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## Note

# Reversed-phase high-performance liquid chromatographic analysis of the reaction mixture occurring in the production of a synthetic diester lubricant

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A simple, rapid reversed-phase liquid chromatographic method has been developed to study the kinetics of esterification in the production of the synthetic lubricant di(2-ethylhexyl)sebacate using an octylsilica stationary phase and methanol–aqueous phosphate buffer eluents. By the use of suitable eluent compositions and the quantity of raw materials (sebacic acid and 2-ethylhexanol), the intermediate monoester and di(2-ethylhexyl) sebacate can be determined.

In a reaction mixture containing diester, monoester, 2-ethylhexanol and sebacic acid, the concentration of the diester and the alcohol can be determined by gas chromatography (GC)[1] or by high-performance liquid chromatography (HPLC)[2,3], but the monoester and sebacic acid can be analysed only by GC after derivatization (esterification or silylation[4,5]). The advantage of the HPLC method developed is that no derivatization of the compounds is needed.

## EXPERIMENTAL

The chromatographic system used consisted of a pump, Model 6000A, a differential refractometer detector (Varian LC 4010), a six-port injection valve (Model 7125, Rheodyne) with a 10-$\mu$l loop and a dual-channel recorder (Varian Model 9176).

The analytical column contained octylsilica (Nucleosil $C_8$), 150 mm × 4 mm I.D., 5 $\mu$m. The column temperature was maintained at 25 ± 0.5°C by means of a water-bath and a water-jacket.

The eluents were prepared as described[6] with an aqueous phosphate buffer of constant methanol concentration and sodium bromide concentration. The pH of the eluents was measured with a combined glass electrode calibrated with aqueous buffers.

The purity of the 2-ethylhexanol used for the preparation of the calibration graph was controlled by capillary GC (99.5%, w/w), and the sebacic acid was ana-

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lysed by LC (>99.5%, w/w). Standard diester [di(2-ethylhexyl)sebacate] was prepared by us and purified in several steps. Its composition was determined by capillary GC based on percentage areas: 94.5% (w/w) diester, 3.6% (w/w) 2-ethylhexanol. An HP5880A GC instrument with flame ionization detection (FID) and a chemically bonded, stationary phase, SE-54, were employed. For the determination of the diester and monoester in the reaction mixtures, the samples were dissolved in 85% (v/v) methanol–aqueous phosphate buffer eluent (5 m*M* sodium dihydrogenphosphate, 40 m*M* phosphoric acid, 20 m*M* sodium bromide). In order to analyse 2-ethylhexanol and sebacic acid, the samples were mixed with 70% (v/v) methanol–20 m*M* aqueous sodium bromide solution in a separation funnel. The diester cannot be dissolved in this solution (lower phase). The sebacic acid and the 2-ethylhexanol can be determined from the upper phase.

## RESULTS AND DISCUSSION

In order to establish the optimum conditions for liquid chromatographic analysis, the retention of the compounds was studied as a function of the methanol concentration of the eluent (Fig. 1). The concentration of the sodium dihydrogenphosphate in the eluent was 5 or 25 m*M* and the concentration of the phosphoric acid was kept constant at 40 m*M*. The pH of the eluent was *ca.* 3.4. It was found that the retention of sebacic acid increased significantly by decreasing the pH of the eluent (pH 5 to 3.5). When the pH of the eluent was >4 the peak of sebacic acid appeared before the dead volume. The retention of the monoester, 2-ethylhexanol and the diester were independent of the eluent pH in range pH 3–5. The peak shapes of the monoester and diester improved slightly with the addition of the buffer. Fig. 1 shows that plots of log $k'$ *vs.* methanol concentration are linear ($k' = V_R - V_0/V_0$ where $V_0 = 1.65$ cm$^3$). This suggests that the extent of retention can be controlled by the methanol concentration of the eluent. The slopes of the plots are significantly different.

The separation and determination of all the components could not be carried out with one particular eluent composition due to the large differences in polarity and solubility of the compounds. In order to decrease the retention of the diester (for a more rapid analysis), an eluent with a methanol concentration of 85% was applied. However, sebacic acid was eluted near the dead volume and was overlapped by the injection peak caused by dilution of the samples in methanol (Fig. 2).

The 85% methanol–aqueous phosphate buffer eluent (5 m*M* sodium dihydrogen phosphate–40 m*M* phosphoric acid–20 m*M* sodium bromide) was suitable for separation of the diester, monoester and 2-ethylhexanol, but not for the quantitation of 2-ethylhexanol because of its small retention volume (2.3 cm$^3$); it was eluted after the injection peak. In order to increase the retention of 2-ethylhexanol and sebacic acid, it is advisable to choose an eluent with a lower methanol concentration (<75%, v/v). By decreasing the methanol concentration to 70% (v/v) (25 m*M* sodium dihydrogenphosphate–40 m*M* phosphoric acid–20 m*M* sodium bromide) the peaks of 2-ethylhexanol and sebacic acid were satisfactory for their quantitation (Fig. 3). This eluent was not suitable for the analysis of the monoester because of the high retention of the latter. The samples were dissolved in 70% (v/v) methanol–aqueous 20 m*M* sodium bromide (instead of the eluent) for the preparation of the calibration graphs for sebacic acid and 2-ethylhexanol and for the investigation of the reaction mixture.

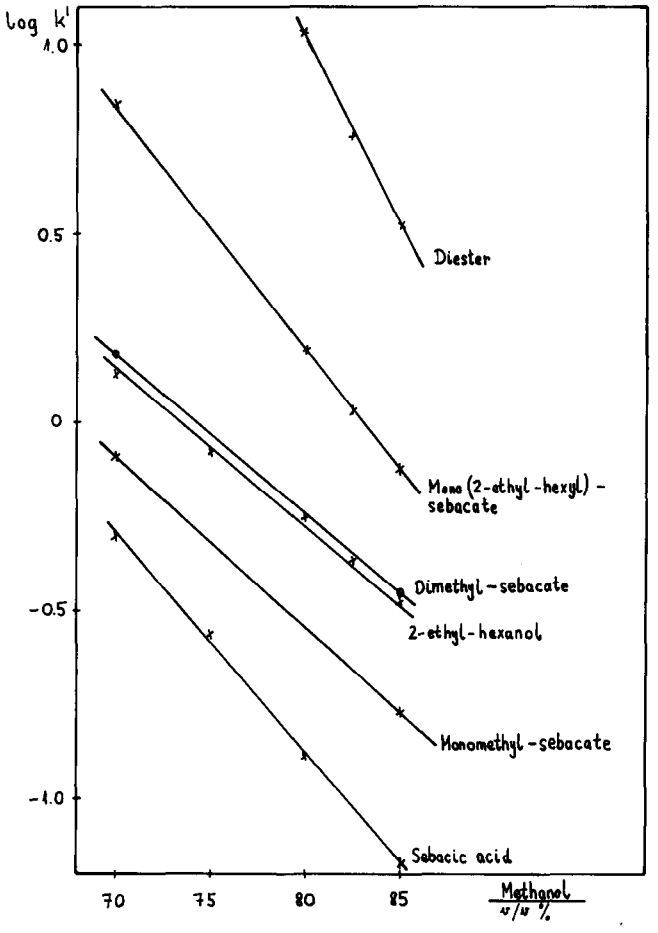


Fig. 1. Plots of log $k'$ *vs.* methanol concentration of the eluent.

After a few days storage of the samples dissolved in the eluent, sebacic acid reacts with methanol forming monomethyl sebacate and dimethyl sebacate owing to acid catalysis of the esterification.

The elution curve of monomethyl sebacate is also shown in Fig. 3. The diester cannot be dissolved in 70% (v/v) methanol–aqueous mixture because it forms another phase. The two phases can be separated in a separation funnel. Standard solutions were used to demonstrate that sebacic acid and 2-ethylhexanol can be determined in the upper phase without any loss.

The determination of the concentration of the monoester in the reaction mixture was more difficult because no standard was available. In order to obtain a calibration graph for the monoester, a reaction mixture was prepared containing *ca.* 60% (w/w) monoester. The actual concentration of the monoester was calculated indirectly as follows:

$$\text{Monoester (\%, w/w)} = 100 - (\text{sebacic acid} + \text{2-ethylhexanol} + \text{diester})$$

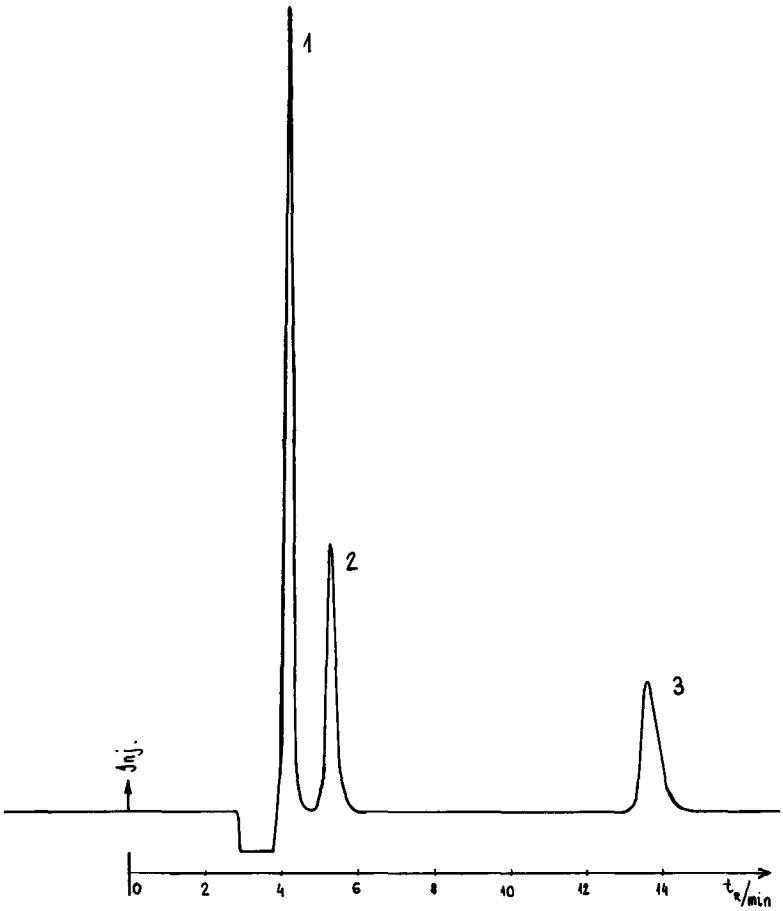


Fig. 2. Chromatogram of the reaction mixture. Eluent: 85% methanol–aqueous phosphate buffer (5 m*M* sodium dihydrogenphosphate, 40 m*M* phosphoric acid, 20 m*M* sodium bromide). Column: Nucleosil $C_8$ (150 mm × 4 mm). Detector: refractive index. Eluent flow-rate: 0.5 ml/min. Peaks: 1 = 2-ethylhexanol; 2 = mono(2-ethylhexyl)sebacate; 3 = di(2-ethylhexyl)sebacate.

The water formed in the esterification process was removed by azeotropic distillation. Traces amount of water were removed by sodium sulphate. The composition of this reaction mixture was: diester, 34.7 ± 0.1 ($n$ = 11); sebacic acid, 1.2 ± 0.05 ($n$ = 7); 2-ethylhexanol, 3.2 ± 0.1 ($n$ = 7); monoester, 60.8 ± 0.1% (w/w) ($n$ = 11). The calibration graph for the monoester was prepared by dilution of this reaction mixture. Data for the calibration were calculated from the peak areas of the compounds. The parameters of the calibration graphs for the four components are summarized in Table I.

The composition of the reaction mixtures was estimated using the equations corresponding to the calibration graphs shown in Table I. Based on the concentration data determined by this method, the optimum technological parameters were estimated. They will be discussed in detail in a subsequent paper.

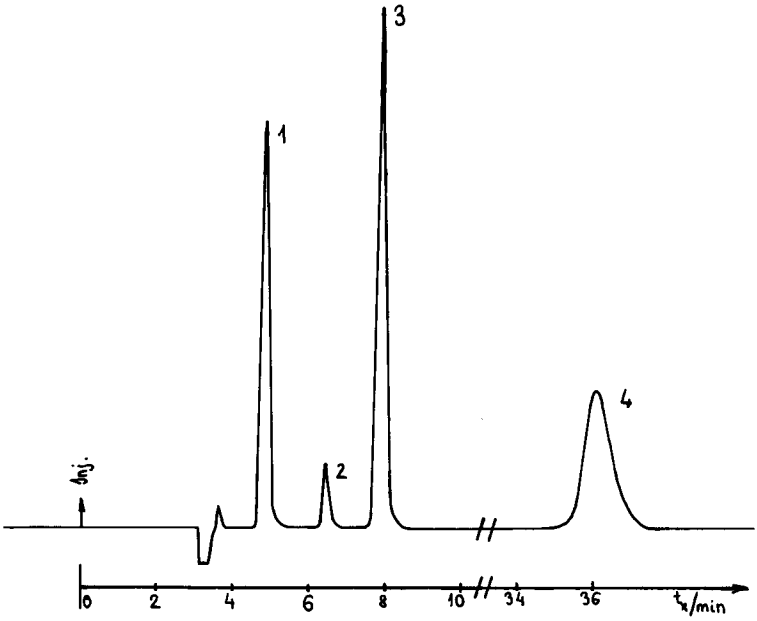


Fig. 3. Chromatogram of the reaction mixture. Eluent: 70% methanol–aqueous phosphate buffer (25 m*M* sodium dihydrogenphosphate, 40 m*M* phosphoric acid, 20 m*M* sodium bromide). Column: Nucleosil $C_8$ (150 mm × 4 mm). Detector: refractive index. Eluent flow-rate: 0.5 ml/min. Peaks: 1 = sebacic acid; 2 = monomethylsebacate; 3 = 2-ethylhexanol; 4 = mono(2-ethylhexyl)sebacate.

TABLE I

PARAMETERS OF THE CALIBRATION GRAPHS FOR SEBACIC ACID, 2-ETHYLHEXANOL, MONOESTER AND DIESTER

$A = a + bc$, where $A$ is the peak area in $mm^2$, and $c$ is the concentration of the injected sample in g/l (injection volume 10 μl).

| *Sample* | *Range tested (g/l)* | *a* | *b* | *Regression coefficient* |
|---|---|---|---|---|
| Sebacic acid* | 0–12 | 1.13 | 84.07 | 0.9999 |
| 2-Ethylhexanol* | 0–12 | −3.02 | 76.06 | 0.9998 |
| Monoester** | 0–15 | 2.13 | 82.83 | 0.9996 |
| Diester** | 0–24 | 11.88 | 97.81 | 0.9995 |

* Eluent: 70% methanol–aqueous phosphate buffer–sodium bromide.
** Eluent: 85% methanol–aqueous phosphate buffer–sodium bromide.

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