

Note

Chromatography of monomers

III. Thin-layer chromatographic separation of C₆–C₁₈ straight-chain acrylates from corresponding methacrylates and alcohols

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Acrylic and methacrylic monomers have become established as major industrial chemicals because of the increasingly broad variety of applications of their polymeric products.

In a previously published paper¹ thin-layer chromatographic (TLC) separations of the esters within the homologous series of C₂–C₁₈ *n*-alkyl acrylates and methacrylates were reported. As a continuation of our studies dealing with the gas-liquid chromatography (GLC)² and liquid chromatography¹ of acrylate monomers, this paper reports the improved separation of longer chain alkyl acrylates from corresponding methacrylates and accompanying alcohols.

EXPERIMENTAL

Reagents

The acrylates and methacrylates, which were either of authentic commercial origin or prepared in our laboratory, were characterized by TLC, GLC and gas chromatography–mass spectrometry (GC–MS)^{1–3}.

Alcohols and other commonly available solvents and chemicals were from Lachema (Brno, Czechoslovakia). 4-Dimethylaminobenzene-4'-azobenzoyl chloride was synthesized in our laboratory as previously reported^{4,5}.

Thin-layer chromatography

Commercially available 20 × 20 cm Silufol silica gel ready-made plates and Lucefol cellulose plates were used (both Kavalier, Votice, Czechoslovakia). For reversed-phase chromatography, the Silufol plates were impregnated with 5% and 10% solutions of paraffin oil in light petroleum (b.p. 50–75°C). The compounds were dissolved in benzene to give 1% (v/v) solution for esters and 5% (v/v) solution for alcohols. Volumes from 2 to 5 μl were applied to the chromatograms. The chro-

matograms were developed with various solvent systems containing solvents as benzene, toluene, trichloroethylene, ethyl acetate, methyl ethyl ketone, carbon tetrachloride, dimethylformamide, methanol and water.

Alcohol identification in the sample of acrylate monomers

The mixture of acrylate monomers and accompanying alcohols dissolved in benzene with 4-dimethylaminobenzene-4'-azobenzoyl chloride and pyridine was refluxed in a sealed ampoule in a water-bath for 90 min. After cooling, the mixture was applied to the chromatogram and developed. Red spots indicated presence of alcohols.

RESULTS AND DISCUSSION

According to our results, only Silufol silica gel plates were suitable for the separation of acrylic and methacrylic acid esters. Silufol was also a more suitable thin-layer material than Lucefol for practical separation of acrylate and methacrylate esters from corresponding straight-chain C₆-C₁₀, C₁₂, C₁₄, C₁₆, C₁₈ alcohols.

We investigated the TLC separation, on Silufol silica gel plates, of C₆-C₁₈ *n*-alkyl chain acrylates from the corresponding methacrylates. The *R_F* values obtained for some pairs of corresponding longer alkyl chain acrylates and methacrylates with various solvent systems as developers are summarized in Table I. In the solvent systems S₁-S₈, methacrylates migrated more rapidly than corresponding acrylates, so that in almost all cases good separations were achieved, the best being in trichloroethylene-methyl ethyl ketone (95:5).

Table II lists the *R_F* values obtained on Silufol plates, impregnated with 5% paraffin oil, for the homologous series of C₈-C₁₈ straight-chain acrylates and methacrylates with dimethylformamide-water in various proportions. It can be seen that

TABLE I

R_F VALUES OF HEXYL, DECYL, TETRADECYL, OCTADECYL ACRYLATE (A6-A18) AND METHACRYLATE (M6-M18) ESTERS ON SILUFOL SILICA GEL PLATES

S₁ = Toluene-dichloromethane (8:2); S₂ = benzene-toluene (9:1); S₃ = trichloroethylene; S₄ = trichloroethylene-ethyl acetate (9:1); S₅ = trichloroethylene-methyl ethyl ketone (95:5); S₆ = carbon tetrachloride-diethyl ether (95:5); S₇ = carbon tetrachloride-ethyl acetate (98:2); S₈ = carbon tetrachloride-ethyl acetate (95:5).

<i>Ester</i>	<i>Solvent system</i>							
	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈
A6	0.49	0.60	0.29	0.68	0.53	0.61	0.30	0.67
M6	0.57	0.65	0.36	0.70	0.68	0.67	0.39	0.77
A10	0.57	0.70	0.35	0.72	0.57	0.70	0.40	0.77
M10	0.65	0.77	0.42	0.76	0.80	0.78	0.48	0.86
A14	0.62	0.73	0.39	0.78	0.59	0.73	0.49	0.82
M14	0.70	0.80	0.45	0.83	0.87	0.83	0.55	0.90
A18	0.67	0.77	0.43	0.82	0.69	0.77	0.54	0.87
M18	0.74	0.83	0.54	0.89	0.92	0.86	0.66	0.92

TABLE II

R_F VALUES OF C_8 - C_{18} *n*-ALKYL CHAIN ACRYLATES (A8-A18) AND METHACRYLATES (M8-M18) ON SILUFOL IMPREGNATED WITH 5% PARAFFIN OIL IN LIGHT PETROLEUM

Ester	Dimethylformamide-water proportion				
	8:1	7:1	6:1	5:1	4:1
A8	0.69	0.67	0.61	0.58	0.41
M8	0.62	0.61	0.58	0.48	0.31
A9	0.64	0.63	0.56	0.52	0.37
M9	0.55	0.53	0.48	0.40	0.22
A10	0.58	0.57	0.42	0.40	0.25
M10	0.44	0.43	0.41	0.34	0.14
A12	0.44	0.42	0.29	0.26	0.14
M12	0.33	0.31	0.26	0.18	0.09
A14	0.26	0.25	0.14	0.12	0.07
M14	0.18	0.16	0.14	0.12	0.06
A16	0.15	0.14	0.07	0.05	0.05
M16	0.14	0.11	0.07	0.05	0.05
A18	0.10	0.07	0.05	0.04	0.03
M18	0.10	0.07	0.05	0.04	0.02

the R_F values of both acrylates and methacrylates increased as the proportion of dimethylformamide increased. As expected, when the reversed-phase technique was used, R_F values of acrylates were higher than those of the corresponding methacrylates. However, this difference of mobilities is small at longer alkyl chain lengths, so that the C_{16} and C_{18} alkyl chain esters were not separated, although different proportions of the two solvents were tried. Moreover, on impregnated phases with solvent systems containing acetic acid, spots were deformed into sharp crescent shapes.

Acrylates and methacrylates were best detected by spraying with a solution of 1% potassium permanganate-2% sodium carbonate. The spots appeared yellow against a violet background, and amounts of *ca.* 0.3 and 1 μ g, respectively, were readily visible on impregnated layers.

Detection based on conversion of esters into hydroxamic acids with hydroxylamine in alkaline media may be recommended only for non-impregnated layers. Chromatograms sprayed with ferric chloride solution showed brown spots against a yellow background.

An alternative method of visualization is to spray with 5% silver nitrate solution in 10% aqueous ammonia, which is almost sensitive as the permanganate reagent, and which produces brown-black spots.

The exposure of developed chromatograms to iodine vapour reveals only unclear spots.

The R_F values of C_8 - C_{18} *n*-alkyl acrylates and methacrylates listed in Tables I and II are useful for their identification, and can be used for the choice of the most suitable solvent system for the separation of a given mixture of acrylate and methacrylate esters.

TABLE III

R_F VALUES OF C_6 - C_{18} *n*-ALKYL ALCOHOLS ON SILUFOL SILICA GEL PLATES IMPREGNATED WITH 5% PARAFFIN OIL IN LIGHT PETROLEUM

Alcohol	Dimethylformamide-methanol-water proportions		
	3:1:1	3:2:1	8:5:1
Hexyl	0.77	—	—
Heptyl	0.75	0.90	—
Octyl	0.68	0.86	0.96
Nonyl	0.63	0.82	0.92
Decyl	0.49	0.75	0.87
Dodecyl	—	0.60	0.77
Tetradecyl	—	0.50	0.72
Hexadecyl	—	—	—
Octadecyl	—	—	—

We also investigated the problem of the chromatographic separation of acrylates and methacrylates from residual alcohols and their reliable identification. Simple systems, such as silica gel with benzene, may be used for the separation of non-volatile acrylates and methacrylates from accompanying alcohols. Detection with a solution of 1% potassium permanganate-2% sodium carbonate, showed yellow spots for both ester and alcohol, of which the one of lower R_F was due to a alcohol.

In order to make possible their TLC identification an attempt was made to separate C_6 - C_{18} alcohols, but none of the solvent systems used was suitable either with Silufol or with Lucefol. Similarly, precoated on Silufol plates with paraffin oil, only limited separation of C_6 - C_{18} straight-chain alcohols was achieved with dimethylformamide-methanol-water in various proportions (Table III).

Because of these poor results from the TLC separation of free C_6 - C_{18} alcohols, they were converted into 4-dimethylaminobenzene-4'-azobenzoates before development. From the R_F values (Table IV), C_8 - C_{18} *n*-alkyl 4-dimethylaminobenzene-4'-

TABLE IV

R_F VALUES OF C_8 - C_{18} *n*-ALKYL 4-DIMETHYLAMINO BENZENE-4'-AZOBENZOATES ON SILUFOL SILICA GEL PLATES IMPREGNATED WITH 10% PARAFFIN OIL

Alkyl azobenzoate	Solvent system	
	Dimethylformamide-methanol (9:1)	Dimethylformamide-water (9:1)
C_8	0.78	0.43
C_9	0.74	0.40
C_{10}	0.71	0.34
C_{12}	0.62	0.27
C_{14}	0.53	0.15
C_{16}	0.45	0.09
C_{18}	0.35	0.05

azobenzoates are well separated on Silufol silica gel impregnated with 10% paraffin oil in light petroleum ether.

For a complete separation of alcohol derivatives, the solvent systems dimethylformamide–methanol (9:1) and dimethylformamide–water (9:1) may be recommended. However, the binary system methanol–water was unsuitable owing to tailing spots. Because of the colour of 4-dimethylaminobenzene-4'-azobenzoates no visualization agent is needed, and less than 0.5 μg can be detected.

When decyl and dodecyl acrylates were treated with 4-dimethylaminobenzene-4'-azobenzoyl chloride under the same conditions as the alcohols (benzene with pyridine in a sealed ampoule heated in a water-bath for 90 min), no decyl and/or dodecyl derivatives were obtained. So this method can be used to determine the purity of acrylates. Further, for the identification of *n*-alkyl acrylates, reliable determination of the alcohol part of esters after their saponification may be made easy.

CONCLUSIONS

For the practical separation of non-volatile acrylates and methacrylates from each other and from the corresponding alcohols, silica gel is a most suitable thin-layer material than cellulose.

Because alcohols can be easily determined by reaction with 4-dimethylaminobenzene-4'-azobenzoyl chloride, the latter can be used for the identification of alcohols in the presence of acrylate esters.

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