Note

Liquid chromatography of benzenedicarboxylic acids and their 2-hydroxyethyl esters on silica gel[*]

L. NONDEK, P. ŠILHAVÝ and J. MÁLEK

Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchdol (Czechoslovakia)

(Received June 7th, 1976)

3-Hydroxyethyl terephthalate (HET) and bis(2-hydroxyethyl) terephthalate (BHET) are known to be main intermediates in the early stage of catalyzed polyesterification of terephthalic acid (TA) with ethylene glycol. In the catalyzed reaction of TA with ethylene oxide, HET is the intermediate which is converted into BHET in the final step. The formation of analogous compounds can also be expected in reactions of isophthalic acid (IA) with ethylene glycol and ethylene oxide. A separation method combined with polarography has been reported for the quantitative analysis of TA–HET–BHET mixtures[1-3] as well as for the analysis of complex mixtures of these compounds with the corresponding neutral and acidic dimers[4,5]. Gas–liquid chromatography has been recommended for the analysis of ethylene glycol solutions of TA, HET and BHET after preceding trimethylsilylation with bis(trimethylsilyl)trifluoroacetamide[6]. Recently, gel permeation chromatography was used to determine the composition of pre-polymeric mixtures resulting from the esterification of TA with ethylene glycol[7]. All of these methods have several disadvantages. The polarographic analysis[1-5] cannot be applied to mixtures of IA, 2-hydroxyethyl isophthalate (HEI) and bis(2-hydroxyethyl) isophthalate (BHEI); gel permeation chromatography[7] modified to separate this three-component mixture is time consuming[8]. The gas chromatographic method requires treatment of the samples with the silylating agent at elevated temperatures and its precision is lowered in the presence of oligomeric products.

In this paper, we report a rapid and simple method for the separation and quantitative analysis of three-component mixtures of IA, HEI and BHEI as well as of TA, HET and BHET in ethylene glycol. The method is based on liquid chromatography of the esterification mixtures on silica gel.

EXPERIMENTAL

Materials

TA (Mobil Oil, Princeton, N. J., U.S.A.) containing 0.07% of *o*-phthalic acid and IA (Amoco Chemicals, Chicago, Ill., U.S.A.) containing 0.29% of TA, both "fiber

---

[*] Esterification of benzenecarboxylic acids with ethylene glycol. Part X.

grade" chemicals, were used without further purification. Pure HET [m.p. 183–184°; acid number 264 (calculated 266.9); saponification number 529 (calculated 533.9)], BHET (m.p. 110.0–110.5°; saponification number 438 (calculated 441.4)) and BHEI (m.p. 77.0–77.5°) were obtained according to previously described procedures[9]. HEI was prepared by the introduction of ethylene oxide into an aqueous suspension of monosodium isophthalate[10] and purified by repeated crystallization until the product melted at 130–131° and its acid number was 272 (calculated 266.9). All of the standard compounds gave satisfactory elemental analyses. Commercial chloroform was dried over phosphorus(V) oxide and distilled under nitrogen. Commercial tetrahydrofuran was allowed to stand over ground potassium hydroxide for several days and then fractionated under nitrogen over sodium bis(2-methoxyethoxy)aluminium hydride (Synthesia, Kolín, Czechoslovakia). Silica gel beads (diameter 40–50 μm) for liquid chromatography[11] were obtained from the Institute for Nuclear Research (Řež, Czechoslovakia). For thin-layer chromatography of standard compounds, Silufol UV$_{254}$ silica gel plates (150 × 75 mm) (Kavalier, Sklárny, Czechoslovakia) were used. The esterification mixtures were obtained[4] by reaction of TA or IA with ethylene glycol (chromatographically pure) (initial molar ratio 1:20) in the presence of tin(II) oxalate (0.2% on the acid used) as catalyst under nitrogen at 180°; samples (1.0 ml) for liquid chromatography were withdrawn from the reaction mixture by means of a heated pipette, placed in an ampoule and diluted with the eluent to give a 2% solution.

Liquid chromatography

The chromatograph consisted of a programmed Micropump 68005 (Development Workshops, Czechoslovak Academy of Sciences, Prague, Czechoslovakia), a 50 cm × 6.0 mm O.D. × 3.5 mm I.D. glass column, a two-beam UV analyzer (254 nm) equipped with 50-μl flow cells (Development Workshops) and a TZ 21S linear recorder (Laboratory Instruments, Prague, Czechoslovakia). The column was dry-packed with silica gel beads and terminated by Swagelok-type fittings. Solute samples (10 μl) were injected as 2% solutions with a microsyringe through a septum. The chromatographic column was operated at a flow-rate of 1.0 ml/min, inlet pressure 15 atm and at room temperature. Degassed chloroform–tetrahydrofuran (1:1) was used as the eluent, to which 1% of glacial acetic acid was added in order to suppress tailing of dicarboxylic acids and their 2-hydroxyethyl esters. A fresh portion of the eluent was prepared immediately before each 8-h series of measurements.

Thin-layer chromatography

Samples of standard compounds were spotted on to Silufol silica gel plates, the spots were developed with chloroform–tetrahydrofuran (2:1) and the chromatograms were rendered visible by irradiation with a UV lamp.

RESULTS AND DISCUSSION

A typical chromatogram of the reaction mixture from the catalyzed esterification of IA with ethylene glycol is shown in Fig. 1; symmetrical peaks of IA, HEI and BHET were obtained in all measurements. The separation of TA, HET and BHET in the reaction mixture from the catalyzed esterification of TA with ethylene glycol gave similar results. The values of the capacity factors, k', for the liquid chromatography
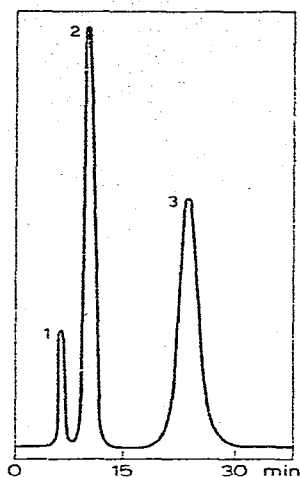
Fig. 1. Liquid chromatography on silica gel of the mixture of IA (1), HEI (2) and BHEI (3) from the tin(II) oxalate catalyzed esterification of IA with ethylene glycol (initial molar ratio 1:20) after reaction for 45 min at 180°.
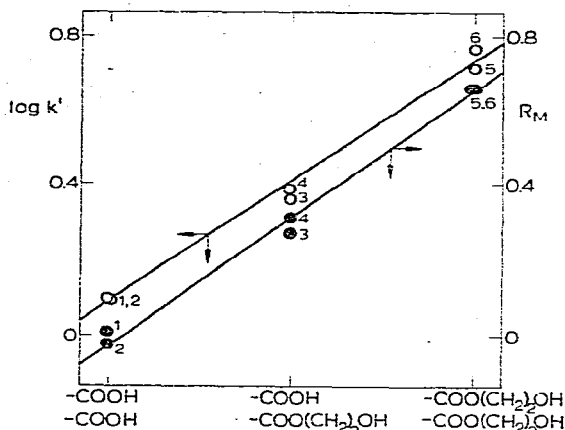
Fig. 2. Linear correlations of the liquid chromatographic capacity factors (k') and thin-layer chromatographic R_M values with the structure in the series TA (1), IA (2), HET (3), HEI (4), BHET (5) and BHEI (6).

and the corresponding R_M values obtained by thin-layer chromatography are presented in Table I. It is noteworthy that IA and TA are eluted in the chloroform–tetrahydrofuran system (1:1) in shorter times than the less polar 2-hydroxyethyl esters and bis(2-hydroxyethyl) esters. The carboxyl group thus behaves in this chromatographic system as a less polar group and is therefore less adsorbed than the 2-hydroxyethyl ester group. This effect is presumably due to the specific solvation of the carboxylic group by tetrahydrofuran; this assumption agrees with the fact that TA, HET and BHET were eluted in reverse order and in accordance with their polarity when chloroform–ethanol (9:1) was used as the eluent[5].

As can be seen from Fig. 2, there are linear correlations between log k' or R_M

TABLE I

VALUES OF k' AND R_M DETERMINED FOR STANDARD COMPOUNDS

Compound	k'*	R_F	R_M**
IA	1.3	0.51***	−0.02
TA	1.3	0.49***	0.02
HEI	2.4	0.33	0.31
HET	2.3	0.35	0.27
BHEI	5.8	0.18	0.66
BHET	5.1	0.18	0.66

* $k' = (t - t_0)/t_0$, where t is the retention time of the solute and t_0 is the retention time (dead time) for unretained perchloroethylene.

** $R_M = \log(1/R_F - 1)$ (ref. 12).

*** Tailing was observed.

and the number of esterified carboxylic groups in the molecule, which express the relationship of the chromatographic behaviour to the structures of the individual compounds in this series.

ACKNOWLEDGEMENT

REFERENCES

1 L. Jadrníčková and J. Krupička, *Chem. Prům.*, 13 (1963) 578.
2 L. Jadrníčková and J. Krupička, *Chem. Prům.*, 18 (1968) 554.
3 F. Mareš, V. Bažant and J. Krupička, *Collect. Czech. Chem. Commun.*, 34 (1969) 2208.
4 M. Krumpolc and J. Málek, *Makromol. Chem.*, 168 (1973) 119.
5 M. Krumpolc and J. Málek, *Makromol. Chem.*, 171 (1973) 69.
6 R. R. Atkinson, Jr., and S. I. Calouche, *Anal. Chem.*, 43 (1971) 460.
7 M. Minárik, G. I. El Diwani and Z. Šír, unpublished results.
8 Z. Šír, unpublished results.
9 P. Čefelín and J. Málek, *Collect. Czech. Chem. Commun.*, 34 (1969) 419.
10 A. E. Ardis and A. A. Vaitekunas, *Ger. Pat.*, 1,198,343 (1965); *C.A.*, 64 (1966) 3430a.
11 M. Tympl, K. Stamberg, V. Baran, V. Urbánek and V. Novák, *Czech. Pat.*, 154,532 (1974); *C.A.*, 82 (1975) 75049.
12 E. C. Bathe-Smith and R. G. Westall, *Biochim. Biophys. Acta*, 4 (1950) 427.