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Thin-layer chromatography of ϵ -caprolactam and its cyclic oligomers

After polycondensation polycapramide contains, at equilibrium, approximately 10% of monomers and oligomers, most of which are cyclic. The paper chromatography of the cycloamide homologue was first reported by ZAHN AND REXROTH¹, who detected it by chlorination and subsequent dipping in *o*-tolidine and potassium iodide mixture. CZEREPKO^{2,3} reported the use of chromogenic reagents for alkaloids, such as potassium bismuth iodide, potassium iodoplatinate and potassium antimony iodide, for the detection of ϵ -caprolactam in paper chromatography. *m*-Dinitrobenzene was also reported to be useful as a detection reagent⁴. The sensitivities of the chromogenic reagents mentioned above were at most about 5 to 10 μ g of ϵ -caprolactam.

It has now been found that the sensitivity of potassium bismuth iodide toward ϵ -caprolactam and its cyclic oligomers was improved approximately ten times and 1 μ g or less of the cycloamides could be detected on thin-layer chromatograms if they are sprayed with diluted sulfuric acid subsequent to Dragendorff's reagent.

Experimental

Apparatus. Standard TLC plates of Tōyō Kagaku Sangyō Co., Ltd., Model HC-20, were used. Glass plates used were 20 × 20 cm.

Materials. Cyclic oligomers (monomer to tetramer) of polycapramide were obtained by fractional vacuum sublimation of an aqueous extract from polycapramide⁵.

Higher cycloamide homologues than the tetramer were synthesized by the procedures described by ZAHN AND DETERMAN⁶.

The adsorbents used were alumina (Aluminiumoxid-G, Merck) and silica gel (Kieselgel-G, Merck, nach STAHL).

Dragendorff's reagent was prepared as follows:

(A) 1.0 g of bismuth subnitrate was dissolved in a small amount of concentrated hydrochloric acid and precipitated with aqueous ammonia. The precipitate formed after filtering was dissolved again in a small amount of concentrated hydrochloric acid and then 3.0 g of potassium iodide were added. The whole was diluted to 50 ml with distilled water.

(B) 25 g of potassium iodide were dissolved in 100 ml of distilled water.

(C) 70% aqueous acetic acid.

A, B and C were mixed in the volume ratio of 5:5:40.

TABLE I

R_F VALUES OF ϵ -CAPROLACTAM AND ITS CYCLIC OLIGOMERS

Solvent systems: A = Isopropanol-methanol-water (1:1:1); B = tetrahydrofuran-petroleum ether (b.p. 100-120°)-water (186:14:10); C = *n*-butanol-acetic acid-water (10:2:5); D = *sec*-butanol-formic acid-water (75:15:10); E = *n*-butanol-concentrated hydrochloric acid-water (100:20:38); F = *n*-butanol saturated with water.

n	Kieselgel						Alumina					
	A	B	C	D	E	F	B	C	D	E	F	
1	0.81	0.75-0.79	0.69-0.75	0.69-0.72	0.70	0.92	0.90	0.91-0.95	0.88	0.87		
2	0.77	0.70-0.78	0.64-0.52	0.56-0.60	0.61	0.86-0.88	0.90	0.94-0.93	0.88			
3	—	0.61-0.65	0.55	0.47-0.49	—	0.83	—	0.92	—			
4	0.74	0.49-0.57	0.39-0.40	0.39-0.43	0.48	0.76-0.77	0.90	0.91-0.92	—			
5	—	0.35-0.48		0.33-0.38	0.39	0.85	0.85	0.87	—			
6	—	0.27	0.24-0.25	0.26-0.35	0.30	0.65-0.66	0.71	0.77-0.80	—			
7	—	—	—	0.25-0.32	0.21	0.54-0.58	—	0.61	—			
8	—	—	—	—	—	0.57	—	—	—			

Procedure. The adsorbent layer was prepared by STAHL's method. The adsorbent slurry was coated on the plates with a standard thickness (0.25 mm), dried in air for 30 min and then for 2 to 3 h at 120°.

The chromatoplates were developed by the ascending technique, and 0.1–2 μ l of a 1% cycloamide methanol solution was applied to the plates by means of a microsyringe.

The time required for development (10 cm) was about 1–2 h. After removing the solvent in a stream of hot air, the plates were sprayed with Dragendorff's reagent, followed by 10% sulfuric acid.

Results and discussion

The results obtained are tabulated in Table I.

When Kieselgel containing thymol was used as adsorbent, the dependence of the R_F value on the content of thymol is shown in Fig. 1.

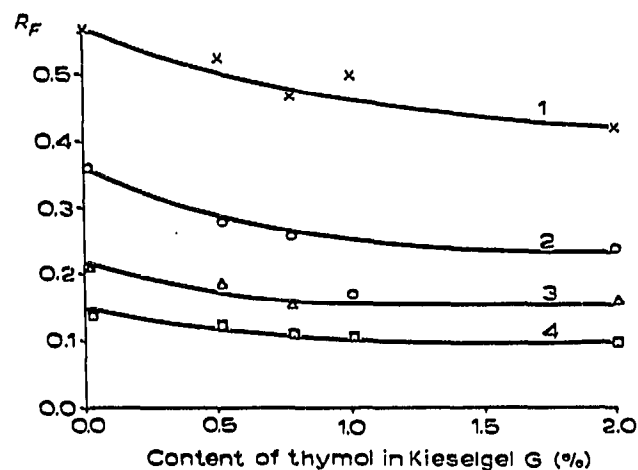


Fig. 1. Dependence of R_F value on the content of thymol in Kieselgel G. 1 = ϵ -Caprolactam; 2 = cyclic dimer; 3 = cyclic trimer; 4 = cyclic tetramer.

Chromogenic reagents. The complex of ϵ -caprolactam with potassium bismuth iodide was reported to be precipitated with hydrochloric acid⁷.

It has now been found that the precipitation behavior of the complex differs depending on the acids used. Acetic acid does not permit formation of the precipitate. In the case of hydrochloric acid, only suitable amounts would precipitate the complex and excess readily redissolve the precipitate. The suitable range of hydrochloric acid concentration was narrow. Sulfuric acid accelerated the precipitation of the complex but only redissolved it with decomposition when a large excess of concentrated sulfuric acid was used.

One of the reasons for the increased sensitivity, we suppose, was the easy formation of insoluble dark red bismuth complexes with cycloamides. Acids which have no function in the formation of the precipitate when used together with Dragendorff's reagent, such as acetic acid, do not show the improvement of sensitivity. A further reason for increased sensitivity may be due to the disappearance of the yellow back-ground formed with Dragendorff's reagent when sulfuric acid is used.

Developing reagents. ϵ -Caprolactam and its cyclic homologues are not separated by non-polar solvents, for example, a chloroform and cyclohexane mixture.

When heterocyclic compounds containing nitrogen, such as pyridine and water, were used as developing reagents, trace amounts of the reagents remained after drying at 100° for several hours and the detection of spots was interfered with.

The system tetrahydrofuran-petroleum ether-water gave good separation of the cyclic oligomers, but the separation of ϵ -caprolactam and its dimer was not sufficient.

The system *n*-butanol-acetic acid-water gave good separation of monomer and dimer, although separation of tetramer and pentamer was incomplete.

sec.-Butanol, formic acid and water or *n*-butanol saturated with water did not show good separations of higher members of the series than the tetramer.

In paper chromatography of cycloamides, CZEREPKO⁸ used paper strips impregnated with thymol. The author utilised this information in the present work. The dependence of the R_F value on the content of thymol in the Kieselgel is shown in Fig. 1, which indicates that the variation in R_F value is small and the separation of members higher than the trimer is extremely poor. Alumina did not give as good a separability as Kieselgel G.

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