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Note

Influence of alkali metal salts on the migration of quaternary ammonium compounds on silica gel layers

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There is little information on the thin-layer chromatography of quaternary ammonium salts on silica gel. Owing to their high affinity for silica gel, these compounds remain close to their starting points even in highly polar developing systems. In general, the mobilities of simple tetraalkylammonium salts increase with increase in the alkyl chain lengths, which enables the separation of tetrabutyl-, tetrapentyl- and tetraalkylammonium salts with longer alkyl chains to be achieved on silica gel using chloroform-ethanol and acetone-N-methylacetamide as solvent systems¹. Quaternary ammonium salts containing shorter alkyl chains, quaternary salts of cyclic amines and quaternary derivatives of alkaloids require more polar solvent systems.

1,5-*endo*-Methylenequinolizidinium tosylate remains on its starting point in chloroform-diethylamine (9:1), chloroform-acetone-diethylamine (5:4:1) and methanol-ammonia (10:3) systems². In the last instance, only by increasing the proportion of ammonia to 1:1 and double development of the chromatograms is the R_F value increased to about 0.1.

In an investigation of lupinine and its derivatives, it was found that in methanol solutions of KI and other alkali metals salts, the R_F values of 1,5-*endo*-methylenequinolizidinium tosylate were considerably higher than those obtained with the methanol-ammonia system, and similar results were obtained for simple tetraalkylammonium halides (tetramethyl-, tetraethyl-, tetrapropyl- and tetra-*n*-butylammonium halides).

EXPERIMENTAL

The solvents used were of reagent grade. 1,5-*endo*-Methylenequinolizidinium tosylate was synthesized according to Podkowińska and Wiewiórowski³, tetraalkylammonium halides (puriss) was purchased from Fluka (Buchs, Switzerland) and lupinine was extracted from *Lupinus luteus*.

Glass plates of dimensions 2.6 × 7.6 cm (microscope slides) covered with a 0.03-cm layer of silica gel G (according to Stahl; Merck, Darmstadt, G.F.R.) were used. Air-dried plates (24 h) were kept in a desiccator over solid KOH and developed in small chromatographic chambers without previous saturation or conditioning². The developing distance was 6 cm and the developing time *ca.* 10 min.

The following solvent systems were used:

- (A) methanol-20% NH₃ solution (10:3) (concentration of NH₃ solution = 2.5 M);
- (B) methanolic solution of KI (0.65 M);
- (B₁) methanolic solution of KI (0.325 M);
- (B₂) methanolic solution of KI (0.137 M);
- (B₃) methanolic solution of KI (0.068 M);
- (C) methanolic solution of CH₃COOK (0.65 M);
- (D) methanolic solution of NaI (0.65 M);
- (E) methanolic solution of LiBr (0.65 M).

The developed chromatoplates were dried in a stream of hot air and sprayed with Dragendorff reagent (modified according to Munier and Macheboeuf⁴).

RESULTS AND DISCUSSION

The changes in the R_F values of the tertiary amine lupinine and 1,5-*endo*-methylenequinolizidinium tosylate on replacement of the solvent system methanol-ammonia with a methanolic solution of KI are presented in Table I. The R_F value of lupinine is only slightly affected while that of 1,5-*endo*-methylenequinolizidinium tosylate increases from 0.00 to 0.56. A large decrease in the KI concentration causes an insignificant decrease in the R_F values.

TABLE I

R_F VALUES OF LUPININE AND 1,5-*endo*-METHYLENEQUINOLIZIDIUM TOSYLATE IN THE SYSTEMS (A) METHANOL-AMMONIA (10:3) AND (B-B₃) METHANOLIC SOLUTIONS OF KI

Solvent system	Lupinine	1,5- <i>endo</i> -methylenequinolizidinium tosylate
A	0.72	0.00
B (0.65 M)	0.78	0.56
B ₁ (0.325 M)	0.75	0.54
B ₂ (0.137 M)	0.74	0.51
B ₃ (0.068 M)	0.72	0.50

The R_F values of simple tetraalkylammonium halides (tetramethyl-, tetraethyl-, tetrapropyl- and tetra-*n*-butyl-) are also higher in a methanolic solution of KI than in the methanol-ammonia system (see Table II, A and B). It is noteworthy that the R_F values of 1,5-*endo*-methylenequinolizidinium tosylate and tetramethylammonium halides in the methanol-ammonia system are zero, and the R_F values of higher tetraalkylammonium halides increase in the order tetraethyl < tetrapropyl < tetra-*n*-butyl; the tetrabutylammonium halides have a relatively high R_F value of 0.54. An increase in the R_F values of the tetraalkylammonium halides in the order tetramethyl < tetraethyl < tetrapropyl < tetra-*n*-butyl was observed in all methanol-alkali metal salts systems (Table II, B-E).

CH₃COOK causes a smaller increase in R_F values than KI of the same concentration (0.65 M) for all the compounds examined.

TABLE II
 R_F VALUES OF LUPININE AND QUATERNARY AMMONIUM SALTS IN THE SYSTEMS (A) METHANOL-AMMONIA (10:3) AND (B-E) METHANOLIC SOLUTIONS OF ALKALI METAL SALTS OF CONCENTRATION 0.65 M

Solvent system	Lupinine	endo-tosylate*	Me ₄ NCl	Me ₄ NBr	Me ₄ NI	Et ₄ NCl	Et ₄ NBr	Et ₄ NI	Pr ₄ NI	<i>n</i> -Bu ₄ NCl	<i>n</i> -Bu ₄ NBr	<i>n</i> -Bu ₄ NI
A	0.72	0.00	0.00	0.00	0.00	0.11	0.12	0.11	0.25	0.54	0.54	0.54
B (KI)	0.78	0.56	0.55	0.55	0.55	0.67	0.68	0.68	0.83	0.92	0.92	0.90
C (CH ₃ COOK)	0.54	0.45	0.20	0.20	0.20	0.34	0.34	0.33	0.66	0.70	0.72	0.70
C (NaI)	0.80	0.69	0.33	0.33	0.33	0.45	0.46	0.45	0.87	0.85	0.85	0.87
E (LiBr)	0.78	0.45	0.16	0.16	0.16	0.36	0.36	0.36	0.77	0.87	0.86	0.86
F**	0.37	0.31	0.40	0.40	0.40	0.36	0.37	0.37	0.50	0.53	0.52	0.53

* 1,5-endo-Methylenequinolizidinium tosylate.

** Solvent system: methanol-1 M NH₄NO₃-1 M NH₃ (3:3:4).

The influence of methanolic solutions of NaI and LiBr is similar to that observed with KI, and its magnitude decreases in the order $KI > NaI > LiBr$ for tetraalkylammonium halides. This order is different with 1,5-*endo*-methylenequinolizidinium tosylate, the highest R_F value being obtained with methanol-NaI.

As reported by Verpoorte and Baerheim Svendsen⁵, methanol-ammonia-aqueous ammonia salt solution systems can be used for separation purposes of some strychnine alkaloids that contain quaternary ammonium groups. We examined one of the solvent systems described by them (Table II, F) and found that it caused an increase in the R_F values of the compounds studied, but to a lesser extent than our solvent systems.

The advantage of the systems proposed here is that they eliminate ammonia, which must otherwise be removed from chromatoplates before spraying them with Dragendorff's reagent.

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REFERENCES

- 1 J. E. Gordon, *J. Chromatogr.*, 20 (1965) 38.
- 2 W. Meissner, H. Podkowińska, H. Kokocińska and W. Stopa, *Sci. Pap. Coll. Econ. Poznań, Poland, Ser. A*, No. 40 (1971) 41.
- 3 H. Podkowińska and M. Wiewiórowski, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, 15 (1967) 467.
- 4 R. Munier and M. Macheboeuf, *Bull. Soc. Chim. Biol.*, 33 (1951) 846.
- 5 R. Verpoorte and A. Baerheim Svendsen, *J. Chromatogr.*, 124 (1976) 152.
- 6 I. Jane, *J. Chromatogr.*, 111 (1975) 227.