36. *The Viscosity of Nitrobenzene.*

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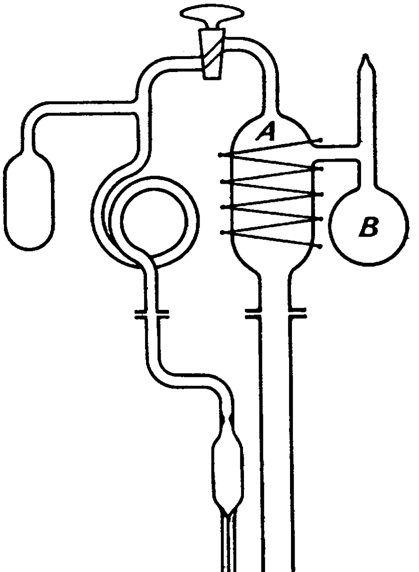
In recent work (Massy, Warren, and Wolfenden, J., 1932, 91) on the physical properties of nitrobenzene in the neighbourhood of the melting point, it was found that the viscosity fell slowly at the rate of about 0·1% per diem; and, although this change seemed to be unaffected by all ordinary precautions to exclude water vapour from the viscometer, it was suggested that the decrease was caused by a minute but continuous absorption of water vapour.

Fig. 1.



In view of Wagner's observation (*Z. physikal. Chem.*, 1903, **46**, 877) that freshly distilled nitrobenzene decreases in viscosity on standing, and of the recent assertions that nitrobenzene exists in two forms above the melting point (Mazur, *Nature*, 1930, **126**, 993; 1931, **127**, 741, 893), it was decided to test directly the truth of our hypothesis as to the cause of the secular fall of viscosity. The opportunity was also taken to show that the viscosity of nitrobenzene rigorously protected from moisture is not affected by thermal pre-treatment, such as might be expected to disturb any internal equilibria in the liquid.

Our previous observations had shown that nothing short of an entirely sealed viscometer achieves complete exclusion of moisture. It had also been shown (by the late Mr. C. H. Carter, in this laboratory) that, if measurements of viscosity are to be made on a liquid before and after warming in the viscometer, significant results can only be obtained if the viscometer (of the Ostwald type) is firmly held by the capillary limb and not by the other limb; the latter arrangement, which has normally been used in this laboratory (Applebey, J., 1910, **97**, 1999), leads to anomalous results owing to the thermal hysteresis in the shape of the viscometer.

Two viscometers were constructed (see Fig. 1) in which contact with the air could be completely avoided; they were held firmly in holders of the Applebey type, modified so as to fix the position of the capillary limb. Rubber bungs are replaced by butt-ended joints sealed together, after the viscometer has been filled, by a vapourless cement of low m. p. The liquid is driven into the upper bulb by air press. due to the electrical heating of the expansion chamber A. The Bulb B contained P_2O_5; the tap was lubricated by H_3PO_4.

$PhNO_2$, prepared by nitration of C_6H_6 carefully freed from thiophen, was washed, dried over $CaCl_2$, and finally distilled twice in vac. from P_2O_5 in an all-glass still at 74·5°. In handling the liquid, a positive press. of dry air was always maintained to exclude moisture. The m. p. was 5·85°

One of the viscometers (I) was filled with $PhNO_2$ and sealed with P_2O_5 in bulb B; the second (II) was filled similarly, but bulb B contained no drying agent and was simply closed by a rubber tube and a glass stopper. Both were mounted in a thermostat at 19·50°. It was anticipated that the time of flow of viscometer (I) would remain const. while that of viscometer (II) would slowly fall owing to the absorption of moisture. Our expectations were realised, as is shown in the following table, which gives a representative series of readings (these are corr. for casual variations of thermostat temp. over a range of ± 0·02° as shown on a Beckmann thermometer).

Time from start, hrs.	Time of flow (secs.).	
	Viscometer I.	Viscometer II.
0·25	1419·26	1053·46
14·0	1419·23	1051·96
24·0	1419·28	1051·83
36·0	1419·35	1050·90
48·0	1419·26	1050·26
60·0	1419·31	1049·30 †
65·0	1419·33 *	1021·20 †
65·25	1419·30 *	—
168·0	1419·20	1013·51

* Between these two observations, viscometer I was removed from the thermostat and heated to 85° in a glycerol-bath.

† Between these two observations, approx. 0·1% of H_2O was added to bulb B in viscometer II.

These results seem to show conclusively that the slow fall in viscosity previously recorded for $PhNO_2$ is entirely due to the absorption of water vapour, which all but the strictest precautions fail to exclude. The invariable absence of any effect on heating the $PhNO_2$ in the sealed viscometer (I) is also indirect evidence of the absence of internal equilibria in it.

We take this opportunity to correct an arithmetical error affecting the viscosities published by Massy, Warren, and Wolfenden (*loc. cit.*, p. 93). The table of results as corrected should read :

Temp.	$10^7/T$.	η.	$\log_{10} \eta$.
19·94°	34,125	2·0272	0·30690
15·04	34,705	2·2231	0·34696
12·14	35,058	2·3650	0·37383
11·03	35,195	2·4256	0·38483
10·08	35,313	2·4659	0·39198
9·66	35,365	2·4947	0·39702
9·32	35,408	2·5152	0·40057
9·07	35,439	2·5185	0·40114
8·85	35,467	2·5370	0·40432
8·51	35,510	2·5530	0·40705
8·08	35·564	2·5711	0·41012
7·37	35,654	2·6140	0·41731
6·64	35,747	2·6613	0·42509
5·69	35,869	2·7090	0·43281

From our own observations in viscometer I, the value of 2·0380 centipoises is obtained for the viscosity of $PhNO_2$ at 19·50°. This is in good agreement with the above values.

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