Journal of Chromatography, 118 (1976) 96–98
© Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 8759

Note

The paper chromatography of a group of secondary amines

ISAO SHIMIZU
Research Laboratory, Mitsubishi Oil Co. Ltd., 4-1, Ohgi-machi, Kawasaki (Japan)
(Received September 22nd, 1975)

Aromatic secondary amines are widely used in aviation gas-turbine oils as antioxidants; since the effects of such amines depend on their chemical structures[1,2], increasing interest is being shown in the structural analysis of these compounds.

The IR spectra of aromatic secondary amines have been studied by several workers[3,4], but this technique is not always suitable for structural analysis of mixtures of those compounds. The separation and identification of aromatic secondary amines have been investigated by partition paper chromatography[5,6] and thin-layer chromatography[7–11], the former technique having been used with satisfactory results. However, previous investigations have not dealt with the systems in which polar solvents are used as both stationary and mobile phases, which are essential to systematic analysis by partition paper chromatography[12–14].

In this paper, the R_F values of aromatic secondary amines with various types of solvent system are reported, and a procedure is described for the systematic analysis of those compounds by partition paper chromatography.

EXPERIMENTAL

Materials

The compounds studied are listed in Table I; they were purified by recrystallization and used at a concentration of 10 g/l.

The organic solvents used as stationary phase were as follows. Liquid paraffin (LP): viscosity 7.789 cS at 98.9°, d_4^{20} 0.8885, n_D^{20} 1.4840, av. mol. wt. 403, S 0.01 % (w/w), aniline pt. 105.2°; chlorinated paraffin (CP): Cl 40.8 % (w/w), viscosity 26.15 cS at 98.9°, d_4^{25} 1.1565, n_D^{25} 1.5020. Dipropylene glycol (DPG) and dimethyl phthalate (DMP) were obtained from Wako (Osaka, Japan). Cresyl diphenyl phosphate (CDP) was obtained from Albright & Wilson (Oldbury, Great Britain) and polyoxyethylene octylphenyl ether (E.O. 10 mol) (PEOE) from Nippon Oils & Fats Tokyo, Japan).

Procedure

Preparation of impregnated paper. A sheet of Toyo Roshi No. 50 filter paper (25 × 12 cm) was dipped in a solution of the stationary phase in a volatile diluent (1:6, v/v), and the solvent was evaporated. Light petroleum (b.p. 30–70°) was used as the diluent for LP and CP, and acetone as that for DPG, CDP, DMP and PEOE.

TABLE I

COLOURS PRODUCED BY VARIOUS AROMATIC SECONDARY AMINES WITH NITRIC ACID AND WITH DIAZO-REAGENT

Amine	*M.p. (°C)*	*Colour of spot*	
		Nitric acid spray	*Diazo-reagent spray*
Diphenylamine	53	Bluish black	Red purple
p-Octyldiphenylamine	—	Dark yellow-green	—
p,p'-Dioctyldiphenylamine	102	Yellow	—
N-Phenyl-1-naphthylamine	62	Olive green	Blue-purple
N-Phenyl-2-naphthylamine	108	Yellowish brown	Light red
N-Octylphenyl-2-naphthylamine	124	Yellowish brown	Light yellowish red
Di-1-naphthylamine	114	Olive green	Blue-purple
Di-1,2-naphthylamine	109	Olive	Purple
Di-2-naphthylamine	171	Yellowish brown	Light red
Phenothiazine	185	Brown	Brown
3,7-Dioctylphenothiazine	166	Reddish yellow	Pale red-purple

Developing procedure. A base-line was drawn 3 cm from one edge of the paper when LP or CP was used as stationary phase, 6 cm when CDP or DMP was used and 8 cm when DPG or PEOE was used. The solutions of the amines were applied at 1-cm intervals on this line, the diameter of each spot being adjusted to about 0.5 cm. The chromatogram was allowed to develop at 20° by the ascending technique until the solvent front had travelled about 10 cm from the base-line.

Detection. After development, the paper was sprayed with concentrated nitric acid or with a diazo-reagent prepared by slowly adding a solution of 3 g of sodium nitrite in 24 ml of water to a solution of 1 g of sulphanilic acid and 8 ml of 36% hydrochloric acid in 20 ml of water, the temperature being maintained at below 5°. Each aromatic secondary amine was revealed as a spot with the characteristic colour indicated in Table I.

RESULTS AND DISCUSSION

The R_F values of the amines studied are shown in Table II. In system B (see Table II), there were large differences between the R_F values of unsubstituted and alkylated aromatic secondary amines, the R_F value decreasing with the number of octyl groups. Further, differences in R_F value between isomers of unsubstituted aromatic secondary amines were evident.

When systems C, D and E were used, large differences between the R_F values of unsubstituted and alkylated amines were also observed, but in these systems the R_F values increased with the number of octyl groups. The R_F value of *p,p'*-dioctyldiphenylamine in system C was too high for identification purposes, but this system separated isomers of unsubstituted aromatic secondary amines. This phenomenon appears to be characteristic of systems containing glycols such as diethylene glycol and DPG, as was reported by Toyoguchi and Shimizu[5] and Delves[6].

System H was unique in that the R_F values were little affected by substitution of an octyl group or the position of the NH radical, but were affected by the number of aromatic rings. This system has polar solvents as both stationary and mobile

TABLE II

R_F VALUES OF AROMATIC SECONDARY AMINES

The chromatographic systems used (stationary phase: mobile phase) were as follows. A, LP: ethanol; B, LP: ethanol–water (80:20); C, DPG: *n*-heptane; D, CDP: *n*-heptane; E, DMP: *n*-heptane; F, PEOE: *n*-heptane; G, CP: ethanol; and H, CP: isopropanol.

Amine	*Chromatographic system*							
	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*
Diphenylamine	0.92	0.85	0.26	0.26	0.23	0.09	0.67	0.59
p-Octyldiphenylamine	0.85	0.50	0.78	0.54	0.56	0.29	0.62	0.61
p,p'-Dioctyldiphenylamine	0.65	0.11	0.95	0.82	0.87	0.62	0.55	0.62
N-Phenyl-1-naphthylamine	0.89	0.74	0.29	0.20	0.17	0.07	0.48	0.39
N-Phenyl-2-naphthylamine	0.91	0.80	0.18	0.18	0.12	0.04	0.49	0.41
N-Octylphenyl-2-naphthylamine	0.83	0.40	0.65	0.43	0.41	0.16	0.45	0.43
Di-1-naphthylamine	0.84	0.56	0.32	0.15	0.12	0.05	0.31	0.22
Di-1,2-naphthylamine	0.88	0.67	0.20	0.14	0.10	0.04	0.33	0.24
Di-2-naphthylamine	0.89	0.71*	0.11	0.13	0.08	0.02	0.33	0.24
Phenothiazine	0.94	0.89	0.07	0.17	0.11	0.02	0.64	0.57
3,7-Dioctylphenothiazine	0.80	0.27	0.82	0.65	0.67	0.26	0.50	0.56

* Tailing.

phases, and the behaviour of the amines in this system may be due to small differences in the polarities of the two solvents.

CONCLUSIONS

Aromatic secondary amines can be identified by separation according to their substitution pattern with a chlorinated paraffin–isopropanol system and then according to the alkyl substituent with a dimethyl phthalate–*n*-heptane system.

ACKNOWLEDGEMENT

I thank Dr. M. Toyoguchi, of Mitsubishi Oil Co. Ltd., for encouragement and valuable discussions.

REFERENCES

1 W. M. Denton and S. A. M. Thompson, *Inst. Petrol. Rev.*, 20 (1966) 46.
2 *Technical Data Sheet*, No. 79, Geigy (U.K.) Ltd., Industrial Chemicals Division.
3 K. Hasegawa, M. Kajikawa and M. Kawaguchi, *Bull. Japan Petrol. Inst.*, 5 (1963) 82.
4 G. I. Jenkins and C. M. A. Humphreys, *J. Inst. Petrol.*, 51 (1965) 1.
5 M. Toyoguchi and I. Shimizu, *Kogyo Kagaku Zasshi*, 61 (1958) 1469.
6 R. B. Delves, *J. Inst. Petrol.*, 48 (1962) 283.
7 N. K. Zubkova, Yu. I. Turskii, V. I. Genkina and G. V. Klyuchko, *Khim. Tekhnol. Topl. Masel*, 9, No. 8 (1964) 60.
8 F. C. A. Killer and R. Amos, *J. Inst. Petrol.*, 52 (1966) 315.
9 R. B. Delves, *J. Chromatogr.*, 26 (1967) 296.
10 J. G. Kreiner and W. C. Warner, *J. Chromatogr.*, 44 (1969) 315.
11 J. P. Coates, *J. Inst. Petrol.*, 57 (1971) 209.
12 I. Shimizu, *Yukagaku*, 16 (1967) 177.
13 I. Shimizu, *Bull. Japan Petrol. Inst.*, 13 (1971) 259.
14 I. Shimizu, *Yukagaku*, 20 (1971) 16.