THE MEASUREMENT OF HIGH MOLECULAR WEIGHTS BY EBULLIOMETRY

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The construction of an ebulliometer for the measurement of molecular weights up to 40,000 is described. A 20-junction copper-constantan thermel and a sensitive galvanometer are used to measure the boiling point elevation to 0·2 mdeg. The apparatus has been used to determine the number average molecular weight of a range of polythene samples from 9000 to 35,000 molecular weight.

Osmotic pressure measurements are unsatisfactory for molecular weights below about 30,000 and existing ebulliometric methods, such as the improved Menzies-Wright apparatus [1, 2] become too inaccurate to be of much value above about 5,000. Since the molecular weights of the majority of the production grades of polythene fall within the range 5,000-30,000 there was an urgent need for a method of measuring molecular weight in this range.

The possibility of using an ebulliometric method depends upon being able to measure a very small temperature difference with sufficient accuracy. With polythene solutions, it is difficult to determine boiling temperatures at concentrations above 3 % because of the frothing which occurs, and it is desirable to work with much more dilute solutions than this because of the marked deviations from ideality which are encountered.

In toluene, which is probably the most suitable solvent for polythene in this connection, it is necessary to measure a temperature elevation of only 3 mdeg. if the solute has a molecular weight of 30,000. If 5 % accuracy is aimed at, it must be possible to measure this to within 0·15 mdeg.; this can be done with a suitable multijunction thermocouple and a sensitive galvanometer.

EXPERIMENTAL

APPARATUS.—The galvanometer was a Tinsley type 4789 long period galvanometer of 12 Ω resistance and sensitivity 1400 mm per μA at 1 m. In order to measure to 0·15 mdeg. it was necessary to use a thermocouple such that 0·15 mdeg. resulted in 0·5 mm deflection (this being the smallest deflection which could be measured accurately, taking into account such factors as vibration). The galvanometer required an external resistance of 200 ohms for critical damping; it can be calculated [3] that the optimum number of junctions, using copper and constantan wires of reasonable sizes, is about 50, but for convenience in construction and handling, it was decided to limit the number of junctions to 20, and the following procedure was adopted.

Selected lengths of 44 s.w.g. double silk-covered copper (resistance 1·4 Ω/m) and Eureka (resistance 97Ω/m) were coated with thin shellac solution and allowed to dry straightened out. 20 portions of each, 10 cm long, were cut, and laid alternately in a row on a piece of card, 20 × .7 cm, and secured in position with pieces of adhesive tape. The ends of the wires, which overlapped the edges of the card, were cleaned, twisted together in pairs and soldered. The junctions were then all trimmed to an overall length of 8 cm and re-insulated with Bakelite varnish. 36 s.w.g. copper was used for the leads. The thermel was then removed from the card and the wires bound together at each end with silk;

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finally the whole was thoroughly coated with Bakelite varnish and dried at 110° C for several hours before being assembled in the ebulliometer. The finished thermel had a resistance of 162 Ω.

The ebulliometer is shown in fig. 1. It consisted of a small boiler A, heated internally by a 2-ohm helix of 0·01 in. Pt wire B mounted on a horseshoe-shaped former. Current was supplied from a Variac transformer at 0-10 V. The Cottrell pump C was mounted with its bell immediately over the heater and arranged to deliver boiling solution on to the lower half of the thermocouple pocket D, which was wrapped with a helix of fine glass rod to promote spreading of the liquid over its surface ; it was protected from cooler reflux by an " umbrella " E with a hole at the top to admit the outlet of the pump. The upper half of the thermocouple pocket was surrounded by a double jacket of vapour, as shown, and the reflux returned to the boiler via a calibrated dripper, F. The outlet from the condenser was connected to a silica gel drying tube. The whole apparatus was placed inside a large Dewar vessel with an opening in the bottom for the outlet tube. The ground joint between the latter and the stopcock outside the Dewar vessel was cemented with shellac as it was only rarely necessary to undo it. The stopcock itself was capillary bore and lubricated with glycerol-dextrin.

The thermel was sealed into its tube with shellac, and the two sets of junctions were embedded in a small blob of bakelite cement which ensured contact with the walls ; also the copper leads from the thermel were coiled in such a way as to ensure contact with the upper part of the thermocouple pocket and thus minimize conduction of heat away from the junctions. These leads were insulated with polythene and brought out to the galvanometer directly ; no switch was incorporated in the main circuit, but to safeguard the galvanometer when a large temperature difference existed between the junctions, as for example when bringing a fresh portion of solvent to the boil, a shorting switch was connected in parallel with it.

The galvanometer was very sensitive both to vibration and fluctuations in ambient temperature ; for these reasons it was mounted on a heavy slab of concrete set in an old air-raid shelter well below ground level ; here a very steady temperature could be maintained and vibration was also minimized.

Water for the condenser was stored in a 20-l. aspirator at room temperature, and flowed by gravity at 5 ml/min into an interchangeable reservoir at a lower level.

FIG. 1.—(Dimensions in mm).

MATERIALS.—*Toluene* was purified by treatment with concentrated sulphuric acid [4] and fractionally distilled in a 50-plate column, collecting the fraction having b.p. 110·5-110·8°/760 mm, and n_D^{20} 1·4968.

Tristearin was recrystallized three times from ethanol and twice from ether. It then had m.p. 57·7°, f.p. 56·9°, mol. wt. (against benzil, in modified Menzies-Wright apparatus) found, 900 ; calc. for $C_{57}H_{110}O_6$, 891·5.

Hexatriacontane was prepared by reaction of octadecyl iodide with excess sodium in ether and recrystallized from methyl ethyl ketone ; m.p. 75·5° ; mol. wt. found, 500 ; cal. for $C_{36}H_{74}$, 506.

METHOD OF OPERATION.—The ebulliometer was charged from a pipette with 15 ml of pure toluene, which was heated to boiling and the current then adjusted to about 2 A. One hour was allowed for the establishment of thermal equilibrium, then the galvanometer shorting switch was opened and a reading taken of the deflection ; this was repeated until it was steady. Experiments were carried out to determine the boiling rate which gave the smallest deflection, and hence the least superheating (table 1). When the correct boiling rate was established and the galvanometer deflection was steady, weighed pellets
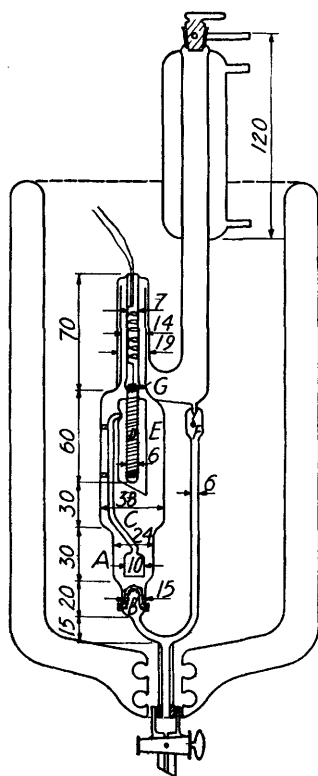
of the sample were introduced successively by dropping them down the condenser and readings taken of the deflection until it was again steady, usually after 15-20 min. At the end of the determination the apparatus was cleaned by refluxing with three portions of fresh toluene, removing each wash by suction through the tap at the bottom; finally a current of dry air was drawn through in the same way for 10-15 min.

CALIBRATION.—The deflection of the galvanometer with pure toluene boiling in the apparatus was measured at various boiling rates and from the results the working current for all the subsequent experiments was chosen. The working current chosen was 2·25 A. The relation between galvanometer deflection and temperature difference was determined by means of the reference compounds tristearin and hexatriacontane. In each case a plot of deflection against concentration was a straight line, so that the constant could be calculated from the equation

$$K = M\Delta d/w,$$

where M = mol. wt. of solute and Δd = change in galvanometer reading per w g solute in 15 ml of solvent. The results showed good agreement:

solute	value of K
hexatriacontane	$\begin{cases}1\cdot771 \times 10^6 \\ 1\cdot800 \times 10^6\end{cases}$
tristearin	$\begin{cases}1\cdot780 \times 10^6 \\ 1\cdot811 \times 10^6\end{cases}$
mean	$1\cdot79 \times 10^6$

MOLECULAR WEIGHT MEASUREMENTS.— Molecular weights were measured for a series of polythene samples ranging from grades 700 to 2. The results were calculated by plotting the values of $\Delta d/w$ against w, and making a straight line extrapolation to $w = 0$ (fig. 2). The molecular weights were then calculated from the relation

$$K/M = \lim_{w\to 0}\{\Delta d/w\}.$$

The results are shown in table 2.

FIG. 2.—Molecular weights of polythene samples.

TABLE 1.—DEFLECTIONS WITH PURE TOLUENE IN EBULLIOMETER

heating current, A	boiling rate, drops reflux per min	galvanometer readings, mm
1·5	8	ca. 40·0
1·75	32	32·5
2·0	60	30·0
2·25	96	29·0
2·5	120	29·0
2·75	160	29·0
2·9	180	30·5
(maximum)		

TABLE 2.—MOLECULAR WEIGHTS OF POLYTHENE SAMPLES

grade no.	intrinsic viscosity †	molecular weight
5	1·09	34,000 *
7	0·90	14,300
20	0·86	12,000
200	0·69	10,000
700	0·54	9,500

* This sample of grade 2 polythene was found to have a molecular weight of 32,000 by osmometry.[5]

† in tetralin solution at 75°.

DISCUSSION
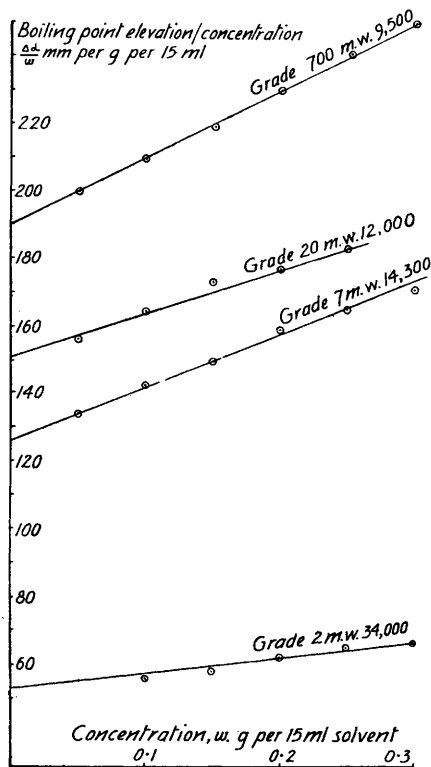
The object of this work was to extend the range of usefulness of ebulliometric measurements up to the point where osmotic pressure measurements could be used.   That this has been achieved is demonstrated by the close agreement between the value found for the molecular weight of grade 2 polythene, and the result obtained on the same sample by osmometry.

It is unlikely that the present apparatus would yield results of any value at all with samples of still higher molecular weight, for at this figure (*ca.* 35,000) the reproducibility of the results was only 10 %, while in the range 5-15,000 it was *ca.* 5 % and individual results were often duplicated within 2 %.

[1] Kitson *et al.*, *Anal. Chem.*, 1949, **21,** 401.

[2] Ray, *Chem. and. Ind.*, 1951, 837.

[3] White, *J. Amer. Chem. Soc.*, 1914, **36,** 2292.

[5] Vogel, *Textbook of Practical Organic Chemistry* (Longmans, 1948, p. 172).

[6] Harris, *J. Polymer Sci.*, 1952, **8,** 353.