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## Note

### Thin-layer chromatography of homologous series of aliphatic C<sub>2</sub>-C<sub>18</sub> alkyl esters of acrylic and methacrylic acids

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Esters of acrylic and methacrylic acids are very important monomers and their industrial production and consumption in various fields is still growing. The importance of their analysis is emphasized by their toxicity. Most work on the analysis of acrylates and methacrylates has involved gas chromatography (GC)<sup>1-3</sup> with few applications of liquid chromatography<sup>4</sup>. Also, few papers<sup>5-7</sup> have been published on the thin-layer chromatography (TLC) of single acrylates and methacrylates, and in the work reported the compounds were derivatized before development. Hence so far the TLC separation of homologous series of aliphatic C<sub>2</sub>-C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub> and C<sub>18</sub> *n*-alkyl acrylates and methacrylates has not been reported.

#### EXPERIMENTAL

##### *Reagents*

Some acrylates and methacrylates were commercially available monomers and the others were prepared by the sulphuric acid-catalysed esterification of commercial acrylic or methacrylic acids and aliphatic alcohols. The purity of all samples was verified by GC-mass spectrometry.

Commonly available solvents and other chemical substances were analytical-reagent grade products from Lachema (Brno, Czechoslovakia).

##### *TLC separation*

Silufol silica gel ready-made plates (Kavalier, Votice, Czechoslovakia) were used. For reversed-phase chromatography, Silufol plates were impregnated with a 5% solution of paraffin oil. A 10 µg/µl solution of each monomer sample was applied. The developed plates were sprayed with 1% potassium permanganate-2% sodium carbonate (1:1).

#### RESULTS AND DISCUSSION

With the Silufol silica gel ready-made plates cyclohexane, carbon tetrachloride, benzene, toluene, di- and trichloromethane, trichloroethylene, diethyl ether, ethanol, methanol, acetone, ethyl acetate, 2-butanone, propanol and their various combina-

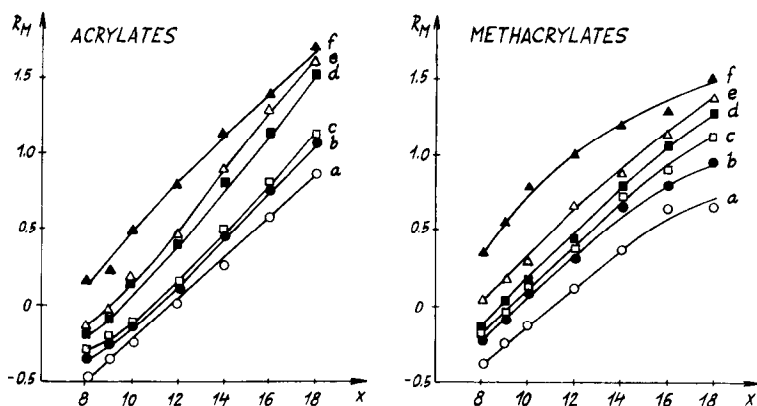


Fig. 1. Dependence of  $R_M$  values on the number of carbon atoms ( $x$ ) in the alcohol chain of acrylates and methacrylates using Silufol impregnated with paraffin oil with dimethylformamide-water as the solvent in the following ratios: (a) 9:1, (b) 8:1, (c) 7:1, (d) 6:1, (e) 5:1 and (f) 4:1.

tions were tested as developing solvents. Of the more than 90 mobile phases explored, it was concluded that benzene (A), toluene (B) and toluene-2-butanone (98:2) (C) were the most satisfactory (Tables I and II).

The poor separation of some neighbouring members of the homologous series of alkyl acrylates and methacrylates led us to use the reversed-phase technique to improve the separation. Using Silufol impregnated with paraffin oil, dimethylformamide-water (9:1) (D) and dimethylformamide-methanol-water (9:5:1) (E) were found to be the best solvents.

The dependence of the  $R_M$  values on the number of carbon atoms in the alcohol chain of higher acrylates and methacrylates (Fig. 1) using Silufol impregnated with paraffin oil and dimethylformamide-water in various proportions as the solvent was investigated.

TABLE I

$R_F$  VALUES OF  $C_2$ - $C_{10}$ ,  $C_{12}$ ,  $C_{14}$ ,  $C_{16}$  AND  $C_{18}$  *n*-ALKYL ESTERS OF ACRYLIC ACID

Acrylate	$R_F$				
	System A	System B	System C	System D	System E
Ethyl	0.39	0.27	0.32	—	—
Propyl	0.46	0.35	0.38	—	—
Butyl	0.52	0.37	0.42	—	—
Pentyl	0.56	0.43	0.46	—	—
Hexyl	0.60	0.45	0.49	—	—
Heptyl	0.62	0.49	0.51	—	—
Octyl	0.63	0.51	0.55	0.75	0.72
Nonyl	0.65	0.53	0.58	0.70	0.68
Decyl	0.70	0.54	0.59	0.65	0.62
Dodecyl	0.73	0.58	0.63	0.51	0.55
Tetradecyl	0.75	0.60	0.64	0.36	0.41
Hexadecyl	0.78	0.63	0.66	0.21	0.29
Octadecyl	0.81	0.64	0.68	0.12	0.17

TABLE II

 $R_F$  VALUES OF  $C_2$ - $C_{10}$ ,  $C_{12}$ ,  $C_{14}$ ,  $C_{16}$  AND  $C_{18}$  *n*-ALKYL ESTERS OF METHACRYLIC ACID

Methacrylate	$R_F$				
	System A	System B	System C	System D	System E
Ethyl	0.43	0.37	0.42	—	—
Propyl	0.51	0.40	0.47	—	—
Butyl	0.54	0.47	0.51	—	—
Pentyl	0.63	0.49	0.55	—	—
Hexyl	0.65	0.55	0.60	—	—
Heptyl	0.68	0.58	0.62	—	—
Octyl	0.71	0.59	0.65	0.71	0.65
Nonyl	0.73	0.61	0.66	0.64	0.59
Decyl	0.75	0.65	0.67	0.57	0.50
Dodecyl	0.79	0.67	0.68	0.44	0.42
Tetradecyl	0.80	0.69	0.70	0.30	0.31
Hexadecyl	0.83	0.70	0.73	0.19	0.24
Octadecyl	0.84	0.73	0.75	0.18	0.15

The  $R_F$  values for series of aliphatic alkyl acrylates and methacrylates in various TLC systems are summarized in Tables I and II. The chromatographic profiles of acrylates in systems A, B and C and in systems D and F are markedly different, and show that the  $R_F$  values increase in accordance with elongation of the alkyl chain in systems A, B and C, whereas in the reversed systems D and E octadecyl esters have the lowest  $R_F$  values. Similarly, the  $R_F$  values of methacrylates in systems A, B and C increase with elongation of the alkyl chain, whereas in systems D and E chain elongation leads to a decrease in the  $R_F$  value.

These results clearly show that the mobility of *n*-alkyl aliphatic esters of acrylic and methacrylic acids simply depends on the number of methylene groups. As can be seen from Tables I and II, one methylene group is sufficient to produce a distinguishable difference in  $R_F$  values in systems D and E; it is difficult, however, in systems A, B and C always to separate two esters that differ only by one methylene group.

From the results, it can be concluded that the TLC systems described here will be useful in identifying esters of acrylic and methacrylic acids in a very simple way.

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