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SIMPLE EBULLIOMETRIC METHOD WITH THE AID OF FOAMING SUBSTANCES

I. Water as Solvent

By C. N. Polydoropoulos

Laboratory of Physical Chemistry, E. M. Polytechnic of Athens

Introduction

Many different methods and different types of apparatus have been proposed for the determination of the boiling point of solutions and the subsequent calculation of the molecular weight of the solute. Of these we can distinguish three main methods: (1) the old one of Beckmann which is no longer in use; (2) Landsberger's method which, although it is theoretically the best, in practice gives satisfactory results only with difficulty; and (3) Cottrell's method[1]. Since then many improvements of Cottrell's method have been presented, some of which are referred to by Swietoslawski.[2] During recent years, the differential thermometers of the Menzies type[3] have also found a large application, because they avoid errors due to changes of barometric pressure.

Common features of all these pieces of apparatus are difficulty of construction and high cost. To overcome these difficulties this paper describes a very simple apparatus prepared from normal laboratory glassware. Nevertheless the results obtained are in all cases entirely satisfactory.

Laboratories not possessing special apparatus will find the determination of molecular weights of unknown substances by the following method to be straightforward.

The apparatus

The apparatus (Fig. 1) is composed of a flask (250 c.c.) a condenser and a thermometer, preferably a differential type with scale in 0·01°, e.g. a Beckmann thermometer. If a Beckmann thermometer is not available, a common one divided into 0·1° can be used, but in that case the use of a lens is necessary for the estimation of the hundredths of a degree.

The horizontal cardboard shield D has proved very effective. If it is absent the gases rising from the flame of the burner heat the stem of the thermometer up to a temperature much higher than that of the room and inevitable slight draughts cause serious fluctuations in the readings. With the shield in place the hot gases cannot reach the thermometer and so the stem is maintained at a temperature not essentially higher than that of the room and the scale readings are perfectly constant.

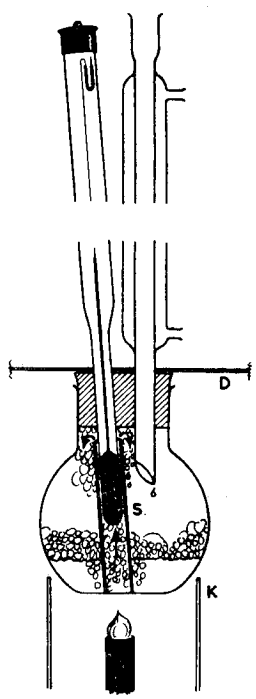

FIG. 1

The vertical cylindrical shield K protects the small flame of the burner.

It is necessary to insert into the flask in a vertical position a piece of glass tubing S so that the thermometer enters into the upper side of S. The lower cross-section of this glass tubing which touches the bottom of the flask should assist the formation of as many centres of boiling as possible. This is easily secured by rubbing this section of the tube on a flat file or on sand-paper.

The usefulness of the foam

As is well known the measurement of the boiling point of a pure substance is readily made by exposing the thermometer bulb to its vapour. The same procedure in the case of a solution does not give the boiling point of the solution but of the pure solvent.

On the other hand, the immersion of the thermometer bulb in the boiling liquid gives, as a rule, high and

unstable readings because superheating is inevitable on boiling.

To avoid superheating of the solution Landsberger proposed to heat it indirectly by condensing in it the vapour of the solvent. In Cottrell's method, on the other hand, the thermometer is placed in the vapour but the solution is continuously pumped over the thermometer bulb through the well-known Cottrell automatic pump.[1]

The advantages of both preceding methods are easily achieved in the present method by the use of a trace of foaming substance. Instead of pure water a very dilute solution of any foaming substance (e.g. common soap) is used as solvent. The apparatus is heated just below the base of the tube S by a small flame of a Bunsen burner. The production of bubbles is greatly facilitated because of the reduced surface tension of the solution and the roughness of the base of tube S. Thus the superheating is almost completely avoided. The foam thus produced ascends through the tube S, flows over the thermometer bulb continuously and pours over the upper edge of the tube S. Then it fills the flask and enters the lower part of the condenser, where it condenses and returns. Thus the thermometer is neither immersed in the solution nor into the steam. It is surrounded by the foam, viz., a mixture of steam and solution which has already reached thermal equilibrium. In addition the foam filling the flask provides further thermal insulation. Thus the thermometer readings become perfectly constant and the estimation of the boiling point elevation, after the addition of solute through the condenser, can be made with a precision of $\pm 0{\cdot}001°$ so that the uncertainty in ΔT should not cause an error of more than 1% in the molecular weight.

Foaming substances

In principle any foaming substance can be used, but those having a high molecular weight are preferable. On the other hand, foaming substances which react with the solute are excluded. For example common soap cannot be used for molecular weight determinations in acid solutions although it is the most available foaming substance. Fish glue nevertheless (also a very common substance) can be used in any case, as is reported below.

Four foaming substances have been tested, belonging to different types: (1) chemically pure sodium stearate, (2) common fish glue, (3) saponin (Kahlbaum), (4) the detergent Teepol.

The concentration of foaming substance must not be lower than a definite limit. For example sodium stearate 0·02%* does not give satisfactory results. The contrary must also be avoided, viz., an excess of foaming substance. Sodium stearate should be used in dilution 0·1% or instead of this an equivalent quantity of common soap. Fish glue also gives very good results in dilution 0·1%, Teepol in 0·05% and saponin in 0·02%.

Teepol has been prepared as follows: the commercial product on evaporation at room temperature deposits large, colourless, transparent crystals. These in dry air lose their water of crystallization, becoming white powder. A 0·05% solution of this powder in water is used here as the solvent. These four foaming substances are referred to as examples. The use of any other foaming substance is not of course excluded.

* Viz., 0·02 g. of sodium stearate per 100 g. of water.

Measurements of molecular weights

50 c.c. of a solution of the chosen foaming substance, which should preferably be fresh, is placed in the flask. Afterwards the tube S and finally the cork are inserted, taking care that the thermometer comes in the upper part of the tube. The end point of the condenser must be lower than the top of the tube S. If the thermometer is not placed quite vertical, the lower edge of S must have a corresponding slope (as in Fig. 1) so that it sits as well as possible on the bottom of the flask in order to obtain as many centres of boiling as possible.

It should be noticed that without the tube S the quantity of foam is significantly smaller. If the base of tube S is carefully roughened and fits well against the bottom of the flask the production of adequate foam is ensured. "Audible" boiling indicates that superheating of the solution is occurring because of inadequate production of bubbles.

The lower end of the thermometer should be 2 to 3 cm. above the surface of the solution.

On using the apparatus heating is continued until the temperature is constant for ten minutes. This is usually realized after heating for 45—60 minutes. The solute in the form of previously weighed pellets is then inserted through the condenser. After about 1 to 4 minutes the temperature again becomes constant. From the temperature difference ΔT the molecular weight may be calculated by the well-known formula.

The whole process requires 60—90 minutes but the actual measurement of the boiling point elevation ΔT is made so rapidly that any appreciable change of barometric pressure is improbable.

The heating can be accomplished either by means of a small flame of a common Bunsen burner just under the base of tube S (Fig. 1) or by means of an electric hot plate. In this latter case a small metal disc of the same diameter as the base of tube S is placed between the plate and the flash just under S so as to localize the heating.

The small quantity of the solute which can adhere to the condenser is usually negligible. Similarly the small quantity of water (0·2 to 0·3 g.) in the vapour state can also be neglected.

Results of the measurements

The method has been tested by means of about one hundred experiments. In Table 1 are presented some results representing mean values. For the calculation of molecular weights the humidity content of specimens has not been taken into account, nor has any correction been made to allow for possible graduation errors of the Beckmann thermometer. Nevertheless the precision

Table I

Foaming substance	Solute, percentage		Mol. weight found	Difference percentage from the stoichiometric value
0·10% sodium stearate	Dextrose	7·2—9·2	180·8±2·8	+0·1
	Urea ..	1·8—2·2	61·9±0·2	+3·2
	KCl ..	2·1—2·4	40·2±1·1	
0·10% fish-glue	Dextrose	4·8—9·0	184·0±2·1	+1·3
	Urea ..	4·5—5·2	62·8±0·8	+4·7
	KCl ..	2·0—6·2	42·8±0·4	
	H_3BO_3	4·0—5·9	62·0±0·6	0·0
0·02% saponin	Dextrose	3·0—5·1	182·6±1·8	+1·1
	Urea ..	2·0—8·0	64·0±0·6	+6·7
	KCl ..	2·2—2·6	41·6±0·9	
	H_3BO_3	2·2—4·7	65·8±0·5	+6·1
0·05% Teepol	Dextrose	3·0—9·0	185·0±2·9	+2·4
	Urea ..	1·6—4·6	63·5±1·0	+5·8
	KCl ..	1·0—6·0	43·2±1·5	
	H_3BO_3	1·0—5·0	64·4±1·2	+3·9

of the results is as good as in the cryoscopic measurements although the ebulliometric constant of water is three times smaller than its cryoscopic constant. For usual molecular weight determinations to within a few % accuracy the effect of the foaming substance on the ebulliometric constant is apparently quite negligible.

The mean value of differences is + 3·2%. In a future paper the possibility of the use of some other solvents, e.g. acetone, will be discussed. Finally the method could be useful in the investigation of foaming substances.

Summary

A simple but precise ebulliometric apparatus can be constructed from common glassware, viz. a flask, a condenser and a thermometer. The thermometer is not immersed in the solution but the circulation of an equilibrium mixture of solution and vapour over the thermometer bulb through a piece of glass tubing is achieved by the addition of a trace of foaming substance.

The experiments have been carried out in Athens in the Laboratory of Physical Chemistry of the E.M. Polytechnic in 1952—53.

References

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[3] Menzies, A. W. C., *J. Amer. chem. Soc.*, 1921, **43**, 2309