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## GAS CHROMATOGRAPHIC ANALYSIS OF ALIPHATIC ALCOHOLS, DIOLS AND ETHERS USING AROMATIC POLYMERS

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## SUMMARY

1. The gas-solid separations of alcohols, diols and ethers on porous aromatic polymers are essentially the same as those using gas-liquid separation on Celite-Apiezon L columns, although the retention times on the latter are much shorter.

2. For liquids with similar boiling points the order of elution is diol, alcohol, ether, which reflects their increasing solubility in the polymer or in Apiezon L.

3. Within a class of compounds there is a linear relationship between  $\log t_r$  and boiling point of the eluent. Small divergencies from linearity arise from changes in the structure of the alkyl sidechain.

4. Modifying PAR-1 with polyethylene glycol has little effect on separation of alcohols and ethers, and the behaviour of the resulting column contrasts strongly with the Celite-PEG 1500 column.

5. Diols are separated on aromatic polymers (e.g. PAR-1) without decomposition.

## INTRODUCTION

Saturated aliphatic alcohols are often separated by gas chromatography using a polar liquid phase such as a polyglycol, an ester or a nitrile derivative. However, HOLLIS *et al.*<sup>1-3</sup> have shown that porous polyaromatic beads can be used. For example, on an ethylvinylbenzene-divinylbenzene (EVB-DVB) column, a mixture of 16 C<sub>1</sub>-C<sub>5</sub> saturated alcohols gave 14 peaks, only mixtures of 2-pentanol and 3-pentanol and of 2-methyl-1-butanol and isopentyl alcohol not separating.

HOLLIS *et al.* suggested that, from elution data, the solubility of the compound in the polymer is the most important factor in determining the order of elution, and that boiling point (or volatility) is of less consequence. As an example, he showed that, on an EVB-DVB polymer, *n*-butyl alcohol eluted before *tert.*-pentyl alcohol although the boiling point of the tertiary alcohol is lower.

In order to investigate the interaction between alcohols and aromatic polymers during gas chromatographic elution of the alcohols, results obtained in this work are compared with results from similar experiments using Celite coated with non-polar and polar stationary phases. Moreover, some analyses of diols and ethers are described in order to compare their behaviour with that of the alcohols.

## EXPERIMENTAL

*Operating conditions of the gas chromatograph*

All results were determined isothermally. The retention times for amines were determined on a Pye 104 gas chromatograph equipped with a flame ionisation detector coupled to an RE 511 (Goerz Servoscribe) recorder. In order to find the corrected retention time ( $t_r$ ) of each compound, the time taken for the carrier gas (nitrogen) to pass through the column was measured using a thermal conductivity cell.

Glass columns (4 mm I.D.) were used, the length being 1.6 m except for the column of Porapak Q which was 0.7 m long. The flow rate for nitrogen was 25 ml·min<sup>-1</sup>.

In some experiments, the gas chromatograph was connected to an A.E.I. MS 12 mass spectrometer.

*Materials*

Solids used for chromatography were PAR-1 (80-120 mesh) (Hewlett-Packard), Porapak Q (100-120 mesh) (Waters Associates Inc.) and Celite (acid washed (A/W) 100-120 mesh) (W. G. Pye and Co. Ltd.). The liquid phases used were PEG 1500 (British Drug Houses Ltd.) and Apiezon L (Apiezon Products Ltd.).

Alcohols, diols and ethers used were all commercially available.

*Column preparation*

A weighed sample of the coating material was dissolved in an excess of solvent, and a known weight of support material was added to the solution. The mixture was evaporated on a rotary evaporator, under reduced pressure, and the column packing was subsequently dried in an oven at 100° for several hours. When preparing columns using alkali-washed (Alk/W) (5% w/w potassium hydroxide) Celite, a weighed sample of potassium hydroxide was dissolved in methanol, and Celite (A/W) was added. The mixture was evaporated under reduced pressure.

The following packing materials were used during this study:

- (I) PAR-1;
- (II) Porapak Q;
- (III) PAR-1 + PEG 1500 (a) 5% w/w, (b) 10% w/w;
- (IV) Celite (Alk/W) + Apiezon L (a) 10% w/w, (b) 20% w/w, (c) 30% w/w;
- (V) Celite (A/W) + Apiezon L 20% w/w;
- (VI) Celite (A/W) + PEG 1500 10% w/w.

## RESULTS AND DISCUSSION

*Separation of aliphatic alcohols and ethers by PAR-1, Porapak Q and Celite-Apiezon L (Columns I, II and IV (a-c))*

The adjusted retention times,  $t_r$ , for aliphatic alcohols and ethers on PAR-1, Porapak Q and Celite-Apiezon L are given in Table I. The retention times on Celite-Apiezon L are shorter than those on the polymers but in most respects the chromatographic properties of the polymers resemble those of conventional Celite-Apiezon L. Thus the order of elution is generally similar for the two polymers and Celite-Apiezon L, although there are instances where the retention times of a pair of alcohols or

TABLE I

ADJUSTED RETENTION TIMES (min) FOR ALIPHATIC ALCOHOLS AND ALIPHATIC ETHERS

Column No.	Column temperature (°)	Column length (m)	PAR-I		Porapak Q	PAR-I		Celite		Celite	
			I	II	III (a)	III (b)	IV (a)	IV (b)	IV (c)	VI	
			150	150	150	150	150	60	60	60	60
			1.6	0.7	1.6	1.6	1.6	1.6	1.6	1.6	1.6
			0.9	0.6	0.7	1.2	1.2	0.3	0.5	0.5	5.8
Methyl alcohol			1.5	1.6	1.3	1.8	1.8	0.4	0.5	0.5	7.6
Ethyl alcohol			1.9	3.2	1.5	2.0	2.0	0.5	1.0	1.2	7.1
Isopropyl alcohol			2.9	5.2	1.9	2.2	2.2	0.7	...	1.7	6.1
tert.-Butyl alcohol			3.4	4.5	2.6	3.6	3.6	1.4	2.0	2.2	16.0
n-Propyl alcohol			4.8	8.4	3.6	4.1	4.1	1.5	3.0	3.6	13.6
sec.-Butyl alcohol			5.3	9.4	4.0	5.1	5.1	1.8	3.5	4.3	23.8
Isobutyl alcohol			5.8	13.2	4.0	4.7	4.7	2.2	5.3	5.4	13.5
tert.-Pentyl alcohol			7.2	11.7	5.2	6.7	6.7	3.4	5.3	6.1	35.3
n-Butyl alcohol			7.4	17.2	5.1	6.8	6.8	3.0	5.1	6.4	26.0
2,2-Methyl-1-propanol			8.4	19.4	6.0	7.2	7.2	3.6	7.7	8.8	27.6
2-Pentanol			8.6	18.3	5.9	6.8	6.8	3.7	8.1	9.3	26.7
3-Pentanol			9.4	29.5	6.7	7.9	7.9	6.0	10.9	12.4	24.9
2-Methyl-2-pentanol			9.6	23.7	7.8	9.5	9.5	5.0	9.8	11.5	51.2
Isopentyl alcohol			9.6	22.9	7.6	9.6	9.6	5.0	10.1	11.6	50.8
2-Methyl-1-butanol			11.2	36.5	7.8	8.9	8.9	7.5	13.3	15.1	40.6
4-Methyl-2-pentanol			11.3	30.9	9.5	12.0	12.0	8.5	14.8	15.8	73.1
n-Pentyl alcohol			17.3	57.2	14.1	17.4	17.4	16.4	27.5	30.6	112.3
2-Ethyl-1-butanol			22.2	66.1	17.0	20.3	20.3	21.0	35.3	37.0	156.2
n-Hexyl alcohol			47.3	...	31.4	35.2	35.2	67.2	...	144.9	237.0
2-Octanol			54.1	...	39.3	44.2	44.2	82.2	142.9	166.3	308.0
2-Ethyl-1-hexanol			2.3	4.0	1.1	1.5	1.5	0.7	2.3	1.9	0.8
Ethyl ether			3.9	8.4	1.9	2.4	2.4	1.3	2.3	3.5	1.2
tert.-Butyl methyl ether			4.0	5.3	1.9	2.4	2.4	1.6	3.0	4.5	1.0
Isopropyl ether			5.0	...	5.2	5.1	5.1	...	...	...	1.9
n-Butyl methyl ether			7.0	12.5	3.8	4.6	4.6	3.7	7.1	10.3	2.3
n-Propyl ether			20.3	...	11.6	13.8	13.8	22.2	42.7	64.3	8.9
n-Butyl ether											

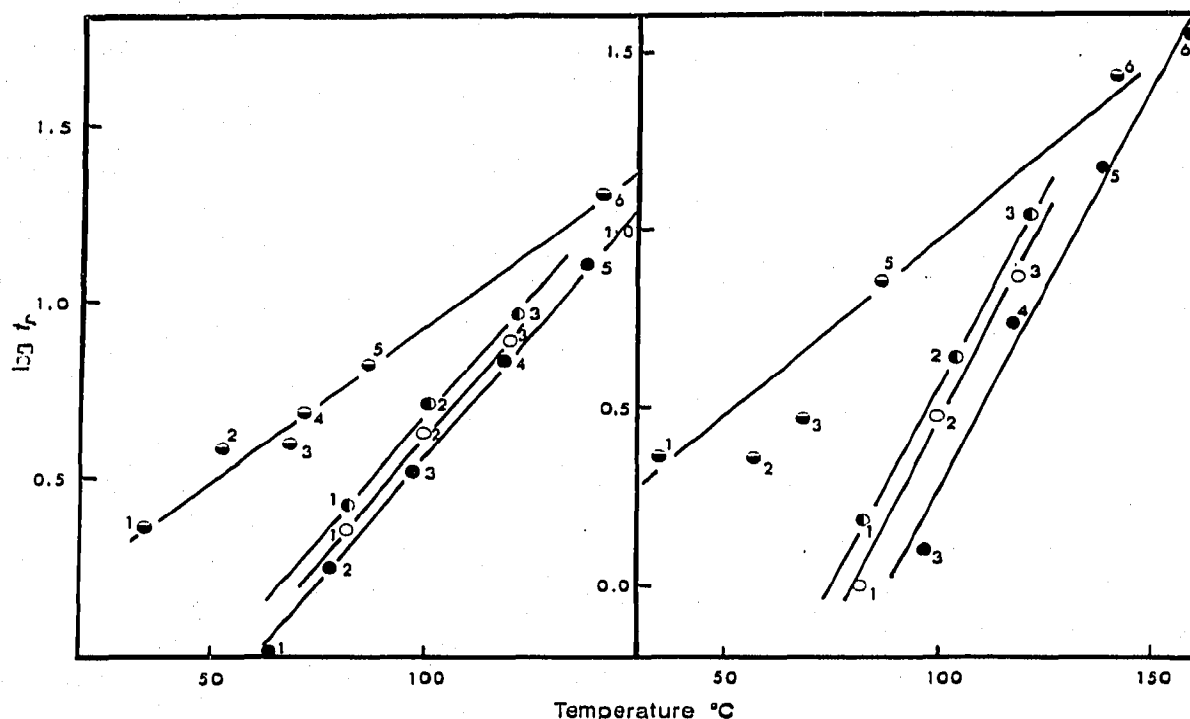


Fig. 1. Plot of  $\log t_r$ —boiling point for aliphatic alcohols and ethers. (a) PAR-1 at  $150^\circ$ . (b) Celite-Apiezon L 20% w/w at  $60^\circ$ . (●) Primary alcohols; 1 = methyl alcohol; 2 = ethyl alcohol; 3 = *n*-propyl alcohol; 4 = *n*-butyl alcohol; 5 = *n*-pentyl alcohol; 6 = *n*-hexyl alcohol. (○) secondary alcohols; 1 = isopropyl alcohol; 2 = *sec.*-butyl alcohol; 3 = 2-pentanol. (◐) Tertiary alcohols; 1 = *tert.*-butyl alcohol; 2 = *tert.*-pentyl alcohol; 3 = 2-methyl-2-pentanol. (◑) Ethers; 1 = ethyl ether; 2 = methyl *tert.*-butyl ether; 3 = isopropyl ether; 4 = methyl *n*-butyl ether; 5 = *n*-propyl ether; 6 = *n*-butyl ether.

ethers are reversed (for example, *n*-butyl alcohol and *tert.*-pentyl alcohol; isopentyl alcohol and 2-methyl-2-pentanol; and *tert.*-butyl methyl ether and isopropyl ether).

The similarity between the columns is further shown by an examination of the linear plots for  $\log t_r$  against the boiling point of the eluent<sup>4</sup> (Fig. 1, a and b). In general, the order of elution of alcohols from these columns parallels the order of their boiling points. The effect of structure on retention time is also illustrated in Fig. 1, where separate lines can be drawn for primary [ $\text{Me} \cdot (\text{CH}_2)_n \cdot \text{OH}$ ], secondary [ $\text{Me} \cdot (\text{CH}_2)_n \cdot \text{CHMe} \cdot \text{OH}$ ] and tertiary [ $\text{Me} \cdot (\text{CH}_2)_n \cdot \text{CMe}_2 \cdot \text{OH}$ ] alcohols. Furthermore, primary alcohols of varying structure [ $\text{Me} \cdot (\text{CH}_2)_n \cdot \text{OH}$  and  $\text{Me} \cdot (\text{CH}_2)_n \cdot \text{CHEt} \cdot \text{CH}_2 \cdot \text{OH}$ ] lie on individual lines (calculated from Table I). This is also seen amongst secondary alcohols [ $\text{Me} \cdot (\text{CH}_2)_n \cdot \text{CHMe} \cdot \text{OH}$  and  $\{\text{Me} \cdot (\text{CH}_2)_n\}_2 \cdot \text{CH} \cdot \text{OH}$ ]. Thus, as seen in Table I, a primary alcohol may be eluted before a tertiary alcohol although the former has a higher boiling point. This effect is even more apparent on Porapak Q where the lines are wider apart than on PAR-1 and on Celite-Apiezon L columns (calculated from Table I).

*n*-Alkyl aliphatic ethers also have a linear relationship between  $\log t_r$  and their boiling point (Fig. 1). However, the line for ethers is considerably displaced from those of the alcohols indicating that replacement of the alcoholic hydrogen by an alkyl group has a much more drastic effect than similar changes in the alkyl side-chain. The longer retention times of ethers relative to alcohols can be attributed to the difference

in solubility of each in the non-polar polymer or Apiezon L, for an ether will be more soluble in a non-polar solvent than an alcohol with a comparable boiling point.

Increasing the concentration of Apiezon L increases the retention times of the alcohols and ethers, but does not affect the isodromos point relative to the boiling point<sup>5</sup>, for normal alcohols and ethers (calculated from Table I).

*The effect of coating PAR-I with PEG 1500 (Column I and III (a) and (b)), and a comparison of PAR-I-PEG 1500 and Celite-PEG 1500 (Column VI)*

Retention times for alcohols on PAR-I are reduced on adding 5% w/w PEG 1500 and are then increased on adding a further 5% w/w of the liquid (Table I). A similar effect is noted for retention times of amines on polymers coated with Apiezon L and with Carbowax 20 M<sup>6</sup>. Such a finding has been attributed to competition between the solid and liquid for the eluent. As the solid becomes progressively more covered with liquid phase, the role played by the solid becomes less important.

Since  $\log t_r$ -boiling point plots for PAR-I-PEG 1500 columns bear a close resemblance to those obtained with PAR-I, it is clear that up to a loading of 10% w/w polyethylene glycol, separation is still due principally to the polymer, and not to the liquid phase (Figs. 1a and 2a). The PEG 1500 coating modifies PAR-I sufficiently to move the plot for ethers closer to that for normal alcohols and as a result the isodromos point, relative to the boiling point, is lowered. Modification of the polymers with a liquid phase may prove useful in the separation of alcohols having similar boiling points but with widely different structures.

The chromatographic properties of alcohols and ethers on PAR-I-PEG 1500 contrast markedly with those on Celite-PEG 1500 (Table I and Fig. 2), for the polar liquid phase on the latter ensures that the alcohols are held back with respect to the

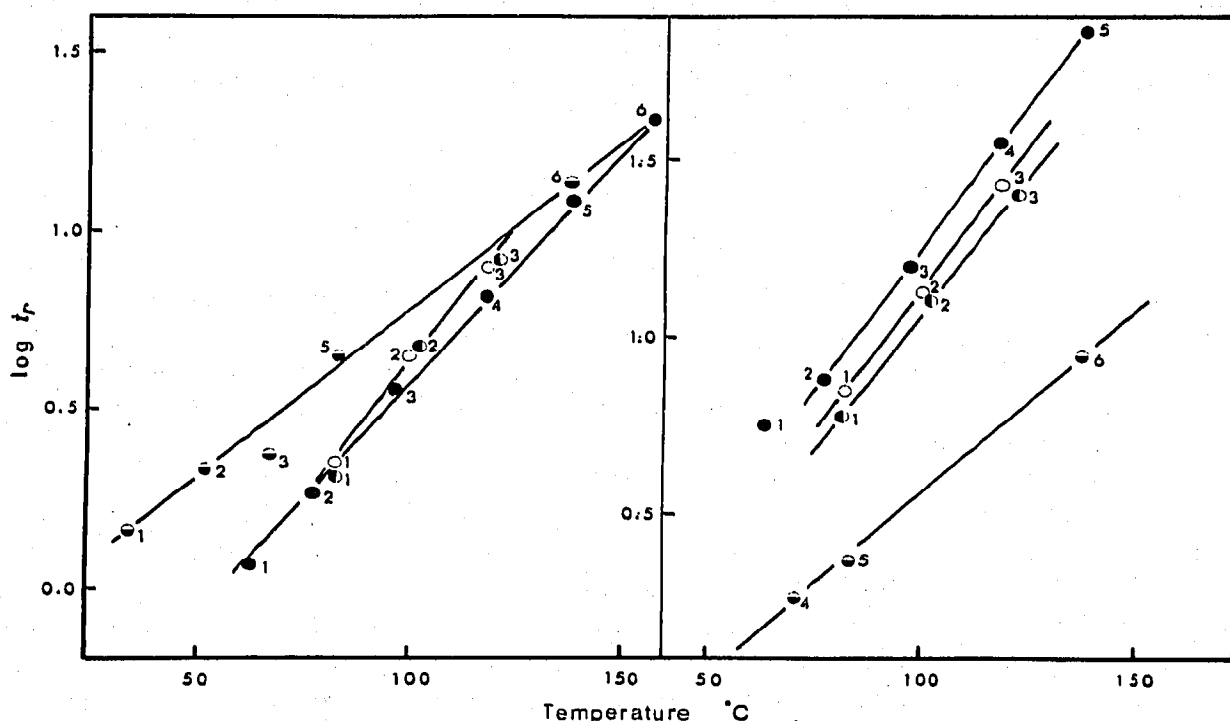


Fig. 2. Plot of  $\log t_r$ -boiling point for aliphatic alcohols and ethers. (a) PAR-I-PEG 1500 10% w/w at 150°. (b) Celite-PEG 1500 10% w/w at 60°.

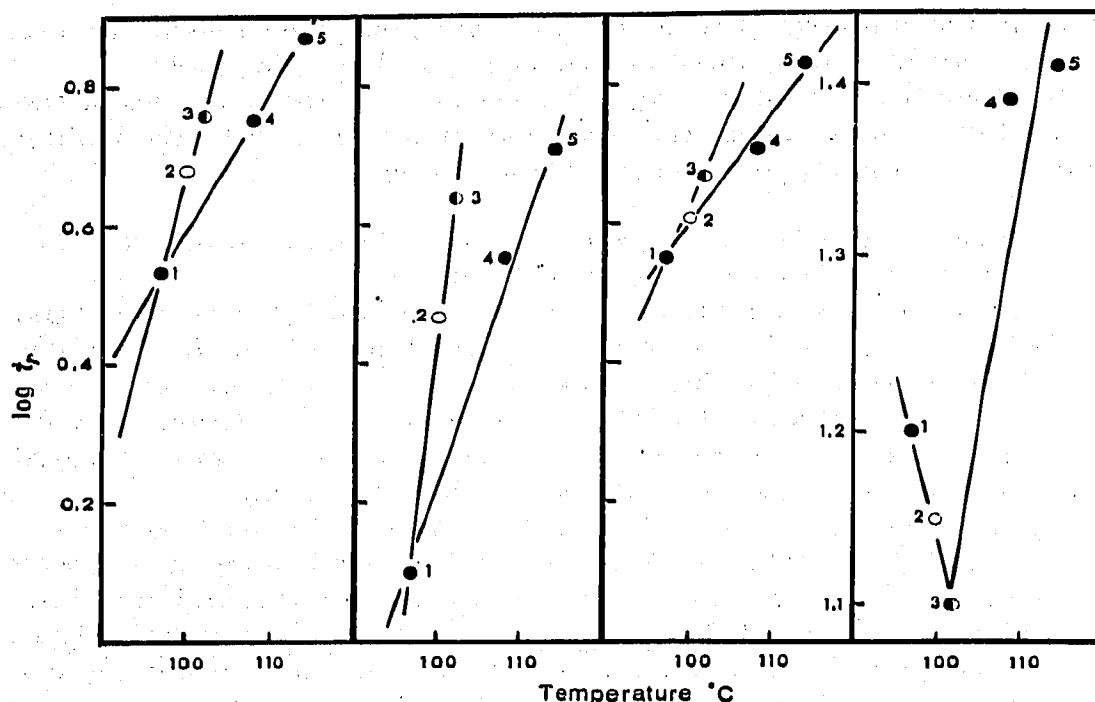


Fig. 3. Plot of  $\log t_r$ -boiling point for aliphatic alcohols. (a) PAR-1 at 150°. (b) Celite-Apiezon L 20% w/w at 60°. (c) PAR-1-PEG 1500 10% w/w at 150°. (d) Celite-PEG 1500 10% w/w at 60°. (●) Primary alcohols; (○) secondary alcohols; (◐) tertiary alcohols. 1 = *n*-Propyl alcohol; 2 = *sec.*-butyl alcohol; 3 = *tert.*-pentyl alcohol; 4 = isobutyl alcohol; 5 = 2,2-methyl-1-propanol.

ethers. Further among the alcohols the primary compounds are held back most and the tertiary least. A particularly striking difference between the Celite-PEG 1500 column on the one hand, and the coated and uncoated polymers and Celite-Apiezon columns on the other, is seen on comparing the retention times, and hence the  $\log t_r$ -boiling point plots, for the alcohols [ $\text{Me}\cdot\text{CR}_2\cdot\text{OH}$  and  $\text{CR}_2\text{H}\cdot\text{CH}_2\cdot\text{OH}$ ] (Fig. 3).

*Separation of diols on PAR-1 (Column I), Porapak Q (Column II), Celite (Alk/W)-Apiezon L 20% w/w (Column IV b), Celite (A/W)-Apiezon L 20% w/w (Column V) and Celite (A/W)-PEG 1500 10% w/w (Column VI)*

The peaks obtained for diols on the Celite columns are grossly distorted whether the liquid phase is polar or non-polar or the support is acid- or alkali-washed. In extreme instances, glycols give double peaks. That this peak asymmetry arises in part from decomposition of the diol was confirmed by mass spectrometric analysis (for example 1,4-butanediol decomposes to tetrahydrofuran). Retention times for the diols were irreproducible on the Celite columns.

Previous investigations into the gas chromatographic separation of diols has concentrated on eliminating this peak tailing by reducing the interaction between the diols and the solid support. This has been attained in two ways, either by using a highly polar liquid phase such as tetrahydroxyethylethylenediamine<sup>7-9</sup>, water<sup>10</sup> or a combination of both<sup>7,10</sup>, or by deactivating the support by silanisation<sup>10</sup>.

In contrast to our results with conventional gas-liquid columns, there appears to be little or no decomposition of diols on Porapak Q, although there is still some tailing. Similar results were obtained for ethylene glycol and 2-methylpentane-2,4-

TABLE II

ADJUSTED RETENTION TIMES (min) FOR ALIPHATIC DIOLS ON PAR-1 AND ON PORAPAK Q AT DIFFERENT TEMPERATURES

	PAR-1			Porapak Q
	150°	180°	200°	185°
Ethylene glycol	8.1	4.7	2.9	6.0
Propane-1,2-diol	...	5.2	3.2	9.0
Butane-2,3-diol	11.6	6.1	3.7	14.0
Propane-1,3-diol	18.6	8.9	5.6	14.3
Butane-1,3-diol	21.0	9.9	6.2	22.0
Butane-1,4-diol	36.8	15.4	9.8	32.5

diol on Porapak S<sup>11</sup>. We found that the most satisfactory separation came from PAR-1, the peaks being symmetrical and there being no evidence of decomposition. Moreover, butane-2,3-diol is separated more satisfactorily from propane-1,3-diol.

Retention times of a series of diols on PAR-1 and on Porapak Q are given in Table II. Linear plots for  $\log t_r$ -boiling point are obtained for diols containing two primary alcohol groups, and for diols with one primary and one secondary group. The separation between these lines is wider than found for aliphatic alcohols, showing that changes of structure in the alkyl side chain have a greater effect than for alcohols. Thus ethylene glycol is eluted before 1,2-propanediol and 1,3-propanediol before 1,3-butanediol, although the boiling points of these pairs of diols are reversed. Similarly, the presence of two secondary groups, as in 2,3-butanediol, causes an even greater *apparent* disparity between boiling point and retention time.

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