12. *The Physical Properties of Nitrobenzene in the Neighbourhood of the Melting Point.*

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A SERIES of recent communications by Mazur suggests a sharp discontinuity in the physical properties of nitrobenzene in the neighbourhood of 9·8°, a temperature some 4° above its m. p. He reports a sharp fall in dielectric constant (*Nature*, 1930, **126**, 993), an arrest

in the heating curve (*ibid.*, 1931, **127**, 741), and a sharp change of slope in the density–temperature curve (*ibid.*, p. 893).

It is not clear from Mazur's papers whether it was ascertained that the temperature corresponding to the fall in dielectric constant was independent of the frequency of the electrical oscillations used; the inference, however, is drawn by Mazur from this discontinuity and the other two that nitrobenzene has two modifications in the liquid state, with a temperature of transition near 9·8°.

Since the dielectric constant is intimately connected with the degree of orientation and capacity for free rotation of the dipoles of the medium, it seemed of interest to measure the related property of the viscosity of nitrobenzene over the critical range described by Mazur. The two later communications led us to extend our measurements to its density and rate of heating.

Our viscosity measurements show no sign of discontinuity near 9·8°, nor have we been able to reproduce the discontinuities recorded by Mazur in the other two respects.

Experimental.

Materials.—Harrington's extra pure nitrobenzene was redistilled twice from phosphoric oxide at 100°. The m. p. of the product, measured with a recently standardised thermometer, was 5·77° ± 0·02°. This compares favourably with the value of 5·5° reported by Mazur, 5·669° by Roberts and Bury (J., 1923, **123**, 2037), 5·689° by Sidgwick and Ewbank (J., 1924, **125**, 2269); Masson (*Nature*, 1930, **128**, 726) reports m. p. 5·85° in a specimen prepared with great care. Exceptional purity is not claimed for our product but, if it is assumed that water is the principal impurity and that the value obtained by Masson corresponds to dry nitrobenzene, it appears that the water content of our nitrobenzene cannot have exceeded 0·03%.

Viscosity Measurements.—The viscosities were measured in a glass viscometer of the type described by Applebey (J., 1910, **97**, 2000), which had been shown to obey Poiseuille's law; the viscometer was held firmly in position by a holder such as is described in the same paper. Both the viscosity and the density measurements were carried out in an electrically controlled thermostat, cooled by a coil in which ice-water circulated. The temperature variations of the thermostat, as registered by a thermo-element of the kind described by Joy and Wolfenden (*Proc. Roy. Soc.*, 1930, *A*, **134**, 413), rarely exceeded 0·002°.

The viscosity was determined by comparing the time of flow of nitrobenzene at various temperatures with that (606·60 secs.) of an equal volume of water at 19·93°. The viscosity of water at 19·93°

was taken as 1·011 centipoises ("International Critical Tables," 1929). The apparent density of nitrobenzene in air at each temperature was obtained from our own measurements described below by correcting for the weight of air displaced at 9·5° and 760 mm. pressure. The apparent density of water was taken as 0·9970 at 19·93°.

It was found that the time of flow of a given specimen of nitrobenzene fell linearly with time, to the extent of about 1 second in 24 hours. This fall we attribute to slow absorption of water by the nitrobenzene in spite of the precautions, such as the use of calcium chloride tubes, taken to exclude water vapour from the viscometer. The water absorption necessary to account for the effect is extremely small; control experiments made with nitrobenzene to which very small amounts of water had been added showed that water absorption at the rate of 1 part in 15,000 parts per day was adequate to account for the fall observed. Since this was linear, a suitable correction was applied according to the length of time the given specimen of nitrobenzene had remained in the viscometer. This correction never exceeded 1 part in 800 parts. The viscometer was refilled at frequent intervals with fresh nitrobenzene from a tube immersed in the thermostat throughout the experiment. In this way both the change of hydrostatic head with temperature and the magnitude of the moisture correction were kept at a sufficiently low value.

The absolute viscosities η, in centipoises (Table I), give a smooth curve when plotted against temperature. The absence of any discontinuity is shown even more conclusively by comparing the

TABLE I.

Temp.	$10^7/T$.	η.	$\log_{10}\eta$.	Temp.	$10^7/T$.	η.	$\log_{10}\eta$.
19·94°	34,125	2·052	0·3121	9·07°	35,439	2·552	0·4069
15·04	34,705	2·257	0·3535	8·85	35,467	2·568	0·4096
12·14	35,058	2·395	0·3793	8·51	35,510	2·587	0·4128
11·03	35,195	2·456	0·3902	8·08	35,564	2·608	0·4163
10·08	35,313	2·497	0·3975	7·37	35,654	2·650	0·4235
9·66	35,365	2·526	0·4025	6·64	35,747	2·689	0·4297
9·32	35,408	2·547	0·4062	5·69*	35,869	2·752	0·4397

* Supercooled.

results with Andrade's equation, $\eta = Ae^{b/T}$ (*Nature*, 1930, **125**, 309), to which unassociated liquids have been shown to conform closely. Conformity with this equation is most clearly tested by plotting $\log_{10}\eta$ against $1/T$, the reciprocal of the absolute temperature, as in Fig. 1 : the linear relationship offers conclusive evidence of the absence of any discontinuity in the viscosity of nitrobenzene over the temperature range studied.

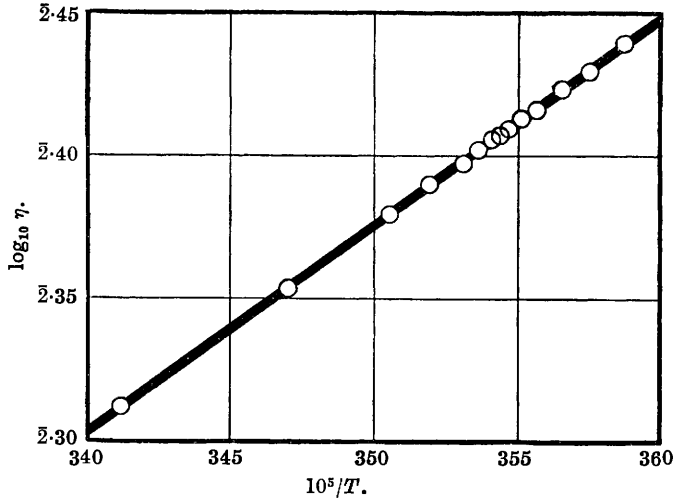
Density Measurements.—A pyknometer of the type described by Hartley and Barrett (J., 1911, **99**, 1072), suitable for use below room

temperature, was employed. Nine measurements were made over the range 6·03—14·02°. The values of $d_4^{t°}$ were as follows:

Temp.	6·03°	7·05°	8·05°	9·08°	10·07°
$d_4^{t°}$	1·2170	1·2161	1·2153	1·2143	1·2134
Temp.	11·05°	12·06°	13·03°	14·02°	
$d_4^{t°}$	1·2124	1·2115	1·2106	1·2097	

These results are plotted in Fig. 2 together with a broken line representing Mazur's values. Our results show no discontinuity over the temperature range measured, and differ from those of

FIG. 1.



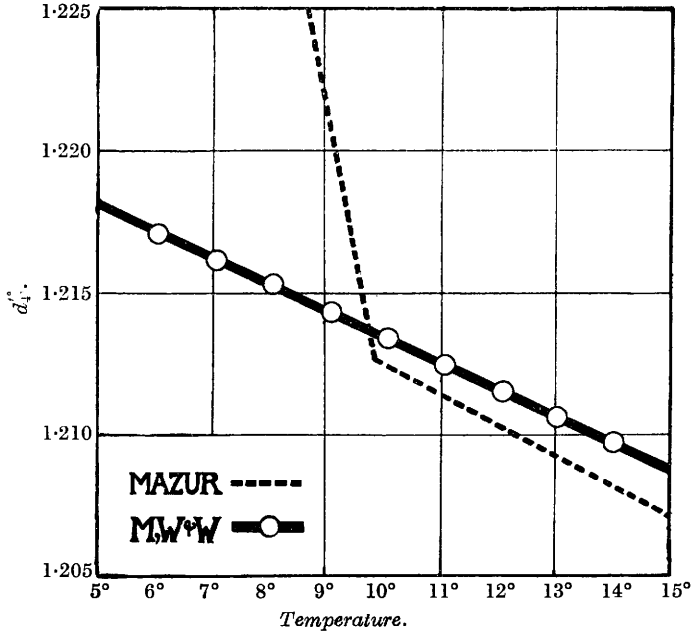
Mazur below 9° to an extent greatly exceeding the experimental error.

Rate of Heating of Nitrobenzene.—In order to detect any arrest in the rate of temperature rise of nitrobenzene under conditions of constant heat influx, some 30 c.c. were sealed up in a dilatometer. The motion of the meniscus along the dilatometer capillary was measured against time while the dilatometer was immersed in a thermostat which supplied heat at a uniform rate, producing a temperature rise of about 4° per hour. In these circumstances the nitrobenzene serves as its own thermometer. Apart from the simplicity of the method, it has the advantage that the heating-arrest, if any, will be emphasised by any change in the slope of the density–temperature curve at the temperature of transition such as is described by Mazur. The graph of volume against time was strictly linear with no trace of a discontinuity between 9° and 11°.

Summary.

The viscosity of nitrobenzene has been measured between 5·69° and 19·94°, and its density between 6·03° and 14·02°. Neither property showed any discontinuity within these ranges. The

FIG. 2.



heating curve of nitrobenzene shows no arrest between 9° and 11°. Hence, none of these physical properties offers any evidence for the existence of two modifications of liquid nitrobenzene.

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