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THE GAS CHROMATOGRAPHIC DETERMINATION OF IMPURITIES AND OXIDATION OF CAPROLACTAM*

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SUMMARY

A gas chromatographic technique has been developed for the determination of the impurities in caprolactam, using Carbowax 20M as the partition liquid and Chromosorb P as the support, treated or untreated with potassium hydroxide. The system was used on a semipreparative scale for the separation of the two main impurities of ε-caprolactam, *viz.* 6-methyl-2-piperidone and octahydrophenazine, after enrichment by continuous crystallization.

To confirm their identity, the two impurities were synthesized and injected into the gas chromatograph. Other impurities were identified by comparison of their retention times with those of known compounds.

A technique was also developed to determine the degree of oxidation of caprolactam by gas chromatography.

INTRODUCTION

Caprolactam is used greatly for nylon 6 production, and can be synthetized in different ways. The most common industrial process is the Beckmann rearrangement of cyclohexanone oxime[1,2], obtained from cyclohexanone. Cyclohexanone oxime is also obtained by the photolytic rearrangement of nitrosocyclohexane[3,4] or by the reduction of the sodium salt of nitrocyclohexane[5].

Another well-known process is its derivation from hexahydrobenzoic acid, which by reaction with nitrosylsulfuric acid directly gives caprolactam[6].

The impurities of caprolactam can be derived from the raw materials used in the process, from side reactions, and from the degradation of caprolactam, which is particularly sensitive to oxygen[7,8].

The commercial products used for nylon 6 production must have a high level of purity. They are usually analyzed by non-specific methods, such as the permanganate test, melting point, colorimetry, alkalinity, acidity and volatile bases determination[9].

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MASTRANGELO[10] added different quantities of cyclohexanone, cyclohexanone oxime, octahydrophenazine and water to caprolactam and determined the corresponding decrease of the freezing point. The ratio between the mole concentration of the impurities and the decrease in freezing point is reasonably constant, but this also is a non-specific method.

In order to check the starting materials used for caprolactam synthesis, IOGENSEN *et al.*[11,12] used a gas chromatographic technique. More recently ONGEMACH AND MOODY[13] described the quantitative determination of caprolactam in the aqueous extracts of polymers, employing SE-30 on Diatoport S.

As the literature does not report any procedure for the detection of caprolactam impurities, we decided to examine the possibilities offered by gas chromatography.

As partition liquids we tried Versamide 900, Carbowax of different molecular weights, XE-60, SE-30, Apiezon L, Polypack, Bentone 34, polyethyleneglycol succinate, and finally high vacuum Dow Corning silicone grease and XE-60 combined in series with Carbowax 6000 and Bentone 34, respectively.

Supports tried were teflon, silylated Gaschrom P, Chromosorb P and W, the last two treated with acids, washed to neutrality, and eventually mixed with phosphoric acid or potassium hydroxide. These supports were variously combined with the above-listed partition liquids.

The impurities present in caprolactam in the range 0.01–0.05% were separated *via* semi-preparative gas chromatography, after enrichment by continuous crystallization. Other impurities, normally below 10 p.p.m., were identified by means of the KOVATS'[14] retention index, modified by MAUME[15] and D'ABRIGEON[16]:

$$I_i = 100\,z' + 100n \cdot \frac{\log \dfrac{(d'_R)_i}{(d'_R)_{z'}}}{\log \dfrac{(d'_R)_{z'+n}}{(d'_R)_{z'}}}$$

This equation is valid for a given partition liquid and at a fixed temperature when a product "*i*" is injected into the gas chromatograph with two homologous compounds, the number of carbon atoms being equal to z' and $z' + n$ respectively, these two being eluted immediately before and after the unknown substance. In our case we used linear aliphatic alcohols as reference products.

In order to confirm their nature, we synthetized the unavailable impurities of caprolactam by procedures already described. 6-Methyl-2-piperidone was prepared by cyclization of δ-xycaproic acid with formamide[17]. Octahydrophenazine was prepared by treating 2-aminocyclohexanone-hydrochloride with sodium hydroxide and hydrogen peroxide[18].

EXPERIMENTAL

Concentration of caprolactam impurities by continuous crystallization

Fig. 1 shows the Pyrex glass continuous crystallizer used for the concentration of caprolactam impurities. Caprolactam was fed in a molten state into "A", cyclohexane was introduced from "B". Caprolactam was completely dissolved in the 52°

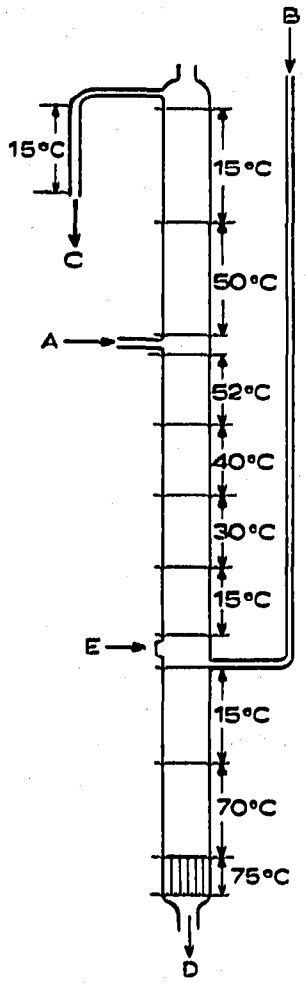

Fig. 1. ε-Caprolactam continuous crystallizer.

zone. The solution obtained, flowing down by gravity through the column, was progressively cooled down to the section below the solvent feed point. The crystals were completely separated in this zone, and sedimented over a layer of previously prepared molten caprolactam. The crystals remelted in the 70° zone and released the greatest part of the occluded solvent. The level of the melt was kept constant by continuously discharging the lactam from the bottom of the column, through a small heat exchanger maintained at 75°.

Above the caprolactam feed point the solution was progressively cooled. The separated caprolactam crystals, going down by gravity, entered the hot zone, redissolving. The cyclohexane solution, enriched with impurities, left the column from "C".

An alternating movement was transmitted by means of a piston, through an elastic membrane in "E" to the liquid column. This prevented the crystals from adhering to the walls of the crystallizer. Nevertheless after a period of time the walls were covered with crystals, which were removed by slowly introducing a metallic scraping ring, rigidly mounted on a stainless steel shaft.

The temperature of the different zones was maintained by circulating water

through the glass jackets. The temperatures indicated in Fig. 1 are those of the solutions in the column.

Gas chromatography

A Carlo Erba Fractovap model C (type AID/f) gas chromatograph, fitted with a flame ionization detector, was used for the analytical work. The recorder was a Leeds & Northrup Speedomax model G. The following operating parameters were used:

Column: 10% (w/w) Carbowax 20M on Chromosorb P 60–80 mesh, with or without 5% potassium hydroxide, 80 cm × 5 mm I.D. stainless steel tube.

Column temperature: 180°.

Evaporator temperature: 250°.

Detector temperature: 250°.

Carrier: nitrogen, with a flow rate of 50 ml/min.

Hydrogen flow rate: 35 ml/min.

Air flow rate: 300 ml/min.

Injection: 4 μl of a 50% (w/v) caprolactam solution in carbon disulfide, gas chromatographic grade (supersaturated solution).

The column treated with potassium hydroxide was prepared according to the following procedure: Chromosorb P was washed four times with hydrochloric acid, the acid being allowed to stay in contact with the Chromosorb each time for 6 h with occasional stirring, then it was washed with distilled water to neutrality. The product was then dried at 300° and mixed with methanolic potassium hydroxide. The solvent was evaporated at 40° under vacuum (20 mm Hg) in order to obtain a fluid paste. Carbowax 20M, dissolved in methylene chloride, was added to the residue. The solvent was evaporated again and the residue was dried at 110° for 2 h.

For the semi-preparative work a Carlo Erba Fractovap model G.P gas chromatograph was used. Effectiveness of separation was checked with the analytical section of the instrument, into which approx. 2% of material was switched. Operating conditions were the same as the analytical ones. The column was 2 m long, with a 10 mm internal diameter, filled with Carbowax 20M supported on Chromosorb P, treated with 5% potassium hydroxide.

DISCUSSION

Among the partition liquids examined Carbowax 20M was judged to be the most effective. We preferred Chromosorb P, with or without potassium hydroxide treatment, as support. From the evaluation of these two types of support we concluded that it was not possible to use only one of them, on account of the different chemical nature of the impurities of the lactam. We used also Chromosorb P mixed with 1% phosphoric acid, but we were not able to obtain reproducible gas chromatograms. Theoretically the use of a support mixed with alkali should have a limitation due to the fact that it should react with acid substances. We confirmed this hypothesis in practice by injecting into the column a series of carboxylic acids.

However analysis of commercial samples of caprolactam with Chromosorb P alone never showed a higher number of peaks. On the contrary with particularly

impure caprolactam we have always observed a higher number of peaks with the "basic" column.

After the identification of the nature of these peaks it was possible to conclude that the performance of this column was due to a better separating power. Taking into account the possible impurities of the raw materials used and the by-products of the different steps of the synthesis of caprolactam, we injected into columns containing the "neutral" or the "basic" support the following substances:

Propionic, butyric, isobutyric, valerianic, adipic and ε-amino caproic acid, ammonia, ethylamine, *n*-propylamine, *n*-butylamine, isobutylamine, pentylamine, aniline, *ortho*- and *para*-toluidine, phenol, nitrobenzene, methylisobutyl ketone, dimethylisobutyl ketone, cyclopentanone, 2-methylcyclopentanone, 3-methylcyclopentanone, cyclohexanone, cyclohexanol, 2-methylcyclohexanol, δ-valerolactone, cyclohexanone oxime, phenazine, N-oxyphenazine, octahydrophenazine, δ-valerolactam, 6-methyl 2-piperidone, isobutyl-isopentanamide, *tert.*-butyl-*n*-butanamide, *tert.*-butyl-isobutanamide, *tert.*-butyl-propanoamide, *tert.*-butyl-*n*-pentanamide, *tert.*-butyl-isopentanamide, isobutyl-isobutanamide, *n*-propyl-*n*-butanamide, *n*-propyl-isobutanamide.

Figs. 2 and 3 show the chromatograms obtained with the neutral and alkaline support, respectively, after injecting a caprolactam sample enriched with the impurities previously found in the commercial product. Methyl myristate was used as a reference for the retention times and is eluted between the toluidines and 6-methyl-2-piperidone. It can also be usefully employed as an internal standard for the quantitative evaluation of the impurities.

Neither of the columns separated the toluidines, which are eluted with retention times of 0.46 and 0.49 with the neutral and alkaline columns, with a detectability limit of 0.5 p.p.m. On the neutral column, they are eluted together with cyclohexanone oxime, which, in its turn, in the alkaline system gives a signal with a retention time equal to 0.11. This very frequent impurity probably decomposes in the alkaline column, as its detectability limit increases from 1 p.p.m. for the "neutral" column approximately to 10 p.p.m. The quantitative evaluation of cyclohexanone oxime can be performed by subtracting the toluidine content determined with the alkaline column from the sum of toluidines and cyclohexanone oxime obtained with the neutral column. This is possible because the correction factor for the toluidines is

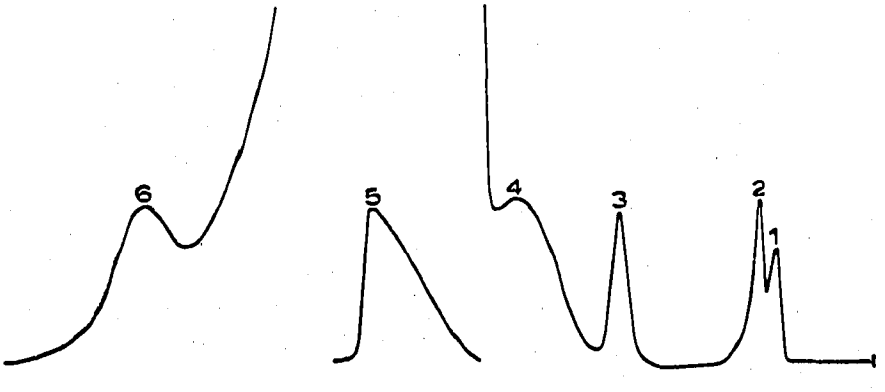

Fig. 2. Caprolactam enriched with typical impurities. Support: Chromosorb P. 1 = Aniline; 2 = *o*- and *p*-toluidine and cyclohexanone oxime; 3 = methylmyristate; 4 = 6-methyl-2-piperidone; 5 = caprolactam; 6 = octahydrophenazine.

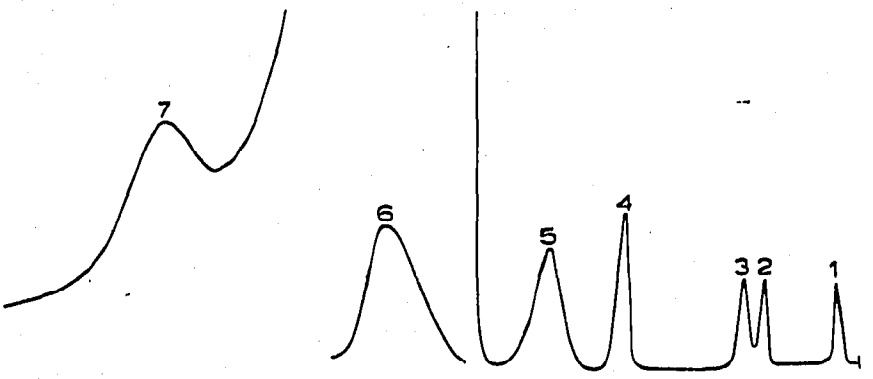

Fig. 3. Caprolactam enriched with typical impurities. Support: Chromosorb P mixed with 5% potassium hydroxide. 1 = Cyclohexanone oxime; 2 = aniline; 3 = *o*- and *p*-toluidine; 4 = methylmyristate; 5 = 6-methyl-2-piperidone; 6 = caprolactam; 7 = octahydrophenazine.

the same as that for cyclohexanone oxime. Aniline is well separated in both systems, with a detection limit of 0.5 p.p.m. and with retention times of 0.39 and 0.41 in the neutral and alkaline columns, respectively.

The separating power of the neutral system is again critical for 6-methyl-2-piperidone. When this product is present in a few p.p.m. it becomes visible as a shoulder on the caprolactam peak. The detection limit increases from 2 p.p.m. on the alkaline support to 10 p.p.m. The retention time is 1.39 with the alkaline system, 1.41 for the neutral column.

Octahydrophenazine leaves the column on the tail of caprolactam, with a detection limit of 20 p.p.m. and retention times of 2.88 and 2.93 in the neutral and alkaline columns, respectively. On the other hand, a few p.p.m. of octahydrophenazine show a high absorption in ultraviolet light, at approximately 290 nm. When this absorption is observed, a small inflection of the tail of the caprolactam peak around the expected retention time may also be sufficient to confirm the presence of this impurity.

In some samples of caprolactam we observed a not very well resolved shoulder before the peak of 6-methyl-2-piperidone. As we had only small quantities of these materials it was not possible to identify this impurity.

The presence of octahydrophenazine and 6-methyl-2-piperidone was confirmed by separating them with a semi-preparative gas chromatograph, the support being treated with alkali. We injected, into the gas chromatograph, a sample of caprolactam enriched with impurities by means of the continuous crystallization system described in Fig. 1. This material contained 30% of caprolactam and 70% impurities. In one step we obtained the two substances with a purity higher than 95%. The products were finally purified to approximately 100% by liquid chromatography on silica gel. To confirm the structure of octahydrophenazine, which has already been separated from caprolactam by SCHAFFLER[19], we compared its physical properties and I.R. spectrum with those of the synthetic product. For 6-methyl-2-piperidone we completed our investigation with an elementary analysis and the N.M.R. spectrum, shown in Fig. 4.

The presence of cyclohexanone oxime, normally below 5–10 p.p.m., is easily explained by the fact that this is the starting product of the last step of the synthesis

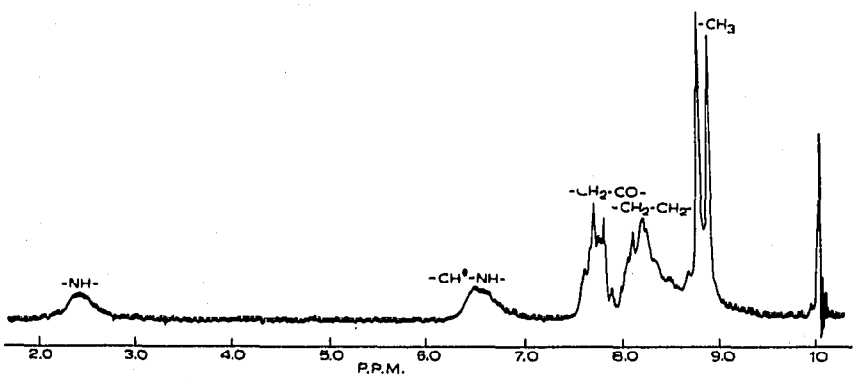

Fig. 4. N.M.R. spectrum of 6-methyl-2-piperidone.

of caprolactam. The identification of aniline, *o*- and *p*-toluidine and octahydrophenazine, always present below 10 p.p.m., confirms the results of SCHAFFLER[19], who separated these products from 300 000 kg of raw material obtained from the Beckmann rearrangement. The origin of these impurities was comprehensively explained by the same experimenters.

Aniline and the toluidines affect the caprolactam polymerization, as their functional groups react with the end groups of the polymer. Octahydrophenazine accelerates caprolactam oxidation and its presence is undesirable.

6-Methyl-2-piperidone, present up to 100 p.p.m., should be the Beckmann rearrangement product of 2-methyl-cyclopentanone oxime, an impurity of cyclohexanone. In fact, we submitted caprolactam to drastic chemical, thermal and oxidative treatment and never identified 6-methyl-2-piperidone among the products obtained. 6-Methyl-2-piperidone does not polymerize with caprolactam and can be easily eliminated from the polymer by common solvents. This agrees with the results of CUBBON[20], SCHAFFLER AND ZIEGENBEIN[21] and HALL AND SCHNEIDER[22]. These authors confirm that polymerization of five- and six-membered ring lactams can be completely inhibited by the presence of substituents in the ring.

Adipimide has been reported as the last step of caprolactam oxidation[7,8]. Imides, on account of their acid nature, are not eluted from the "alkaline" system proposed by us for the caprolactam analysis. This should preclude the use of this column for oxidized caprolactam, but this is not confirmed experimentally.

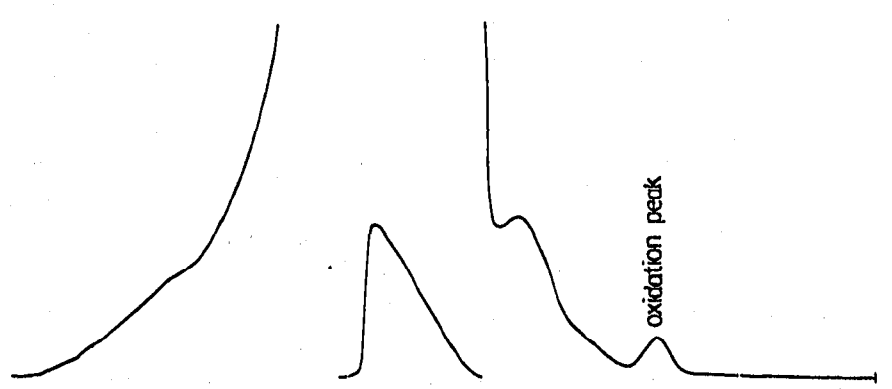

Fig. 5. Oxidized caprolactam. Support: Chromosorb P.

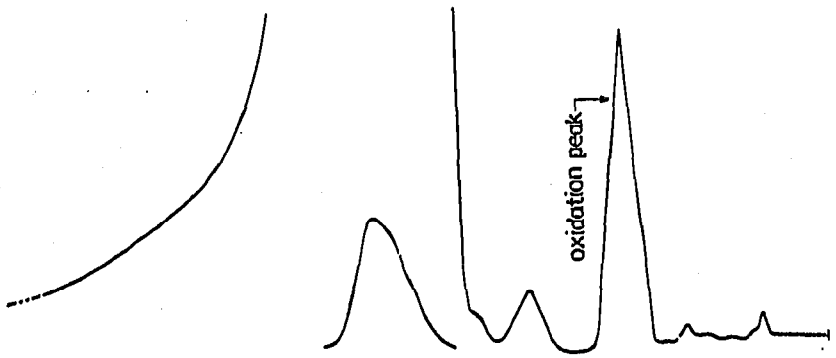

Fig. 6. Oxidized caprolactam. Support: Chromosorb P mixed with 5% potassium hydroxide.

Figs. 5 and 6 show chromatograms obtained with Chromosorb P or Chromosorb P mixed with alkali, respectively. The sample injected was oxidized caprolactam, prepared by bubbling air into the product heated at 100° for 24 h. In Fig. 5, before the 6-methyl-2-piperidone peak, another peak appears with a retention time of 0.44. (This retention time is with reference to caprolactam. Methyl myristate overlaps with the new peak.) The area of this peak during the first stage of the oxidation process increases almost proportionally with the time of oxidation.

Fig. 6 shows the same peak, with a retention time of 0.46, but with a larger area. We will consider this as the "oxidation peak". There are other peaks in the chromatogram not revealed by the neutral system. Differences are more evident as the oxidation proceeds.

From our data it is possible to draw some preliminary conclusions:

The support mixed with potassium hydroxide is preferable for the analysis of oxidized caprolactam.

The oxidation mechanism of caprolactam reported by others[7,8] cannot be considered completely satisfactory.

The oxidation kinetics can be studied by means of a characteristic "oxidation peak", which increases almost linearly with time up to a constant value. At this point the areas of other peaks suddenly increase.

Caprolactam can be oxidized under controlled conditions (for example bubbling for 6 h at 100° 20 l/h of air). After injection of the sample into a gas chromatograph, it is possible to judge its stability to oxidation from the area of the oxidation peak.

From the data obtained with a series of samples of different origin we concluded that oxidation stability of commercial caprolactams decreases as the purity of material increases.

We classified the purity of the samples examined by gas chromatography and U.V. absorption, as they were not differentiated by other analytical techniques. Our hypothesis was confirmed by submitting a sample twice crystallized from cyclohexane to the oxidation test. Crystallization was performed by cooling the solution obtained at room temperature to −20° and collecting the crystals under nitrogen. The pure material was many times more sensitive to oxidation than the original caprolactam.

We are continuing our research in order to identify the oxidation products of caprolactam.

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