The separation and identification of some alkanolamines and their salts by thin-layer chromatography

Alkanolamines, in particular ethanolamines and isopropanolamines, are often used in hydraulic brake fluids and cutting oils as corrosion inhibitors. Also when combined as soaps with fatty acids (usually oleic and stearic acids) they are used extensively as emulsifiers and detergents. The separation and identification of alkanolamines and their salts in such products can be time-consuming and it is advantageous to have a rapid method for doing this.

Amines have been separated by paper and thin-layer chromatography[1–6] and the R_F value for monoethanolamine in various solvents has been reported. The paper chromatographic methods suffer from the disadvantages of long development times and diffuse substance zones. Thin-layer chromatography, however, is ideally suited to the separation of alkanolamines and the development of a suitable procedure for separating and identifying ethanolamines and isopropanolamines and some of their salts in commercial formulations is described below.

Experimental and discussion

Solvent system/adsorbent/locating agent. Most of the solvent systems reported in the literature for separating amines consist of an alcohol and a base (usually ammonia). For the separation of simple mixtures of ethanolamines and isopropanolamines these systems work fairly well but they do not give a very good separation of complex mixtures. However, if methylene chloride is incorporated into the alcohol–base solvent mixture a much better separation is obtained and also the developing time

TABLE I

COLOURS AND R_F VALUES OF SOME ALKANOLAMINES AND THEIR CARBOXYLIC ACID SALTS

Compounds	*Colour of zones*		*R_F values*
	Ninhydrin	*Ninhydrin, then alizarin*	
(1) Monoethanolamine	Crimson	Crimson	0.26
(2) Diethanolamine	White	Blue-purple	0.43
(3) Triethanolamine	Grey	Grey-purple	0.60
(4) Monoisopropanolamine	Crimson	Crimson	0.47
(5) Diisopropanolamine	White	Blue-purple	0.63
(6) Triisopropanolamine	Green	Grey-purple	0.71
Oleates of alkanolamines (1)–(6)*	Blue/yellow fringe Red	Blue Red	Baseline 0.60
Naphthenates of alkanolamines (1)–(6)*	Yellow Red	Blue Red	Baseline 0.60
Oleic acid**	Yellow Faint red	Blue Faint red	Baseline 0.60
Naphthenic acids** (equivalent weight: 300)	Yellow Faint red	Blue Faint red	Baseline 0.60

* A zone due to the particular alkanolamine used was also observed.
** The R_F values of the carboxylic acids are recorded for comparison.

is decreased. The solvent system finally adopted was methylene chloride–ethanol (95 %)–ammonia (0.880) in the proportions 43:43:15 by volume. Of the various adsorbents examined for the separation neutral silica gel was the most suitable. Solutions of 0.2 wt. % ninhydrin and alizarin in acetone were used to locate the separated alkanolamines.

Procedure. The usual thin-layer chromatographic (TLC) procedure was used to separate the alkanolamines. 0.1 % solutions of the alkanolamines in ethanol were spotted on the TLC plate of neutral silica gel (250 μm thickness), 1 cm apart. The plates were then developed by the ascending technique, heated for 10 min at 110°, sprayed with ninhydrin solution and finally heated for a further 5 min at 110° to locate the separated alkanolamines. Respraying with alizarin solution gave a further identification.

When an alkanolamine salt is subjected to chromatographic techniques zones are obtained for both the alkanolamine and acid moieties. The alkalonamine salts used included oleates and naphthenates. All of these salts gave a distinct yellow zone at the baseline and a red zone at about R_F 0.60. The R_F values of the alkanolamines separated are given in Table I and the separation is illustrated in Fig. 1.

Application of the method to commercial formulations. A number of hydraulic brake fluids and cutting oils were examined by the procedure.

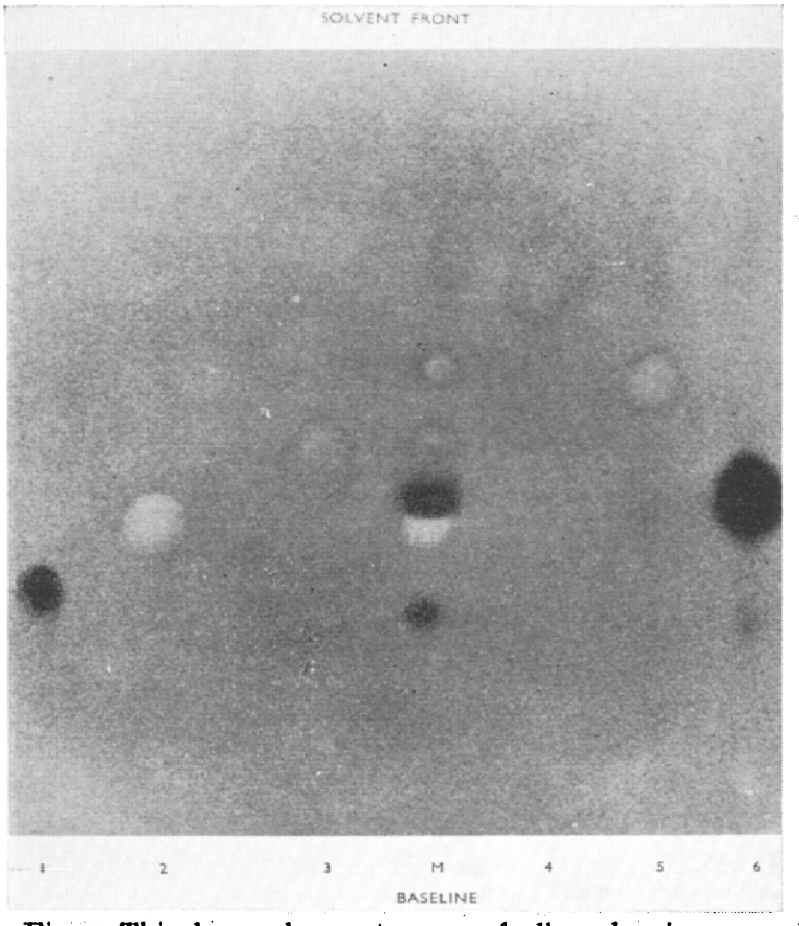

Fig. 1. Thin-layer chromatogram of alkanolamines. 1 = Monoethanolamine; 2 = diethanolamine; 3 = triethanolamine; 4 = triisopropanolamine; 5 = diisopropanolamine; 6 = monoisopropanolamine; M = mixture of 1–6.

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TABLE II

THE DETECTION OF ALKANOLAMINES AND THEIR SALTS IN VARIOUS COMMERCIAL FORMULATIONS

Formulation	*Colour of zones*		*R_F values*	*Inference*	*Alkanolamine found by chemical analysis*
	Ninhydrin	*Ninhydrin, then alizarin*			
1	Crimson	Crimson	0.26	Monoethanolamine	
	White	Blue/purple	0.43	Diethanolamine	
	Red	Red/purple	0.60	Triethanolamine Alkanolamine salt	Triethanolamine oleate
	Yellow	Blue	Baseline	Alkanolamine salt	
2	Crimson	Crimson	0.26	Monoethanolamine	
	White	Blue/purple	0.43	Diethanolamine	Diethanolamine
	Red	Red	0.60	Alkanolamine salt	Diethanolamine oleate
	Yellow	Blue	Baseline		
3	Crimson	Crimson	0.26	Monoethanolamine	
	White	Blue/purple	0.43	Diethanolamine	Triethanolamine
	Grey	Grey/purple	0.60	Triethanolamine	
	Yellow	Blue	0–0.20	Unknown	
4	Crimson	Crimson	0.47	Monoisopropanolamine	
	Red	Red	0.60	Monoisopropanolamine salt	Monoisopropanolamine naphthenate
	Yellow	Blue	Baseline		
5	Crimson	Crimson	0.26	Monoethanolamine	
	White	Blue/purple	0.43	Diethanolamine	
	Red	Red/purple	0.60	Triethanolamine Alkanolamine salt	Triethanolamine Triethanolamine naphthenate
	Yellow	Yellow	0.36	None	
	Yellow	Blue	0–0.20	Unknown	

The results given in Table II show that whenever triethanolamine was incorporated in a formulation, mono- and di-ethanolamine were present as impurities. When the chromatogram is sprayed with ninhydrin the red zone (R_F 0.60) due to a carboxylic acid overlays and conceals the zone of triethanolamine (R_F 0.60) when both the acid and amine are present in a mixture. However, if triethanolamine is present it can be confirmed by the distinct purple hue of the red zone when sprayed with alizarin solution. Sometimes the other components of a formulation cause the acid constituent to appear as a red streak from $R_F \sim 0.3$ to $R_F \sim 0.6$ but this does not prevent identification of the alkanolamine constituents.

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1 H. ROSENBERG AND A. N. ENNOR, *Biochem. J.*, 73 (1959) 521.
2 C. E. ROWE, *Biochem. J.*, 73 (1959) 438.
3 J. FRANC AND M. HAJKOVA, *Coll. Czech. Chem. Commun.*, 24 (1959) 423.
4 J. BLASS AND A. SARRNOFF, *J. Chromatog.*, 3 (1960) 168.
5 E. A. MISTRYUKOV, *J. Chromatog.*, 9 (1962) 314.
6 K. TEICHERT, E. MUTSCHLER AND H. ROCHELMEYER, *Deut. Apotheker-Ztg.*, 100 (1960) 283.

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Paper chromatography of sugar phosphates and three-carbon phosphates. Extension and modification of the Agarwal procedure*

Many methods[1–6] have been developed for the paper chromatographic separation of phosphorylated metabolic intermediates. While using one of these procedures[6], originally designed for the chromatography of hexose phosphates, in the study of organic phosphates in honey[7], it was found that this procedure would also separate sugar phosphates from some three-carbon phosphates as a group. In addition, with the modification described here, some separation of the individual three-carbon phosphates was obtained.

Experimental

Reagents. All reagents were analytical grade and used as supplied.

Standard sugar phosphates and three-carbon phosphates. These standards were converted to their ammonium salts by the method of AGARWAL *et al.*[8]. The amount of salt used produced a 0.05 *M* solution of free acid or ester. The standards are listed with their name, source and abbreviation used in the text**.

* From a thesis submitted by MARY H. SUBERS in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry at Saint Joseph's College.

** Mention of trade or company names does not imply endorsement by the Department over others not named.