

CAMPBOR CRYOSCOPY BY DIFFERENTIAL THERMAL ANALYSIS

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The determination of the freezing point depression of organic solutions with camphor as solvent was performed by means of DTA. Amounts of 50–100 μg substance and 1–2 mg camphor were weighed on a platinum wire, the camphor being pressed to a pellet by a glass press. The temperature difference between the glass tubes with pure camphor and with solution was recorded versus temperature, while the samples were cooled in a previously heated aluminium block. The difference between the recorded deviations from a straight line was found to be a measure of the freezing point depression. Errors less than 5% were computed for various samples.

The microcryoscopic method is a simple and useful way to determine the molecular weight of organic compounds [1]. Many improvements of this method have been made since Rast [2] first used the camphor cryoscopy of Jouniaux [3] on the micro scale.

Some of these improvements should be mentioned:

New solvents with lower melting point and larger cryoscopic constant K have been found for a large number of compounds [1, 4, 5]. Many of these solvents – like camphor – do not exhibit the undesirable supercooling phenomenon.

The amount of substance needed to perform a molecular weight determination has been reduced to 50 μg or even less [6].

New improved methods of temperature measurement have been proposed by the use of thermocouples or thermistors [7–9].

The use of a microscope has made the observation of the appearance of the first crystals easier [10].

The use of heating curves rather than of cooling curves has been proposed in order to avoid supercooling [11].

Automatic recording of cooling curves [12] has been successfully introduced.

Closed systems with inert gas to avoid the influence of air, oxygen or moisture [13] have been constructed for sensitive compounds.

In this paper the differential thermal cooling curves of samples in camphor as solvent were used to determine the freezing point depression ΔT by improving a method first conceived in 1962 [14]. The temperature difference δT between a glass tube containing pure camphor and another one containing the solution was recorded versus the temperature of the heating block by means of an X–Y re-

order. The high sensitivity of DTA [15], reaching 0.002° for the temperature difference, and 0.1 mg for the sample weight [16], allows the replacing of subjective observation by objective record in microcryoscopy.

By this method only one single cooling curve is needed to obtain ΔT directly.

Experimental

Apparatus. The heating and cooling of the samples was performed in a cylindrical aluminium block Al, shown in the vertical section in Fig. 1. The lower part of the block held glass tubes of outer diameter 2.5–3.0 mm containing the solution and

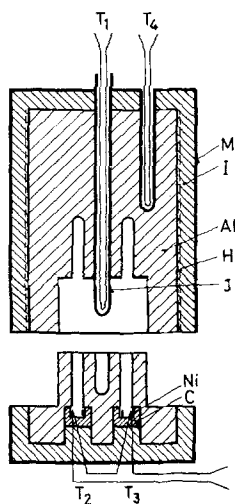


Fig. 1. DTA device. Al — aluminium block; T_1 , T_2 , T_3 , T_4 — thermocouples; Ni — nickel rings; C — teflon cups; J — glass jacket; H — heater; I — asbestos insulation; M — metal jacket

the pure solvent, while the upper part was heated by an 80 W electric heater. Through a perforation of this upper part an iron–constantan thermocouple T_1 in a glass jacket J was pushed into a boring in the lower part of the block, and served to give the X-function of the graph. Around the lower end of the glass tubes two nickel rings Ni welded to the iron–constantan thermocouples T_2 and T_3 ensured a good thermal contact between the tubes and the thermocouples. These two thermocouples were connected differentially and gave the Y-function of the graph. The nickel rings with the thermocouples were inserted into small teflon cups C in order to isolate them thermally and electrically from the heating block. A fourth thermocouple was connected to a thermoregulator V capable of switching on the heater at low temperatures (140° for camphor as solvent) and of switching it off at higher temperatures (about 200° for camphor).

The electrical scheme is given in Fig. 2a for the heater, and in Fig. 2b for the X-Y recorder input. The ends of the thermocouples were welded to copper wires, and the weldings were kept at constant temperature in a thermos flask *Th*. The thermal insulation *I* of the aluminium block allowed a cooling rate of about 2°/min and adjustable heating rates up to 3°/min.

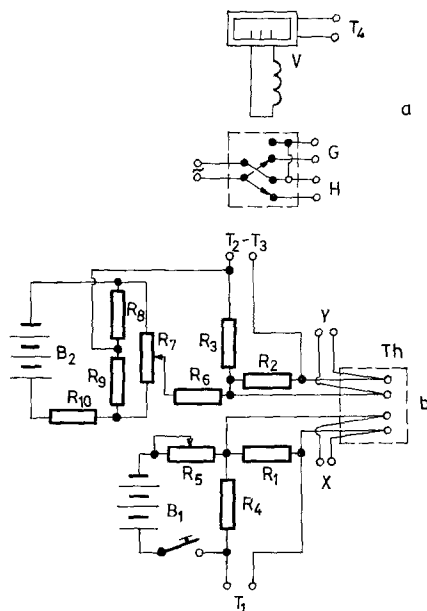


Fig. 2. Electrical scheme. *a*) Automatic switch; T_4 — connections to thermocouple T_4 (see Fig. 1); V — millivoltmeter for temperature regulation with mercury switch; G — connections to the galvanometer light source of the X-Y recorder; H — to the heater. *b*) Compensation of the thermoelectric voltage: B_1 , B_2 — 4.5 V batteries; R — resistors and potentiometers; T_1 , T_2 , T_3 — connections to the thermocouples; Th — Thermos flask; X and Y — connections to the X-Y recorder

Records were made photographically by means of a galvanometric X-Y recorder.* The X and Y functions were both adjustable zero and adjustable range. The size of the graph was 9 × 24 cm on spectrographic plates or photographic paper. The whole length of the paper was covered by about 60°, between 140° and 200°.

Procedure. The glass tubes with the solution and the solvent were put into their holes, so that they touched the nickel rings, and were then covered by the upper part of the aluminium block. When the power was switched on, the millivoltmeter switched on the heater *H* and switched off the light source of the X-Y plotter *G*, avoiding the plotting of the heating curve. Once the upper temperature limit was reached, the millivoltmeter *V* switched off the heater and switched on the light

* The X-Y recorder was made in the workshop of the Department.

source of the X–Y recorder. Thus, the differential cooling curve was plotted as δT versus T . As soon as the temperature reached the preset lower limit, the thermostat V was again put in operation and heating started, while the light source of the plotter was turned off. This cycle repeated itself until the power was switched off.

During the heating of the block the samples could be exchanged and the zero of the Y axis adjusted so as to draw the next cooling curve at a suitable distance from the preceding one. On the same photographic paper up to 15 curves could be plotted.

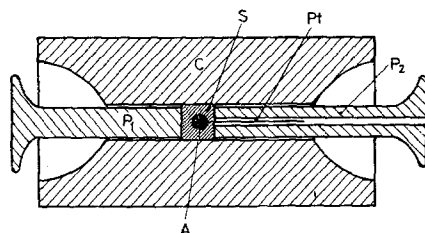


Fig. 3. Pellet press for camphor: C — capillary tube; P_1 , P_2 — pistons; Pt — platinum wire; A — substance drop, S — camphor

The exchange of the samples could be made at any time during the ten minutes of heating. The exact moment of the exchange is not critical for correct plots.

The tube sizes were chosen to fit the holes of the Boetius microscope in order to allow a comparison of the freezing point depression observed visually and that obtained from the differential thermal plots.

The samples contained about 20 mg of camphor and 1–2 mg of the compound to be studied, weighed in a conventional manner by the use of a microbalance.

Some of the samples contained only 50 μg of the compound, weighed with a torsion microbalance following the prescriptions of Sobotka [6]. The camphor was introduced into the tubes by a special technique. Small pellets of camphor were pressed in a capillary glass press (C in Fig. 3) with inner diameter 1.2 mm. The piston P_2 of the press had a capillary bore along its axis, in which a piece of known weight was introduced. The curl of the wire — eventually with the weighed pearl of the compound — was seized in the pellet S by pressing and then the pellet with the wire was weighed with the microbalance again. After weighing, the pellet was put into the tube together with the wire. During this operation no loss of camphor by sublimation was observed. The amount of camphor in the reference tube was about 1 mg and was kept unchanged.

The differential thermal cooling curve exhibited a maximum and a minimum corresponding to the freezing process of the pure camphor and of the solution, respectively. The difference between the beginning of the two deviations was a measure of the freezing point depression ΔT . After a proper calibration, ΔT could be read directly from the cooling curves.

Results and discussion

Fig. 4 shows several differential thermal cooling curves. While curves 11, 12 and 13 were plotted with solutions containing 20 mg of camphor and 1–2 mg of benzoic acid, curve 14 was plotted for a sample of about 50 μg benzoic acid and 2 mg camphor. The maxima and the minima are still large enough to be observed

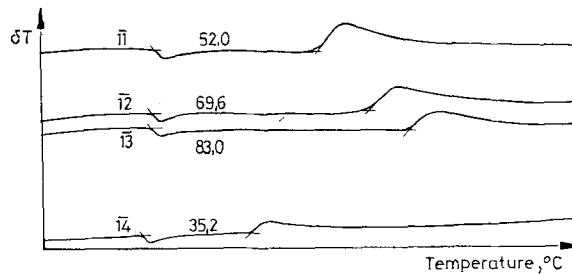


Fig. 4. Cooling curves. First figures are sample numbers, last figures give ΔL in mm

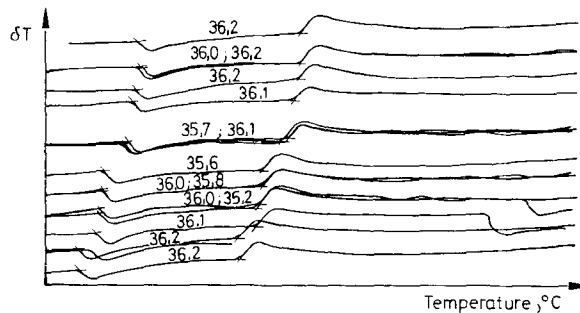


Fig. 5. Reproducibility of the cooling curves. Recording was repeated with the sample containing 0.056 mg benzoic acid in about 2.2 mg camphor

even with such small samples. The figures above the plots are the ΔL values in mm as measured between the two intersection points at the beginning of the temperature deviations on the curves. ΔL is proportional to the freezing point depression ΔT . The errors on the Y axis are smaller for small samples, and therefore the method is suited for molecular weight determinations on the ultramicro scale.

The reproducibility of the measured ΔT for a given sample is good (Fig. 5), as shown by the standard deviation of -0.6% computed for the set of 16 cooling curves in Fig. 5.

A calibration curve of L by T measured with a Boetius microscope is given in Fig. 6. The plot is a straight line, but a slight asymmetry of the thermocouples

causes an intersection of the ΔL axis 1.4 mm off the zero point. The plot was drawn by the least squares method. The slope of the calibration line was 3.3 mm/degree. The standard deviation of the slope was 5% and this can be accepted as a measure of the precision of the method. It should be mentioned that

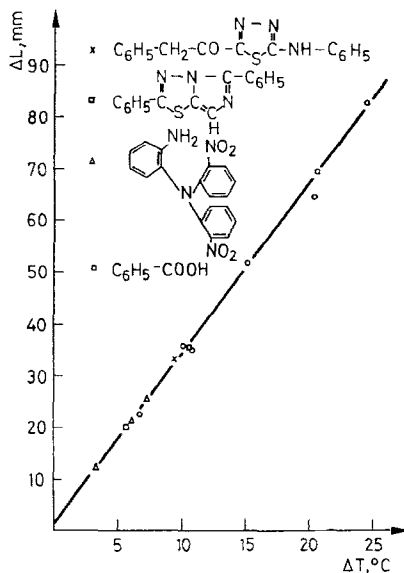


Fig. 6. Calibration curve

measurements were made using tubes of various diameters and wall thicknesses as well as various compounds. The precision of the method can therefore still be improved.

DTA cryoscopy has many advantages, such as high sensitivity (which allows working on the ultramicro scale), rapidity (one complete determination including weighing, needs about 30 minutes), and objective recording (errors due to subjective observation are avoided). Furthermore the method is open to improvements, so as to be fully automated.

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RÉSUMÉ — Emploi de l'ATD pour déterminer l'abaissement du point de congélation de solutions organiques où le camphre est utilisé comme solvant. On pèse 50 à 100 μg de substance et 1 à 2 mg de camphre sur un fil de platine, le camphre étant comprimé sous forme de pastille à l'aide d'une presse en verre. On enregistre en fonction de la température la différence de température entre les tubes de verre contenant le camphre pur et ceux contenant la solution, pendant le refroidissement d'un bloc d'aluminium préalablement chauffé. La mesure de l'abaissement du point de congélation est effectuée d'après la hauteur séparant la tracé d'avec l'horizontale. L'erreur est inférieure à 5% pour plusieurs échantillons.

ZUSAMMENFASSUNG — Die Bestimmung der Gefrierpunktserniedrigung von organischen Lösungen mit Campher als Lösungsmittel läßt sich mit Hilfe der DTA-Methode besser ausführen. 50—100 μg der Substanz und 1—2 mg Campher werden zu einer Pille gepreßt an einem Platindraht eingewogen. Die Temperaturdifferenzen zwischen den Glastuben mit reinem Campher und mit der Lösung werden im Laufe des Abkühlens gegen die Temperatur in einem vorgeheizten Aluminiumblock registriert. Die Differenz zwischen der registrierten Abweichung von einer Geraden gilt als Maß der Gefrierpunktserniedrigung. Der Fehler ist niedriger als 5%.

Резюме — Методом ДТА определено понижение температуры замерзания органических растворов с использованием в качестве растворителя камфоры. 50—100 мг вещества и 1—2 мг камфоры взвешивают в виде маленьких шариков и помещают на платиновую проволоку. Разницу температуры между стеклянными трубками с чистой камфорой и с раствором регистрируют в зависимости от температуры в процессе охлаждения, происходящем в заранее нагретом алюминиевом блоке. Установлено, что разница между зарегистрированными отклонениями от прямой линии является величиной понижения температуры замерзания. Ошибка составляет менее 5% для различных образцов.