# TERPENOIDS

## LXXXII. EVALUATION OF POLYESTERS AS STATIONARY PHASES IN GAS–LIQUID CHROMATOGRAPHY OF TERPENOIDS*

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In an earlier communication[1] on our study of polyesters as stationary phases in gas–liquid chromatography (GLC) columns, it was observed that the number of methylene groups between the two carboxyl groups of the acidic fragment of the polyester has a profound influence on the degree of separation. The retention times of hydrocarbons are nearly proportional to the number of methylene groups present. This linearity was found to be valid up to brassylic acid [HOOC-$(CH_2)_{11}$-COOH] and deviated to some extent with higher dicarboxylic acid polyesters. On the same basis of these findings it was felt necessary to study the effect of the temperature gradient more closely and also to find out the effect of equimolar proportion of the different polyesters on the degree of separation. At one stage it was suspected that using equimolar proportion of different polyesters, the retention times for a particular hydrocarbon may become identical; but results of actual experiments presented in this paper will show that this is not really so, and that the number of methylene groups spaced between the carboxyl groups of the dicarboxylic acid moiety plays a more important part than the molecular weight of the polyester. There may be other factors as well.

### EXPERIMENTAL

(1) Apparatus: Griffin & George MK II VPC apparatus was used with modifications as described in our previous communication.

(2) The same columns were employed for the study of temperature gradient.

(3) Retention time data were recorded as previously[1] between 70 to 120° at intervals of 5° approximately.

(4) Polyesters of succinic, adipic, azelaic, and brassylic acids were chosen for the present investigation.

(5) α-Pinene, β-pinene, limonene, p-cymene and n-amyl acetate were used as reference compounds.

(6) Specific retention volumes ($V_g$ values) were calculated according to standard procedure[2] and used for the construction of graphs as described in the discussion.
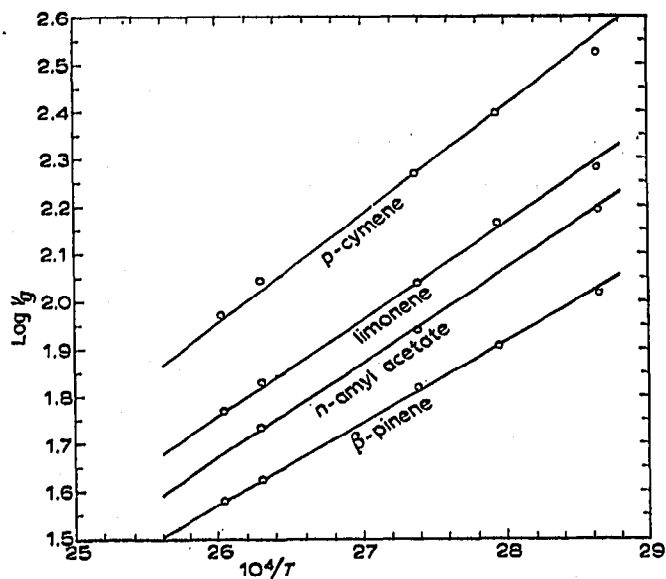
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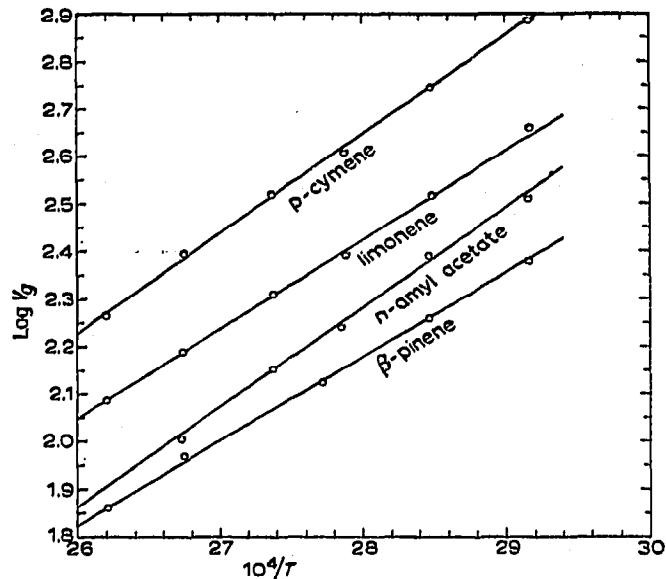Fig. 1. Succinic acid–diethyleneglycol polyester.
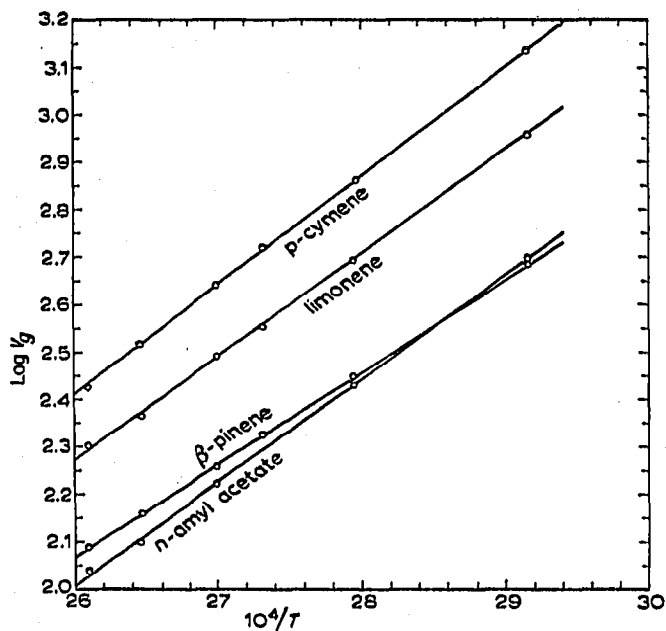


Fig. 2. Adipic acid–diethyleneglycol polyester.



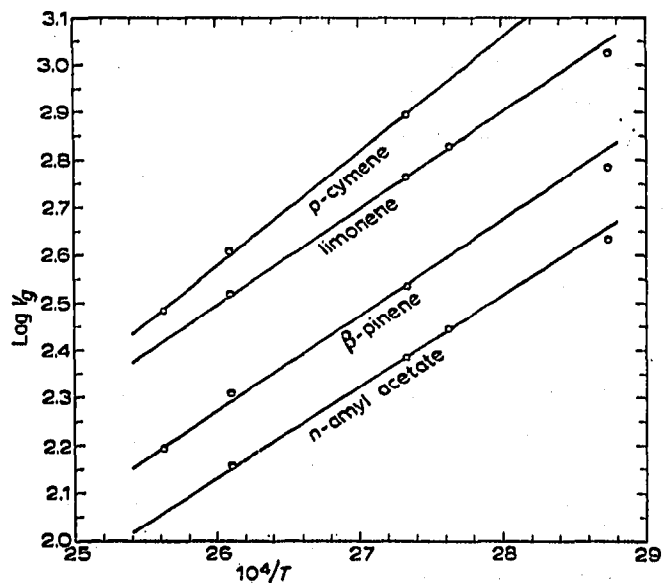Fig. 3. Azelaic acid–diethyleneglycol polyester.



Fig. 4. Brassylic acid–diethyleneglycol polyester.

## RESULTS AND DISCUSSION

During the study of the influence of temperature gradient, $V_g$ values were calculated[2] and log $V_g$ against $10^4/T$ was recorded in Figs. 1 to 4. At different temperatures, values of log $V_g$ of the required compound were then read out from each graph. The difference between the two values for a particular compound on two different phases furnished the ratio for the two specific retention volumes. Such ratios for the two terpenic compounds, $\beta$-pinene and limonene, have been calculated and are shown in Table I. The maximum deviation in each case has also been calculated and is shown in the same table. The deviation is found to lie generally within the permissible experimental limits and is about 10 % in an extreme case.

TABLE I

| Ratio of the number of methylene groups | Temperature $10^4/K$ | | | | | Maximum deviation |
| --- | --- | --- | --- | --- | --- | --- |
| | 26.20 | 26.80 | 27.0 | 27.50 | 27.9 | |
| Compound: $\beta$-pinene: | | | | | | |
| 11/2 = 5.50 | 5.129 | 5.346 | 5.309 | 5.495 | 5.697 | 6.75 |
| 11/4 = 2.75 | 2.851 | 2.927 | 2.951 | 3.020 | 3.020 | 9.82 |
| 11/7 = 1.57 | 1.603 | 1.596 | 1.614 | 1.622 | 1.641 | 4.52 |
| 7/2 = 3.50 | 3.20 | 3.273 | 3.289 | 3.388 | 3.467 | 8.57 |
| 7/4 = 1.75 | 1.778 | 1.82 | 1.828 | 1.862 | 1.90 | 8.57 |
| Compound: limonene: | | | | | | |
| 11/2 = 5.50 | 5.433 | 5.383 | 5.559 | 5.249 | 5.129 | 6.75 |
| 11/4 = 2.75 | 2.851 | 2.825 | 2.917 | 2.950 | 2.884 | 6.05 |
| 11/7 = 1.57 | 1.641 | 1.589 | 1.648 | 1.585 | 1.514 | 4.97 |
| 7/2 = 3.50 | 3.311 | 3.388 | 3.296 | 3.311 | 3.888 | 5.82 |
| 7/4 = 1.75 | 1.738 | 1.778 | 1.770 | 1.862 | 1.90 | 8.57 |

The deviation observed may be due to the following possible reasons:

(1) Fluctuations in the column temperature, which in our case, using the Griffin & George MKII VPC apparatus was about $\pm 1°$ (ref. 3).

(ii) Slight fluctuations in the flow rate[2].

(iii) Since the same columns as were used previously have been used in the present investigation, the weight of the stationary phase may not be exactly the same, because the rate of bleeding of different polyesters is most likely to be different[4].

(iv) It is also worth noting that the lower polyesters are viscous liquids, whereas the higher polyesters are low melting solids. The densities of these polyesters will not be the same at any particular temperature. This is likely to affect the partition coefficient and thus introduce a source of deviation.

The behaviour of $n$-amyl acetate is found to be interesting. On a succinic acid polyester column, this compound emerges after $\beta$-pinene; the same occurs with an adipic acid polyester column. However, on an azelaic acid polyester column these two compounds almost overlap and on a brassylic acid polyester column it actually emerges before $\beta$-pinene. This gives a good clue to the separation of a mixture of compounds of different natures.

*Influence of molar proportion of the polyester*

Average molecular weights were taken on the basis of two closely agreeing experimental values and new column fillings were prepared. The columns were adjusted in such a way that each column contained 1/500 mole of the polyester. These columns were conditioned at 80° for 1.5 h and the retention times of reference compounds determined as usual. The results are tabulated in Table II. The retention

TABLE II

| Compound | Number of methylene groups | Molecular weight | Weight of the liquid | Retention time | Contribution per gram, per methylene group |
|----------|----------------------------|------------------|----------------------|----------------|---------------------------------------------|
| α-Pinene | 2 | 1249 | 2.448 | 2.03 | 0.4146 |
|          | 3 | 340  | 0.676 | 0.99 | 0.4879 |
|          | 4 | 1154 | 2.266 | 3.75 | 0.4138 |
|          | 7 | 398  | 0.791 | 2.55 | 0.4605 |
| β-Pinene | 2 | 1249 | 2.448 | 3.60 | 0.7352 |
|          | 3 | 340  | 0.676 | 1.55 | 0.7640 |
|          | 4 | 1154 | 2.266 | 6.63 | 0.7316 |
|          | 7 | 398  | 0.791 | 4.08 | 0.7369 |
| $Δ^3$-Carene | 2 | 1249 | 2.448 | 4.56 | 0.9313 |
|          | 3 | 340  | 0.676 | 1.99 | 0.9811 |
|          | 4 | 1154 | 2.266 | 8.50 | 0.9380 |
|          | 7 | 398  | 0.791 | 5.31 | 0.9590 |
| Limonene | 2 | 1249 | 2.448 | 6.55 | 1.338 |
|          | 3 | 340  | 0.676 | 2.80 | 1.380 |
|          | 4 | 1154 | 2.266 | 11.93 | 1.316 |
|          | 7 | 398  | 0.791 | 7.18 | 1.296 |
| Camphene | 2 | 1249 | 2.448 | 2.81 | 0.5738 |
|          | 3 | 340  | 0.676 | 1.35 | 0.6655 |
|          | 4 | 1154 | 2.266 | 5.33 | 0.5882 |
|          | 7 | 398  | 0.791 | 3.28 | 0.5294 |

times were not identical indicating thereby that molar proportion was not the deciding factor. However, when the retention time was divided by the actual weight of the stationary phase used and then by the number of methylene groups which may be considered as contribution per gram per methylene group, the values were nearly constant. These values are tabulated in Table II under "contribution".

This is in agreement with the linearity factor observed previously, though it may be worth remembering that in the earlier communication equal weights of the stationary phases were used.

SUMMARY

The study of polyesters was extended over a wider range of temperature. The ratio of the specific retention volumes on two different polyesters for a typical hydrocarbon is nearly equal to the number of methylene groups spaced between the two

carboxyl groups of the acidic fragment of the polyester. Further it has also been found that the molecular weight plays a less important part than the number of methylene groups present in the acidic fragment of the polyester.

REFERENCES

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