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## Note

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### Determination of caprolactam and its oligomers by means of liquid chromatography

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The separation of a mixture of caprolactam oligomers and their identification by paper chromatography was investigated by Katorzhnov<sup>1</sup>. The determination of the components of such a mixture by various analytical methods has been reviewed<sup>2</sup>. Caprolactam has been analyzed by gas chromatography<sup>3-7</sup>, and its oligomers separated by gel permeation chromatography<sup>7-10</sup> using various types of Sephadex and Bio-Gel. For this study, we have used liquid chromatography in columns packed with silica gel.

#### EXPERIMENTAL

##### *Chemical*

Technical caprolactam (purity 99.9%, Spolana, Neratovice, Czechoslovakia) was purified by crystallization three times from benzene and dried at 260 Pa; m.p. 67-69°. The cyclic dimer of caprolactam was obtained by repeated crystallization of a technical mixture of caprolactam oligomers from water; m.p. 342°. These substances were employed as the standards.

A mixture of caprolactam oligomers was prepared from the water extract obtained in the production of polycaprolactam chips (Povážské Chemické Závody, Žilina, Czechoslovakia), which comprises a suspension of 5.8% of undissolved compounds. The solid part, containing<sup>11</sup> 49% of caprolactam and 51% of prevalently cyclic oligomers, was filtered, dried and repeatedly extracted with benzene. The content of monomer decreased after each extraction. For the testing of the analytical method, the monomer and cyclic dimer were added to the final mixture. Paper chromatography<sup>12</sup> was used to detect the presence of individual oligomers.

##### *Liquid chromatography*

A simple apparatus constructed in the Institute of Macromolecular Chemistry was equipped with a Model 2025-50 through-flow differential refractometer (Knauer, Oberursel, G.F.R.) and with two types of glass column. The column (120 cm × 2 mm) used for the eluent tetrahydrofuran-heptane-water (93:7:5) was packed with Sil-pearl (Kavalier, Votice, Czechoslovakia), particle size 30-40 μm; the operating pressure was 2.5 MPa, the flow-rate 0.5 ml/min and the temperature 25°. The column

(30 cm  $\times$  5 mm) used with the system 1-butanol–glacial acetic acid–water (7:3:1) was packed with the globular porous silica gel SG50II-7.5KP, which was prepared in the Institute of Macromolecular Chemistry; the operating pressure was 1.5 MPa and the flow-rate 0.7 ml/min at 26°. The amount of injected material ranged from 5 to 10  $\mu$ g.

## RESULTS AND DISCUSSION

The analysis of caprolactam and its oligomers was investigated by means of liquid chromatography in columns packed with silica gel. The results for the oligomers were obtained with the eluent tetrahydrofuran–heptane–water (93:7:5). Owing to the limited solubility of the oligomers, it was necessary to add several drops of formic acid to complete the dissolution of the analyzed substrate. The presence of formic acid does not interfere with the determination of the individual oligomers (Fig. 1). However, if the monomer is also present in the mixture, its identification is disturbed by the peak of formic acid. An unambiguous assignment of the presence of the cyclic dimer of caprolactam in a mixture with the monomer is also difficult due to the small difference between their elution times. The dimer peak overlapped that of the caprolactam present in large excess in the mixture. The tetrahydrofuran–heptane–water eluent may be used for determining the composition of a mixture of caprolactam oligomers free from monomer.

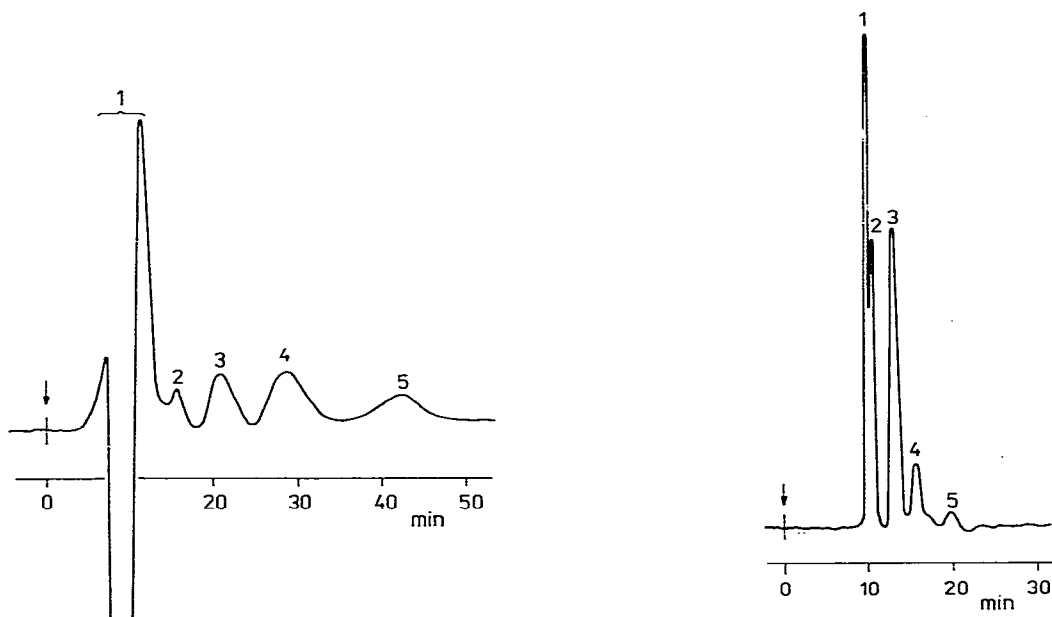


Fig. 1. Chromatogram of the separation of a mixture of caprolactam oligomers on silica gel using tetrahydrofuran–heptane–water (93:7:5) as eluent in the presence of formic acid. Peaks: 1 = formic acid; 2 = dimer; 3 = trimer; 4 = tetramer; 5 = pentamer.

Fig. 2. Typical chromatographic separation of a mixture of the monomer and oligomers of caprolactam on silica gel using 1-butanol–glacial acetic acid–water (7:3:1) as eluent. Peaks: 1 = monomer; 2 = dimer; 3 = trimer; 4 = tetramer; 5 = pentamer.

A complete dissolution and separation was attained with the eluent 1-butanol-100% formic acid-water (75:20:10). However, formic acid is a potential source of corrosion of some parts of the chromatographic apparatus, and acetic acid is more suitable. In 1-butanol-glacial acetic acid-water (7:3:1), complete dissolution of caprolactam and its oligomers occurred and a good separation was achieved (Fig. 2). The applicability of the method was verified with mixtures containing the monomer and oligomers up to the pentamer and having a known ratio of monomer to dimer.

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