Thin-layer chromatographic study of *p*-toluenesulphonates of some amines

Separation of amines by TLC has been carried out by several workers[1–9]. Yasuda[10] has reported on the identification of N-nitroso- and nitrodiphenylamines by this technique. Teichert and coworkers[11] have reported on a study of their 3,5-dinitrobenzamides, whereas Seiler and Weichmann[12] investigated their 1-dimethylaminonaphthalene-5-sulphonates.

The present paper describes the resolution and identification of some amines in the form of their *p*-toluenesulphonates. This was achieved by directly converting a mixture of amines on thin-layer plates into their tosylates and subsequently running the chromatograms. Thus, in a mixture of six to eight amines it was possible to characterize distinctly 1–2 μg of each amine in the form of its *p*-toluenesulphonate.

Experimental

All the solvents used were freshly dried and distilled. Kodak photographic glass plates (20 × 28 cm) were used. An ascending irrigation technique was employed.

Preparation of p-toluenesulphonates. The individual amine (1 mole) was dissolved in pyridine (10 moles) and to this *p*-toluenesulphonyl chloride (1.1 mole except in the case of ethylenediamine 2.1 moles) in pyridine (5 moles) added. The clear solution was heated for half an hour on the water bath under anhydrous conditions. After the reaction, the contents were poured into an excess of cold water, and the resultant crystalline precipitate filtered, washed with aqueous sodium carbonate followed by dilute hydrochloric acid and water. The product was dried and repeatedly crystallized from hot ethanol. Their melting points are as follows:

aniline-*p*-toluenesulphonate, m.p. 103°; *o*-toluidine-*p*-toluenesulphonate, m.p. 108°; *m*-toluidine-*p*-toluenesulphonate, m.p. 114°; *p*-toluidine-*p*-toluenesulphonate, m.p. 118°; *o*-nitroaniline-*p*-toluenesulphonate, m.p. 110°; *m*-nitroaniline-*p*-toluenesulphonate, m.p. 138°; *p*-nitroaniline-*p*-toluenesulphonate, m.p. 190°; α-naphthylamine-*p*-toluenesulphonate, m.p. 157°; β-naphthylamine-*p*-toluenesulphonate, m.p. 133°; ethylenediamine-N,N′-di-*p*-toluenesulphonate, m.p. 160°; piperidine-*p*-toluene-

TABLE I

DETAILS OF THIN-LAYER COATINGS OF VARIOUS ADSORBENTS

*Adsorbent**	*Quantity of adsorbent used for slurry (g)*	*Solvent used for slurry*	*Quantity of adsorbent per cm² (mg)*
A	30	Chloroform (55 cc.)–methanol (28 cc.)	7.5
B	30	0.5 *N* oxalic acid (20 cc.)–methanol (70 cc.)	6.8
C	30		
D	30	Water (60 cc.)	6.2
E	30		

* A–D, see text.

TABLE II

R_F VALUES OF VAROUS AMINE *p*-TOLUENESULPHONATES

Solvent systems: (I) chloroform; (II) chloroform–xylene (80:20); (III) chloroform–xylene (95:5); (IV) petroleum ether–ether (50:50).

No.	*p-Toluenesulphonates of the following amines*	*Silica gel G*			*Buffered silica gel G with N/2 oxalic acid*			*Neutral alumina*			*Basic alumina*			*Acidic alumina*		
		I	*II*	*III*	*I*	*II*	*III*	*I*	*II*	*IV*	*II*	*III*	*IV*	*II*	*III*	*IV*
1	Aniline	0.8	0.36	0.49	0.63	0.38	0.52	0.77	0.26	0.48	0.23	0.33	0.26	0.17	0.27	0.28
2	*o*-Toluidine	0.93	0.43	0.52	0.74	0.44	0.62	0.86	0.47	0.74	0.36	0.48	0.33	0.26	0.38	0.50
3	*m*-Toluidine	0.76	0.34	0.41	0.47	0.40	0.53	0.85	0.30	0.56	0.27	0.31	0.30	0.10	0.20	0.34
4	*p*-Toluidine	0.53	0.33	0.35	0.43	0.35	0.50	0.30	0.68	0.53	0.32	0.40	0.28	0.20	0.31	0.40
5	*o*-Nitroaniline	0.98	0.58	0.64	0.50	0.60	0.72	0.57	0.17	0.26	0.50	0.60	0.38	0.06	0.15	0.09
6	*m*-Nitroaniline	0.38	0.22	0.24	0.27	0.24	0.34	0.20	0.08	0.21	0.14	0.23	0.14	0.03	0.10	0.06
7	*p*-Nitroaniline	0.41	0.18	0.21	0.22	0.20	0.30	0.10	0.03	0.07	0.09	0.14	0.10	0.02	0.08	0.03
8	*α*-Naphthylamine	0.53	0.36	0.57	0.45	0.41	0.54	0.50	0.22	0.42	0.31	0.43	0.24	0.14	0.23	0.20
9	*β*-Napthylamine	0.60	0.30	0.47	0.40	0.30	0.55	0.54	0.16	0.39	0.21	0.28	0.21	0.10	0.16	0.23
10	Ethylenediamine	0.58	0.33	0.42	0.42	0.34	0.50	0.70	0.25	0.50	0.29	0.38	0.25	0.16	0.25	0.32
11	Piperidine	0.62	0.50	0.58	0.55	0.52	0.66	0.58	0.61	0.94	0.64	0.86	0.23	0.63	0.70	0.87
12	*m*-Chloroaniline	0.55	0.63	0.38	0.43	0.38	0.47	0.42	0.66	0.33	0.23	0.33	0.53	0.18	0.30	0.16
13	Diphenylamine	0.70	0.32	0.70	0.70	0.66	0.73	0.50	0.33	0.70	0.40	0.45	0.43	0.62	0.51	0.17
14	*p*-Anisidine	0.62	0.38	0.39	0.39	0.34	0.57	0.80	0.51	0.40	0.20	0.30	0.15	0.12	0.21	0.36

sulphonate, m.p. 96°; *m*-chloroaniline-*p*-toluenesulphonate, m.p. 138°; diphenylamine-*p*-toluenesulphonate, m.p. 141°; *p*-anisidine-*p*-toluenesulphonate, m.p. 114°.

Adsorbents. The following adsorbents were employed:

(A) Silica gel G (E. Merck)
(B) Silica gel G (E. Merck), buffered with 0.5 *N* oxalic acid
(C) Alumina, neutral (M. Woelm)
(D) Alumina, basic (M. Woelm)
(E) Alumina, acidic (M. Woelm).

Preparation, spotting and irrigation of plates. The plates were coated by pouring a homogeneous slurry of the adsorbant in a suitable solvent on to them and tilting

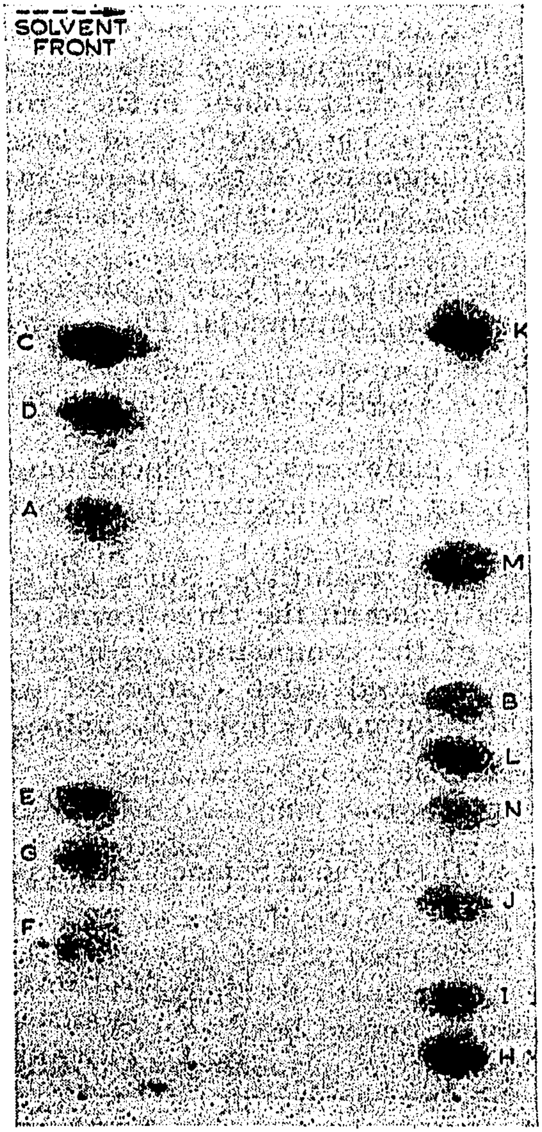

Fig. 1. Thin-layer chromatogram (photograph taken under U.V. light) showing the resolution of mixtures of the following amines as their *p*-toluenesulphonates: A = *p*-anisidine; B = diphenylamine; C = *m*-chloroaniline; D = piperidine; E = ethylenediamine; F = *β*-naphthylamine; G = *α*-naphthylamine; H = *p*-nitroaniline; I = *m*-nitroaniline; J = *o*-nitroaniline; K = *p*-toluidine; L = *m*-toluidine; M = *o*-toluidine; N = aniline. Adsorbent: neutral alumina (Woelm). Irrigating solvent: chloroform–xylene (80:20). System: ascending.

them from side to side. The plates were left overnight at room temperature and were activated at 110° for 1 h. They were then weighed and the quantity of adsorbent per cm^2 was noted down. Details are given in Table I. The amine solutions (each containing 1–2 μg) in pyridine–petroleum ether (1:1) were spotted on the plate with a micro-capillary, and on the same spots a solution of *p*-toluenesulphonyl chloride (equivalent to 1.1 mole of amine, or when it was a mixture of amines to 1.5 moles) in pyridine was applied. The authentic *p*-toluenesulphonates were also spotted alongside. The plates were left for 4 h in an oven at 60°, after which they were irrigated with suitable solvents. The spots were observed under U.V. light using a "chromatolite" lamp. Table II gives the R_F values of various amine-*p*-toluenesulphonates.

Discussion and results

It was observed that when the amines were spotted as mixtures or individually and were then converted on the plates into their *p*-toluenesulphonates on subsequent irrigation, they resolved distinctly. Thus, a mixture of six to eight amines, in the form of their *p*-toluenesulphonates, was readily resolved (Fig. 1). The R_F values of these compounds corresponded to the authentic *p*-toluenesulphonates of the amines investigated. The individual compounds proved to be single spots on two-dimensional thin-layer chromatography.

It was found that cellulose–calcium sulphate, Kieselgel G, and 5–10% olive oil impregnated cellulose were not good adsorbents for these compounds. There was profuse tailing with the majority of these compounds.

The tosylates could be directly observed under U.V. light and there was no necessity for a spray reagent as in the case of amines.

Polar solvents when employed for irrigation of the plates either produced long tailing or highly diffused spots. Non-polar solvents and their mixtures produced excellent resolution of the compounds.

Thin coatings of the adsorbents produced very good resolutions. Silica gel G (unbuffered), silica gel G (buffered with *N*/2 oxalic acid), and all the three forms of alumina gave good results. In general, the mobility of the compounds on acidic alumina in chloroform–xylene solvent mixtures was reduced when compared to basic and neutral alumina. On buffered silica gel G, chloroform gave lower R_F values than on unbuffered silica gel G.

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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 REXROTH[1], 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 reagent[4]. The sensitivities of the chromogenic reagents mentioned above were at most about 5 to 10 μg 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 μg 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 Tôyô Kagaku Sangyô 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 polycapramide[5].

Higher cycloamide homologues than the tetramer were synthesized by the procedures described by ZAHN AND DETERMAN[6].

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.