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The Diamagnetism of Nitrobenzene at Different Temperatures.

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1. *Introduction.*

Very little work seems to have been done so far on the influence of temperature on the diamagnetism of liquids. Water has been studied by a number of investigators, whose results, however, do not show any mutual agreement.[1] A number of liquids, both aliphatic and aromatic, have been studied by Mathur,[2] who finds generally, an appreciable decrease in the case of some of the aromatics and no change in the case of aliphatics as the temperatures are increased. The result for the aliphatic liquids seems theoretically justifiable since Oxley,[3] and Vaidyanathan[4] found very little change at the points of liquefaction and boiling respectively. But both these observers, speaking generally, found relatively larger *increases* in the case of some aromatics. The slow

[1] For details see Wills and Boeker, Phy., Rev., 42, 687, 1932.

[2] Ind. Jour. Phys., 6, 207, 1931.

[3] Phil. Trans. Roy. Soc., 214, 109, 1914.

[4] Phy. Rev., 30, 512, 1927; Ind. Jour. Phys., 2, 135, 1927, and 3, 391, 1929.

process of the destruction, partial or complete, of the structure in the case of liquids as the temperature is increased suggests therefore that in the case of these aromatics, increase of temperature should be accompanied by a sensible increase in the specific diamagnetic susceptibility. It was felt therefore that it would be worth while investigating one of the typical liquids like nitrobenzene at some length, taking carefully into account the conditions under which the measurements were taken.

2. *Experiment.*

Quincke's capillary ascension method was used. The experimental tube and the arrangements are shown in Fig. 1.

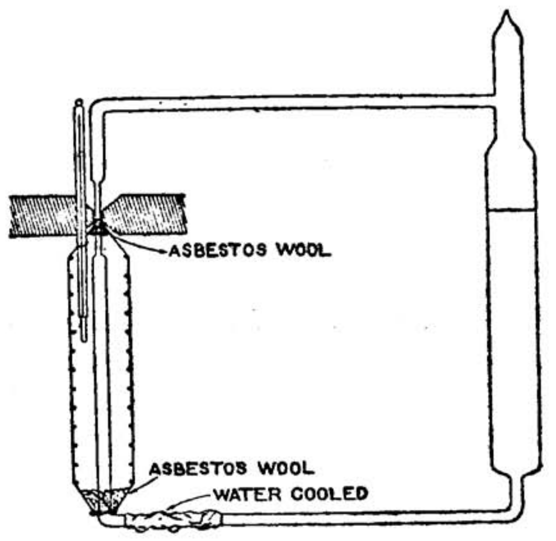

FIG. 1

We have used a closed tube with only the liquid and its vapour inside. This avoids all uncertainties regarding the presence of dissolved air in the liquid. The tube was thoroughly cleaned in the following order, benzene, sodium hydroxide solution, boiling water, nitric acid, boiling water again, distilled water and absolute alcohol. The greatest care was taken to purify the liquid by repeated drying and distillation and to check its purity by the usual physical properties. The tube was filled up to the required height with the hot liquid just fresh after distillation and sealed after evacuation and heating the liquid to facilitate the exit of all dissolved air.

The lower part of the tube between the pole-pieces was surrounded by an electric heater. The full details are apparent from the figure. The pole-pieces were wrapped with cotton wool and kept damp throughout the measurements. In certain experiments a second heater was used above the pole-pieces but in practice it was found that it did not modify the results in any manner.

A thermometer T gave the temperature of the space within the heater, the heating current being adjustable with great nicety. The question as to whether at a constant heating current, the average temperature of the tube was the value read on the thermometer, was carefully investigated. A platinum wire was doubled and wound around the tube within the heater and its resistance measured on a sensitive bridge at different heating currents. It was found that at moderate temperatures there was satisfactory agreement (to within 2°), between the thermometer reading and the temperature calculated from the resistance. When the second heater was used the temperature within it was adjusted to be equal to that of T.

As the heater was raised to any definite temperature, the level in the capillary was brought to the right position, by lowering the main tube which was clamped to a stand and rendered movable up and down by a delicate screw arrangement. The height through which the level was lowered due to the magnetic field was measured by a microscope with an eyepiece scale, and corresponded to nearly 200 divisions on this scale.

After several preliminary trials, the best method of taking consistent measurements was found to be as follows. Several readings of the depressions were taken at the laboratory temperature. The heating current was then increased by small values at a time. The temperature and the depressions due to the field were noted alternately, the times at which these readings were taken being noted simultaneously. If graphs are now drawn between time as the abscissa and the other two quantities as ordinates, it is easy to find the steady readings corresponding to definite temperatures.

Four different tubes were used and in all 30 sets of measurements were taken with increasing and decreasing temperatures. The magnetic field was constant and was about 4,500 gauss. It is well known that if δ is the depression of the level due to a field H,

$$\rho \, \delta \, g = \tfrac{1}{2}(k-k_{0})H^{2}$$

Where the terms have the usual significance. Since the vapour inside has a constant pressure, ρ_{0} (vapour value) may be taken as constant. We obtain therefore for the specific susceptibility the expression,

$$\chi = \frac{2\,\delta\, g}{H^{2}} + \frac{\chi_{0}\,\rho_{0}}{\rho}$$

The second term is usually very small and hence we assume the same molecular susceptibility for the vapour as for the liquid. The density of nitrobenzene at different temperatures was taken from the measurements of Tyrer,[5] extrapolated for temperatures above 75°C. With all the precautions taken, the error in the susceptibility values did not exceed $\frac{1}{4}$ %.

[5] Jour. Chem. Soc., Trans., 107, 2534, 1914.

3. *Results.*

The diamagnetic susceptibility of nitrobenzene at 30°C. was taken as 1 and the values at other temperatures were calculated taking this to be the standard. The results are shown in the following table. It may be mentioned here that as a check on the apparatus used, the susceptibility of nitrobenzene at atmospheric temperature was compared with that of water at the same temperature using a water tube. Assuming the χ value of water to be 0·72[6] at 30°C, the specific susceptibility of nitrobenzene at the same temperature was found to be 0·505 in fairly close agreement with 0·510 obtained by one of us with Sivaramakrishnan [7] by the Curie balance method.[8]

Temperature °C.	χ_t/χ_{30}
30	1·000
34	0·998
44	0·991
54	0·975
69	0·953
77	0·952
95	0·972
102	0·977

Fig. 2 shows how the susceptibility varies with the temperature. It will be seen that this quantity attains a minimum value at about 75°C and shows a gradual rise after that

[6] All values of χ should be multiplied by 10^6.
[7] Ind. Jour. Phys., 6, 509, 1932.
[8] Oxley's results (*loc. cit.*) give 0·502 at 20°C and 40°C.

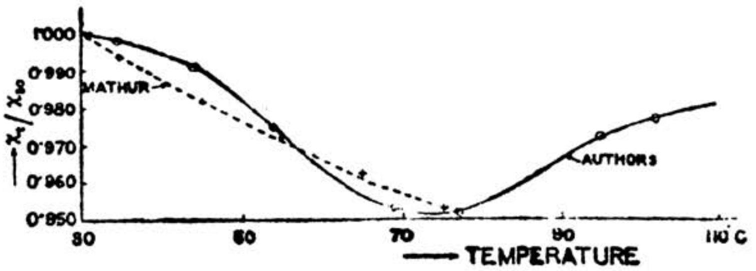

FIG. 2

temperature. This rise however becomes smaller as the temperature is raised. The temperature at which the minimum occurred was consistently obtained (to within 3° on either side of 75°C) in a large number of measurements. Mathur's results [8] were obtained between 15° and 75°C and in the range between 30°C and 75°C, there is fair agreement between our values, although the shape of his curve is different from ours.

4. *Discussion.*

It is interesting to compare these values with those of one of us [9] on the optical anisotropy of nitrobenzene at different temperatures. It is found that as the temperature is increased from 30°C, the anisotropy falls down rapidly after about 40°C, attains a minimum value at about 100°C and thereafter shows a tendency to rise with temperature. It is a strange coincidence that the susceptibility-temperature curve on Fig. 2 should do the same, only the minimum value is obtained at 75°C. There seems to be very little doubt that the same cause accounts for both the phenomena. It was mentioned in that paper that the anomalous behaviour of nitrobenzene might be

[8] *Loc. cit.*
[9] Ind. Jour. Phys., 8, 90, 1933.

due to molecular association and evidence from other sources [10] seems to point to the same conclusion. The large decrease in the diamagnetism of nitrobenzene with temperature is most probably also due to decreasing association.

Oxley's results show that on liquefaction, nitrobenzene shows an increase of 12% in its diamagnetic susceptibility. We know very well that a crude structure persists in liquids also and it follows therefore that, other conditions remaining the same, the disruption of this structure should be accompanied by an increase in the diamagnetism. In the range 30° to 75°C, we find the susceptibility values decreasing since association decreases also ; but above 75°C we find that the susceptibility increases slowly, just what would follow from a proper interpretation of Oxley's results. In the case of benzene, Oxley obtained no change in the diamagnetic susceptibility on liquefaction while toluene (melting point −92°C) showed only a 5% increase ; and Boeker's [11] recent work shows that benzene and toluene suffer hardly any diamagnetic variation with temperature (range 20°C to 50°C).

There is however one point of difference in the anisotropy and susceptibility variations for nitrobenzene. The temperatures at which the minimum values occur are not the same in both the cases. The experiments have been performed under different conditions and the errors in optical experiments are more serious ; it is therefore a problem whether too much significance should be attached to this inconsistency.

It is too early at this stage to develop any reasonable theory regarding the susceptibility variation of liquids with temperature. A careful study with more liquids is necessary before even definite generalisations are permissible. It is proposed to leave this work at this stage and await an early opportunity to continue this investigation.

[10] S. W. Chinchalkar, Ind. Jour. Phys., 7, 491, 1933.

[11] Phys. Rev., 43, 756, 1933.

Summary.

The diamagnetic susceptibility of nitrobenzene has been determined at different temperatures ranging from 30° to about 110°C by a modified Quincke's method. The specific susceptibility is found to decrease as the temperature is increased from 30°C, a flat minimum is attained at about 75°C and then the value shows a gradual rise. Attention is drawn to the similarity in behaviour of the magnetic property with the variation of the optical anisotropy of nitrobenzene with temperature. Molecular association is mentioned as the probable cause of the anomalous behaviour.