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Abstract

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DETERMINATION OF THE PURITY AND CRYSTALLIZATION TEMPERATURE OF CERTAIN HYDROCARBONS IN AMOUNTS OF 1-2 ML

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Of the majority of published works on determining the purity of organic compounds from crystallization curves, the studies of Rossini (1,2) appear to be the most accurate and the most theoretically well founded. Unfortunately, newly synthesized organic substances are very often obtained in small amounts, and Rossini' s method proves practically inapplicable, since a fairly large amount of substance is needed to determine purity by this method (40-50 ml).

This circumstance has prompted attempts to reduce the amount of sample without violating the basic requirements of Rossini' s method. Among the conditions of Rossini' s method, the most essential is the requirement that thermodynamic equilibrium be maintained between the liquid and crystalline phases during the crystallization process.

In practice, this condition is fulfilled by stirring the substance, in most cases by means of an ordinary stirrer. This condition makes it difficult to reduce the amount of substance. A number of attempts have been made in this direction, the most serious of which is apparently the work of Peshkov (3), who, by altering the design of Rossini' s stirrer and using a copper-constantan thermocouple instead of a resistance thermometer, reduced the sample volume to 7-8 ml and obtained crystallization curves of a substance with an accuracy of up to ±0.01°.

In the joint work of Peshkov with Tilicheev and Yuganova (4), the sample volume was reduced to 3.5 ml, but in this case the stirrer was replaced by a red-copper grid inserted into the reaction vessel to equalize temperature gradients, which is an inferior substitute for stirring.

In a number of works by other investigators who attempted to reduce the amount of substance under study, stirring of the substance is not used (5), which violates Rossini' s condition and makes the application of his calculation method unjustified.

Our work is devoted to an attempt at a further reduction of the sample size to 1-2 ml without violating Rossini' s condition of thermodynamic equilibrium between the crystals and the liquid during crystallization. This is achieved by reducing the size of the reaction vessel and by somewhat changing the design of the stirrer.

The simplest Rossini stirrer consists of a nichrome wire twisted at one end in the form of a spiral (1). Such a stirrer is unsuitable for working with small amounts of substance, since the gap between the thermocouple sheath and the inner walls of the reaction vessel becomes very small, and the substance is smeared over the walls of the vessel. As a result, during crystallization of the substance, the thermocouple junction is not in the substance but in the air layer formed between the walls of the thermocouple sheath and the substance smeared over the vessel walls, and the thermocouple measures the temperature of this air layer rather than that of the substance under investigation, which leads to distortion of the results.

In the present work we use stirrers of two types. In some cas—

in some cases the stirrer is a nichrome wire, bent at one end into a closed ring according to the diameter of the reaction vessel (Fig. 1a); in others, three pieces of the same nichrome are soldered to the ring of nichrome wire at equal distances from one another (Fig. 1b), and these stir the substance.

The stirrer is driven by a motor and moves vertically with an amplitude of 20-25 mm and at a speed of 60–85 strokes per minute.

In general, the measurement scheme remains the same as that described in the first paper (6). The crystallization temperature is measured with a copper-constantan thermocouple calibrated against a standard resistance thermometer. Unlike the previous one, the thermocouple is made of thinner wires (7), approximately 0.05 mm in diameter, and is placed in a glass sheath with an outer diameter of 2.5 mm. Since, owing to its small diameter, the sheath is comparatively fragile, the thermocouple must be well centered so that the stirrer does not touch it during stirring. For this purpose the reaction vessel is made so that its upper part is wider than the lower part, where the substance under investigation is located (Fig. 1c). In the upper part of the vessel there is a centering plug and the fastening of the thermocouple in the plug closing the vessel with the substance. When working with substances crystallizing at temperatures from −65 to −140°, where the coolant is liquid nitrogen, a vacuum of 10^{-2}–10^{-3} mm Hg is created in the jacket of the reaction vessel in order to slow the rate of cooling. The crystallization curves are recorded automatically with an accuracy of ±0.05° on the tape of a reconstructed self-recording potentiometer EPP-09 (8), which serves as a null instrument for the low-resistance potentiometer PMS-48, compensating the part of the emf developed by the thermocouple up to the recording of the curve on the recorder and measuring the thermoelectric emf at the required point of the curve.

Fig. 1
(labels in the figure: "to the vacuum pump" ; "to the millivoltmeter" ; a, b, c)

Because of the small amount of the substance under investigation, the plateau on the curve is small and therefore inconvenient for calculations. To obtain a good curve it is necessary to increase the speed of motion of the chart tape of the recorder by two to three times in comparison with that used in recording curves for samples in amounts of 7-10 ml. Thus, for *n*-octane the tape speed had to be increased from 180 to 360 mm/hour when the volume of the sample under investigation was decreased from 10 to 1.5 ml. For *n*-heptane it was increased from 180 to 720 mm/hour.

The amount of impurities in the substance and its crystallization temperature under the condition of complete absence of impurities are determined from the formulas given in the works of Rossini ([1], [9], [10]). The simplest of them ([9]) is:

$$N_2 = A(t_{f_0} - t_f), \tag{1}$$

where N_2 is the amount of impurity in mole fractions, A is the cryoscopic constant, t_{f_0} is the crystallization temperature of the absolutely pure substance (i.e., under the condition of complete absence of impurity), t_f is the crystallization temperature of the initial sample, and

$$t_{f_0} = t_f + (t_f - t_r), \tag{2}$$

where t_r is the crystallization temperature of the initial substance at that point of the curve at which half of the substance has already crystallized.

The cryoscopic constant A is determined by measuring the lowering

of the freezing temperature of the initial sample as a result of adding to it a measured amount of a suitable artificial impurity [9], such that the resulting solution obeys Raoult' s law. Then the following relation holds:

$$A = \frac{N_2^* \left(1 + \frac{1}{2} N_2^*\right)}{t_f - t_f'}, \tag{3}$$

where t_f' is the crystallization temperature of the initial sample with the artificial impurity, and N_2^* is the artificial impurity, in mole fractions.

By the method described, five hydrocarbons were investigated: *n*-hexane*, *n*-heptane, *n*-octane, methylcyclopentane**, and 2,5-dimethylhexane***, in amounts of 1.2-2 ml. For all substances the amount of impurities, the crystallization temperature of the initial sample, and the crystallization temperature of the absolutely pure substance calculated from the experimental data were determined. The reproducibility of the crystallization curves of *n*-hexane, *n*-heptane, *n*-octane, and 2,5-dimethylhexane is ±0.05°, and that of methylcyclopentane is ±0.1°. The results obtained are summarized in Table 1.

Table 1

Substance	Amount of substance studied, ml	A, mole fraction/degree (authors' data)	A, mole fraction/degree (data [2])	Freezing temp., °C: initial sample (authors' data)	Freezing temp., °C: absolutely pure (authors' data)	Freezing temp., °C: absolutely pure (data [2])	Amount of impurity, mol.% (authors' data)
n-Hexane	1.2	0.050	0.0495	−95.63	−95.30	−95.347	1.60
n-Heptane	2.0	0.0504	0.0507	−90.98	−90.57	−90.610	2.05
n-Heptane	10.0	0.050	0.0507	−91.00	−90.58	−90.610	2.10
n-Octane	1.4	0.0544	0.0531	−56.94	−56.73	−56.798	1.15
n-Octane	8.0	0.050	0.0531	−56.97	−56.73	−56.798	1.20
2,5-Dimethylhexane	1.2	0.0477	0.0467	−91.37	−91.21	−91.200	0.75
2,5-Dimethylhexane	5.0	0.0480	0.0467	−91.38	−91.20	−91.200	0.80
Methylcyclopentane	1.5	0.0455	0.0488	−142.65	−142.43	−142.455	1.00
Methylcyclopentane	6.0	0.0454	0.0488	−142.68	−142.46	−142.455	1.00

For verification and comparison, the same samples of the listed substances were studied in parallel in amounts of 6–10 ml. The discrepancies between the results obtained when working with 1.2–2 and 6–10 ml of sample do not exceed the experimental error. Our data on the crystallization temperatures of absolutely pure substances and the cryoscopic constants of the substances studied, both for samples in amounts of 1.2–2 ml and for samples in amounts of 6–10 ml, and the data on the crystallization temperatures of absolutely pure substances and the cryoscopic constants for these same substances [2], agree well within the indicated accuracy (Table 1).

Thus, the possibility has been demonstrated of determining the purity of organic substances in amounts of 1–2 ml.

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