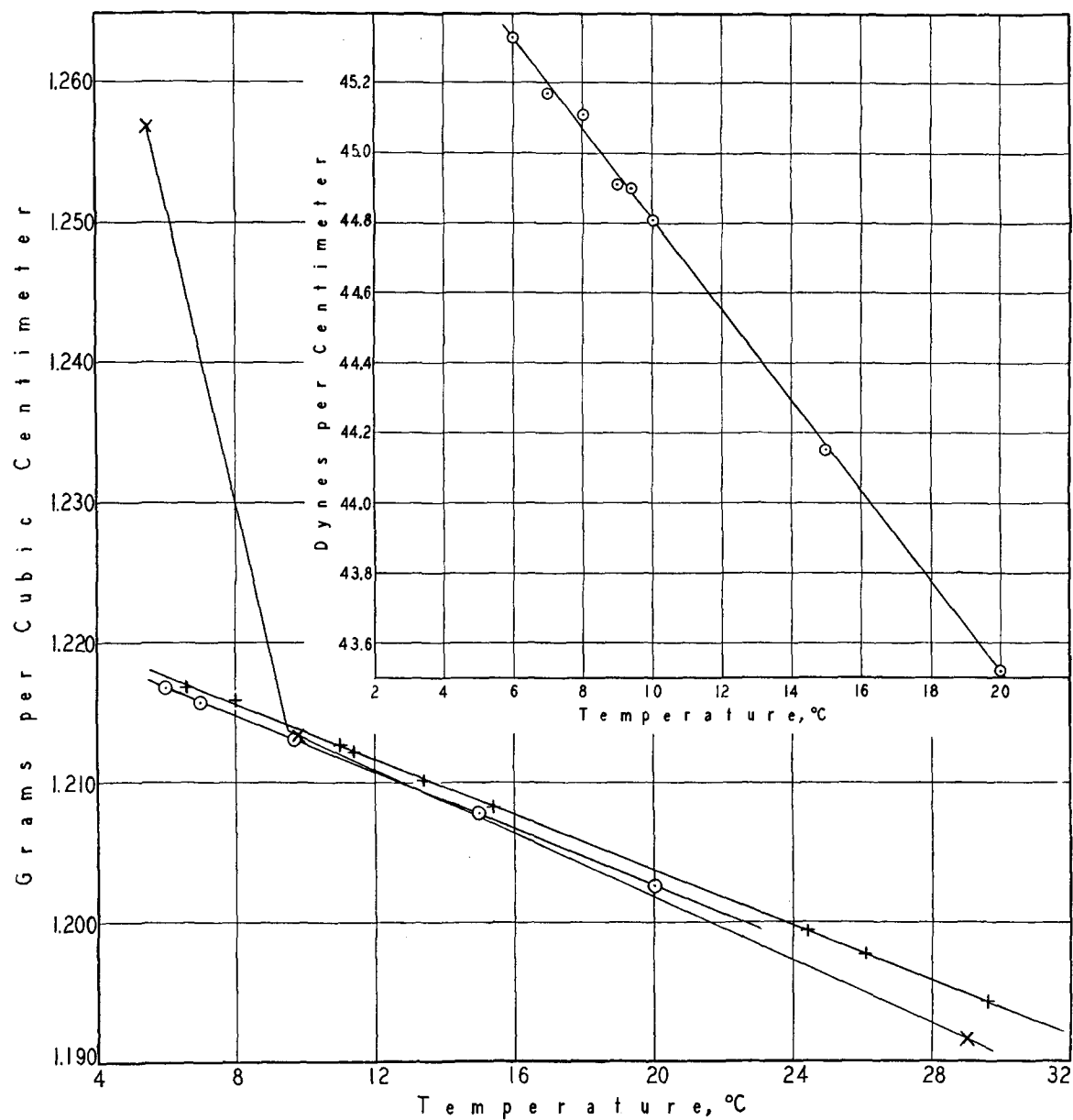


FIG. 1. Surface tension and density values. Mazur,\* crosses; Friend, plus signs; Lind and Young, circles.

\* Mazur, *Nature* **127**, 893 (1931); slightly different data are given in *Acta Phys. Pol.* **1**, 53 (1932).

Ziemecki<sup>4</sup> nor Thorne and Bayley<sup>10</sup> found any indications of a discontinuous variation with temperature. Stewart<sup>11</sup> reports that his x-ray diffraction measurements indicate "noticeable changes in the cybotactic groups" for nitrobenzene at 9.5°C, and rapid changes for ethyl ether at -105.4°C. The experiments which he reports, however, cannot confirm the existence of discontinuities characteristic of changes of state.

Allotropy of liquid nitrobenzene, whether due to changes in molecular aggregation or to other causes, would probably affect surface tension.

Measurements of this property in the neighborhood of 9.5°C seemed desirable to supplement the existing evidence for and against a transition at this temperature.

#### EXPERIMENTAL

A sample of Eastman's best grade of nitrobenzene was fractionated. A large portion was obtained which boiled within a range of 0.05°C at 211.4°C, and froze within a range of 0.06°C at 5.5°C.

For the measurement of surface tension, a drop weight apparatus of the type described by Harkins and Brown,<sup>12</sup> Gans and Harkins,<sup>13</sup> and others, was adopted. The tip used was of Pyrex glass. Its diameter, as determined with a travelling microscope, was 0.4980 cm. The supply bottles were also made of Pyrex glass.

Fresh calcium chloride was kept in the drop weight box at all times, and any air entering due to temperature changes when the box was immersed in the thermostat, passed through a calcium chloride tube. Since much of the work was done at temperatures lower than that of the room, the box was not opened after removal from the thermostat until it had come to temperature equilibrium with the room. This was necessary in order to prevent the condensation of moisture upon the contents of the box. Thermostat temperatures, maintained constant to  $\pm 0.01^\circ\text{C}$ , were determined to  $\pm 0.05^\circ\text{C}$ .

<sup>10</sup> A. M. Thorne and P. L. Bayley, *Phys. Rev.* **41**, 376 (1932).

<sup>11</sup> G. W. Stewart, *Phys. Rev.* **39**, 176 (1932).

<sup>12</sup> W. D. Harkins and F. E. Brown, *J. Am. Chem. Soc.* **41**, 499 (1919).

<sup>13</sup> D. M. Gans and W. D. Harkins, *J. Am. Chem. Soc.* **52**, 2289 (1930).

For the determination of the factor<sup>14</sup> required for calculating surface tension from drop weights, the density is required. In order that our density data might be compared with those of Mazur and of Friend, they were determined carefully with a Pyrex glass pycnometer. Surface tension and density values are given in Table I, and are

TABLE I.

Temperature	Density	Drop weight	Surface tension
6.0 <sub>0</sub>	1.2168	0.04369	45.33
7.0 <sub>0</sub>	1.2158	0.04353	45.17
8.0 <sub>0</sub>	(1.2148)	0.04347	45.11
9.0 <sub>0</sub>	(1.2138)	0.04327	44.91
9.4 <sub>0</sub>	(1.2134)	0.04326	44.90
9.7 <sub>0</sub>	1.2131	—	—
10.0 <sub>0</sub>	(1.2128)	0.04317	44.81
15.0 <sub>0</sub>	1.2078	0.04252	44.15
20.0 <sub>0</sub>	1.2025	0.04190	43.52

represented graphically in Fig. 1, together with the densities reported by Mazur and by Friend. Density values enclosed in parentheses were interpolated.

Density studies were continued as follows. Dilatometers were filled, one with nitrobenzene as used in our previous investigations, a second with slightly moist nitrobenzene, and a third with nitrobenzene intensively dried over phosphorus pentoxide; these were sealed and immersed in the thermostat. The last sample darkened somewhat on standing. Each sample contracted uniformly between 15°C and 6°C. Because of the possibility of a delayed transition, the dilatometers were kept at 6°C for twenty-four hours, but no further contraction in volume occurred.

#### DISCUSSION OF RESULTS

It will be observed that our density curve differs but little from Friend's, and, like his, shows no such break as that of Mazur. Neither does the surface tension curve exhibit any irregularities (all points lie within less than 0.1 percent of the curve).<sup>15</sup> It must be recognized, of course,

<sup>14</sup> International Critical Tables, Vol. IV, p. 435, McGraw-Hill, New York (1928).

<sup>15</sup> Our value, 43.52 dyne/cm at 20°C, is in good agreement with the 43.38 of Harkins, Clark and Roberts,

that it is possible that our material lacked a catalyst necessary to produce transition from a metastable to a stable state, or that it contained an impurity sufficient to mask the effect, as sug-

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J. Am. Chem. Soc. **42**, 702 (1920), and the 43.35 reported by Hennaut-Roland and Lek, Bull. soc. chim. Belg. **40**, 177 (1931). The estimate in the International Critical Tables, Vol. IV, p. 454, for 20°C was based largely on less precise data, and now appears to be about 0.4 dyne/cm too high.

gested by Dobinski.<sup>16</sup> On the other hand, Mazur's liquid may have contained an impurity which produced a spurious effect<sup>9</sup> (possibly due to limited solubility). Further work is necessary to establish the existence or non-existence of discontinuities in any of the properties of pure liquid nitrobenzene. At the present time, it seems to us that there is a preponderance of evidence against the contentions of Mazur.

<sup>16</sup> S. Dobinski, Nature **130**, 662 (1932).