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DIELECTRIC CONSTANT,
VISCOSITY, SURFACE TENSION,
AND CRITICAL DATA OF BORON
TRIBROMIDE, DIOXAN, AND
ETHYLENE DICHLORIDE

BY

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Although the physical properties of pure liquids have been investigated in a great number of cases, the relationship between these properties of the bulk liquid and the properties of the molecules themselves is not yet completely clear. Presumably the reason is that the actual shape of the molecules is important, i. e. they cannot be regarded as spheres. Again, large molecules are often flexible and, due to the possibility of twisting single bonds, they may take up a number of shapes; ethylene dichloride is a simple example. Ring structures like dioxan must, however, be more rigid. Inorganic molecules are generally simple in shape and rigid, but they have been comparatively little investigated for several reasons, one being that the liquid state is seldom realised at room temperature. Boron tribromide is, however, a liquid at ordinary temperatures, and therefore suitable for study. The three examples quoted are insufficient for a generalisation to be made.

Experimental.

Purification. The purification of ethylene dichloride has been described previously (1). Dioxan marked "Exluan 07" was frozen, dried over sodium and distilled to give four fractions at melting points 11.75, 11.76, 11.80, and 11.55 °C. respectively. According to TIMMERMANS and ROLAND (2), 11.80 is the correct melting point. Boron tribromide was distilled twice in a stream of pure hydrogen and then a fraction was distilled in vacuo, in a sealed all-glass apparatus, into a conductivity cell and four ampoules. The melting point was found to be -47 °C.; STÖCK and KUSS (3) found -46 °C.

Dielectric Constant. The dielectric constant of ethylene dichloride has been determined earlier (1); since then SUGDEN (4)

has made a more accurate determination. The dielectric constant of dioxan has also been determined by several investigators, but that of boron tribromide has not been measured previously. The above conductivity cell of large capacity was used, and the dielectric capacity measured by means of an apparatus described elsewhere (5). It was also proved that boron tribromide is a perfect insulator. The dielectric constants for twice- and thrice-distilled boron tribromide were in agreement; measurements were made at several temperatures between -70 and $+80^{\circ}\text{C}$. For the liquid state, the following formula was found to be valid:

$$\epsilon = 2.58 - 0.0028t \pm 0.03$$

where ϵ is the dielectric constant at temperature $t^{\circ}\text{C}$. The dielectric constant of the solid is not very different from that of the liquid, but the formation of bubbles prevented a very accurate determination. The dipole moment is certainly not larger than $0.15 \cdot 10^{-18}$ e. s. u., and is presumably zero. Zero moment was found for boron trifluoride by WATSON, RAMASWAMY and KANE (6). ANDERSON, LASSETTRE and YOST (7) have studied the Raman spectra of BF_3 , BCl_3 , and BBr_3 and explain the results on the basis of a plane model in which the three halogen atoms form a regular triangle with the boron atom at the centre. The present data are in accordance with these findings.

Viscosity and Surface Tension. These were both measured by means of the same apparatus. As emphasised by RAASCHOU (8) a modified Ostwald viscometer is very useful for the determination of surface tension by the capillary rise method. The apparatus used here was provided with standard ground joints for the inlet and outlet so that boron tribromide could be distilled into it and kept under dry hydrogen all the time. The liquid was raised by means of hydrogen pressure and then both gas spaces were connected, and the time of outflow of a definite volume between two marks was measured by a stopwatch. After the lapse of some time the meniscus in the narrow tube had attained its equilibrium position, and the capillary rise was measured by means of a cathetometer. The apparatus was calibrated for both purposes by means of water. In the

case of dioxan several different volumes of liquid were used, thus varying both the height of fall in the viscometer and the position of the meniscus for the capillary rise measurements. In this way both viscosity and capillary rise measurements were controlled, and it was proved that the effect of kinetic energy on the viscosity measurements is insignificant. As the walls of the capillary tube are wetted during the flow of liquid, it is fairly certain that the contact angle is zero. The measurements were carried out at several temperatures between -45 and $+70^{\circ}\text{C}$. The viscosity η in gm./cm. sec. was found to vary with the absolute temperature T according to the following logarithmic formulae:

$$\begin{aligned} \text{Ethylene dichloride } \log_{10} \eta &= \frac{532}{T} - 3.88; \\ \text{Dioxan } \log_{10} \eta &= \frac{625}{T} - 4.02; \\ \text{Boron tribromide } \log_{10} \eta &= \frac{346}{T} - 3.33; \end{aligned}$$

In the case of ethylene dichloride the present values lie between those of THORPE and ROGER (9) and those of FAUST (10). For dioxan the agreement with TIMMERMANS and ROLAND (2) is very good, whereas the data of HERZ and LORENTZ (11) deviate considerably. The viscosity of boron tribromide has not been measured before.

The theory of the logarithmic formula for viscosity has been gradually evolved; in part it dates back to MAXWELL (12) and later contributions are due to RAMAN (13), DUNN (14) and ANDRADE (15). It is in fact a consequence of DEBYE'S (16) theory of the "quasicrystalline structure of liquids". The first constant in the formula is a measure of the critical increment of energy required for the mutual passage of molecules, and the second constant is a measure of the velocity with which the molecules move during the passage. Due to its great molecular weight boron tribromide moves more slowly than the other molecules, but the critical increment is smaller because the dimensions of the molecule are small, and the molecule as a whole is of a suitable shape.

The variation of the surface tension γ with the temperature

in °C is not quite linear; for the sake of simplicity, however, a linear formula is given:

$$\text{Ethylene dichloride } \gamma = 36.3 - 0.14t \text{ (dynes/cm.)}$$

$$\text{Dioxan } \gamma = 36.1 - 0.14t;$$

$$\text{Boron tribromide } \gamma = 32.1 - 0.13t.$$

These data agree with older data of SCHIFF (17) and TIMMERMANS and ROLAND (2), but not with data of JAEGER (18), WORLEY (19) or HERZ and LORENTZ (11). The surface tension of boron tribromide has not been previously determined.

The Orthobaric Curve. In the T—D (or the T—V) diagram the orthobaric curve gives the relationship between the temperature and the density of saturated vapour or boiling liquid. With the vapour pressure curve in the P—T diagram or the border curve in the P—V diagram it defines the equilibrium between the liquid and gaseous states. Two of these curves determine the third. As will be shown below the orthobaric curve and the vapour pressure curve (to the vicinity of the critical point) may be determined by means of simple devices, whereas the investigation of the border curve requires a complicated apparatus.

The present apparatus for determining the orthobaric curve is constructed by combining suggestions of CENTNERSZWER (20) and GOUY (21). Varying amounts of the material are sealed (air-free) into ampoules 8 cm. long of internal diameter 2 mm. and external diameter 4 mm. An ampoule is placed in the central bore of an electrically heated copper cylinder, and rests on a screw mounted loosely in the cylinder, so that the ampoule may be shaken and moved up and down to make the meniscus visible through the observation hole. Light from an incandescent lamp passes through an inlet into the cylinder, is reflected by the meniscus, and passes out again through the observation hole, which is at an angle to the inlet such that only the reflected image and not the lamp itself is visible. The image is observed during slow heating until it disappears, showing that the meniscus disappears, and the corresponding temperature is read on a thermometer placed in a hole in the copper cylinder. On subsequent slow cooling the temperature of reappearance of the meniscus is also read. The whole arrangement is calibrated by determining the melting points of tin, bismuth and

cadmium contained in glass tubes in place of the ampoule. The ampoules are tested before use, but the observation hole is covered by mica and metal gauze to protect the eye from possible damage due to fragments of an exploding ampoule.

When the meniscus disappears or reappears at the bottom of the ampoule, this is filled with saturated vapour; when it is at the top of the ampoule, this is filled with liquid at the boiling point; and when the meniscus disappears inside the ampoule, the critical state is approached. It follows that the temperature of disappearance of the meniscus, and the density of the contents of the ampoule, are the data to be plotted in a diagram to give points on the orthobaric curve. The weight of the material is obtained by breaking the ampoule into two parts, evaporating the contents, and weighing before and after. The volume of the ampoule is determined by filling the two parts with water and weighing. In this determination, however, the effect of temperature and pressure on the volume is neglected.

Orthobaric curves for ethylene dichloride, dioxan, and boron tribromide obtained in the above manner are shown in Fig. 1. For each density, two temperatures are marked, the higher being for the disappearance and the lower for the appearance of the meniscus; the difference of 2°C. is a measure of the accuracy. As CENTNERSZWER has emphasised the orthobaric curve is very sensitive to the degree of purity of the material. Slight decomposition of ethylene dichloride at the high temperature used is unavoidable, but dioxan is stable and presumably pure. Most samples of boron tribromide were of twice distilled material only, but four ampoules were filled with thrice distilled material. Of these, only one withstood heating, fortunately one in which the contents had nearly the critical density. The critical temperature of 300°C. found by means of this sample is considered to be the best value; it is 2°C. below the maximum of the curve drawn through the other values. The critical density was estimated by means of the law of the rectilinear diameter of CAILLETET and MATHIAS (22). The following critical data have been found:

	t_c	d_c
Ethylene dichloride	290 °C.	0.44
Dioxan	312	0.36
Boron tribromide	300	0.90

Older data are available only for ethylene dichloride; PAWLEWSKI (23) found $t_c = 283^\circ\text{C}$. and NADEJDINE (24) found $t_c = 288.4^\circ\text{C}$. and $d_c = 0.419$.

Vapour Pressure. The vapour pressure curve of dioxan shown in Fig. 2 has been determined by a new method de-

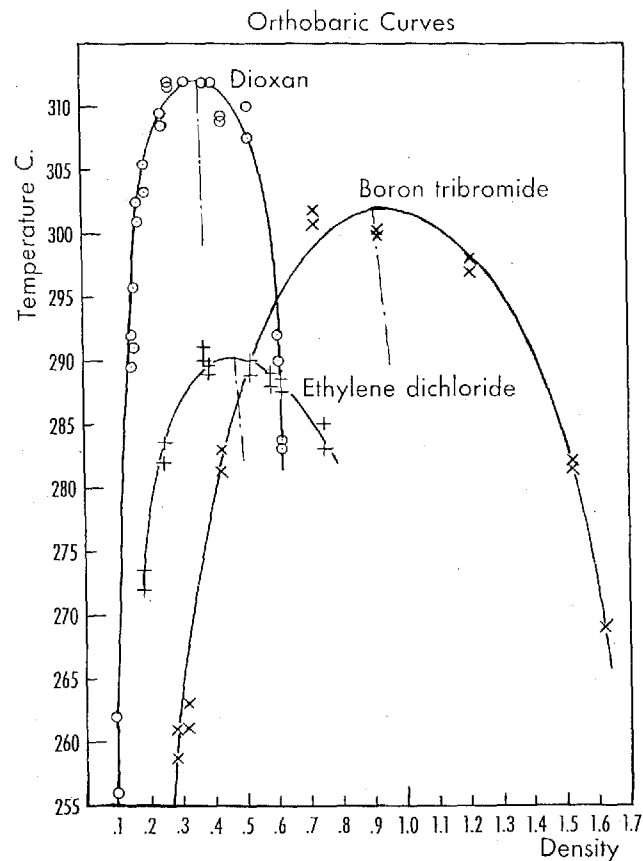


Fig. 1.

pending on a balance of vapour pressures. A U-shaped glass tube is filled with mercury in the bend. The substance to be investigated (here dioxan) is placed on top of the mercury in one branch, and benzene in the other branch. Air is boiled out of each branch before sealing it, and the closed U-tube then contains four phases, namely dioxan liquid, mercury, benzene

liquid, benzene vapour. If now the dioxan branch is heated, a sudden shift will take place at that temperature at which the vapour pressure of the dioxan exceeds that of benzene at room temperature. After the shift the sequence of phases will be:— dioxan vapour, dioxan liquid, mercury, benzene liquid. The difference in height of the mercury column and columns of other liquids will of course exert an influence, but in the vicinity of the critical pressure this will only require a small correction. In the actual measurements each branch of the U-tube was placed in an electrically heated copper cylinder like that described above. For the purpose of following the change of phases the interface benzene-mercury was kept outside, and the temperatures of the two heating baths were raised alternately. When the interface benzene-mercury began to move the heating was reversed, and it was often possible to obtain a balance of pressures with vapour in both branches of the U-tube. The corresponding temperatures of the two heating baths were then read. From the known vapour pressure curve for benzene as determined by YOUNG (25), with a small correction for the heights of the columns of mercury and the other liquids, the vapour pressure curve of dioxan was determined. Systematic errors were to some extent eliminated by interchange of heating baths.

The vapour pressure curve of dioxan is shown in Fig. 2. The difference between the points marked with circles and those marked with crosses lies in the interchange of heating baths. Inside the experimental error of some 2 per cent, the vapour pressure of dioxan may be expressed by the curve shown in the diagram drawn according to the formula:

$$\log_{10} p = 4.69 - \frac{1750}{T}$$

where p is the pressure in bar and T is the absolute temperature. Extrapolating to the critical temperature 312°C (as determined above), the critical pressure is found to be 50 bar with a possible error of some 3 bar.

Summary.

1. The dielectric constant of liquid and solid boron tribromide has been measured over a wide range of temperatures. The dipole moment is small and presumably zero.

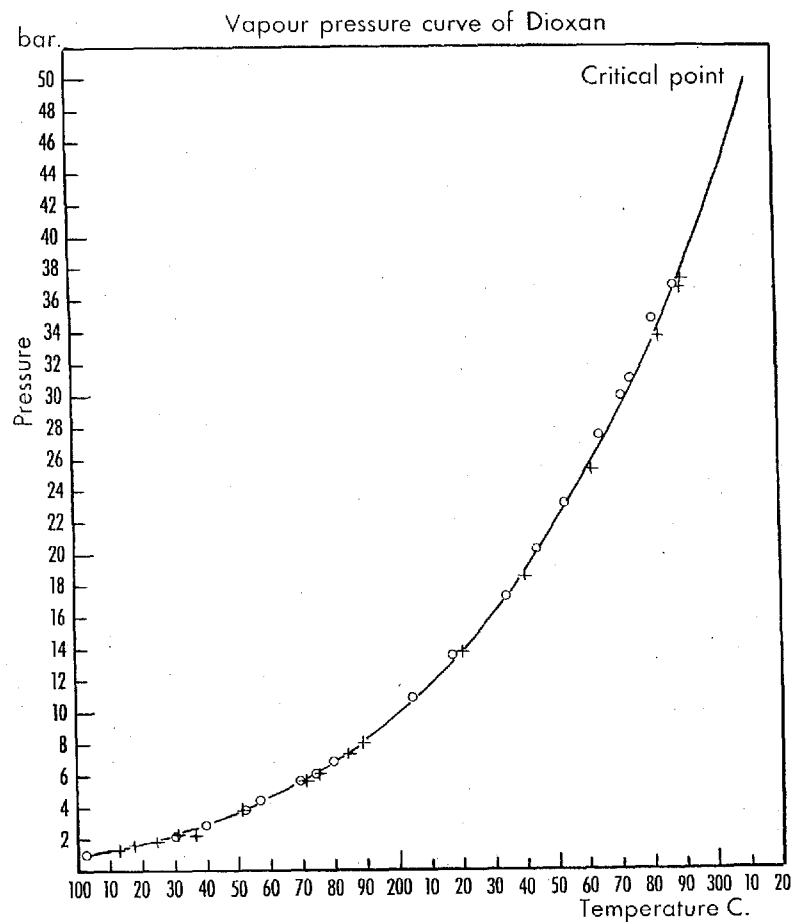


Fig. 2.

2. The surface tension of a sensitive liquid such as boron tribromide is conveniently measured by the capillary rise method in a modified Ostwald viscometer. Viscosity and surface tension data for boron tribromide, dioxan and ethylene dichloride have been obtained over a wide range of temperatures.

3. Simple methods and apparatus have been devised for determining the orthobaric curve and the vapour pressure curve in the vicinity of the critical point. The method of determining the vapour pressure by means of a balance of vapour pressures is particularly new. The bend of a U-tube is filled with mercury, and the substance to be investigated (dioxan) is enclosed (air-free) in one branch and a standard liquid (benzene) in the other. Each branch is placed in a separate heating bath, and the two are warmed alternately until the visible mercury-benzene interface moves rapidly, showing that vapour is present in both branches. By temperature regulation the motion is brought to a standstill, and the temperature of both baths is read. Knowing the vapour pressure curve of the standard liquid, that of the liquid under investigation may be determined.

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References.

- (1) HØJENDAHL, *Z. physikal. Chem. B.* 1933, **20**, 58.
- (2) TIMMERMANS and ROLAND, *J. Chim. Phys.*, 1937, **34**, 725.
- (3) STOCK and KUSS, *Ber.*, 1914, **47**, 3113.
- (4) SUGDEN, *J. Chem. Soc.*, 1933, 773.
- (5) HØJENDAHL, *D. Kgl. Danske Vidensk. Selskab, Mat-fys. Medd.* XVI, **2**, 9, 1938.
- (6) WATSON, RAMASWAMY & KANE, *Proc. Roy Soc.*, 1936, **A**, 156, 130.
- (7) ANDERSON, LASSETTRE & YOST, *J. Chem. Physics*, 1936, **4**, 703.
- (8) RAASCHOU, *Ind. Eng. Chem., (Anal)*, 1938, **10**, 35.
- (9) THORPE and ROGER, *Phil. Trans.*, 1894, **185 A**, 397.
- (10) FAUST, *Z. physikal. Chem.*, 1912, **79**, 101.
- (11) HERZ and LORENTZ, *Z. physikal. Chem. A.*, 1929, **140**, 406.
- (12) MAXWELL, *Phil. Mag.*, (4) 1868, **35**, 133.
- (13) RAMAN, *Nature*, 1923, **111**, 532.
- (14) DUNN, *Trans. Faraday Soc.*, 1926, **22**, 401.
- (15) ANDRADE, *Nature*, 1930, **125**, 309.
- (16) DEBYE, "Der feste Körper", 1938.
- (17) SCHIFF, *Annalen*, 1884, **223**, 72.
- (18) JAEGER, *Z. anorg. Chem.*, 1917, **101**, 1.
- (19) WORLEY, *J. Chem. Soc.*, 1914, **105**, 274.
- (20) CENTNERSZWER, *Z. physikal. Chem.*, 1904, **49**, 199.
- (21) GOUY, *J. Physique.*, (3), 1897, **6**, 479.
- (22) CAILLETET and MATHIAS, *Compt. Rend.*, 1886, **102**, 1202.
- (23) PAWLEWSKI, *Ber.*, 1883, **16**, 2633.
- (24) NADEJDINE, *Rep. d. Physik.*, 1887, **23**, 639.
- (25) YOUNG, *J. Chem. Soc.*, 1889, **55**, 486.

HINDERED ROTATION IV

THE RAMAN SPECTRUM OF DEUTERATED ETHYL BROMIDES

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