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EVALUATION OF THE PROPERTIES OF POLYETHYLENE GLYCOLS AS STATIONARY PHASES IN GAS-LIQUID CHROMATOGRAPHY

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SUMMARY

This paper reports an evaluation of the retention characteristics of polyethylene glycols used as liquid phases in gas chromatography.

Eight different grades of polyethylene glycol were tested (Carbowax 300, 400, 600, 1000, 1540, 4000, 6000 and 20M) and their retention volumes for various homologous series were measured (*n*-alkanes, 1-alcohols, methyl alkyl ketones and linear chloro-, bromo- and iodoalkanes).

Effects of the molecular weight, of temperature, and of the position of the hydroxyl group were examined, and the activity coefficients calculated.

INTRODUCTION

Polyethylene glycols (PEGs) are widely used as liquid phases in gas chromatography. Their ability to separate "polar" compounds has made their use very frequent. A survey of liquid phases in use¹ showed that, until 1970, about 300 articles have been published containing retention data measured on polyethylene glycol 20M, and that this material has been the third most frequently used phase. Other PEGs of lower molecular weight have been also widely used.

A series of PEGs having different intervals of molecular weight is known under the trade name of Carbowax (Union Carbide, New York, N.Y., U.S.A.). In Table I are reported the properties of the different grades of Carbowax, and the highest temperatures for their use as stationary phases.

Other information on the chemistry of PEGs used in gas chromatography have been reported recently², and the infrequent use of the lower-molecular-weight products emphasized, owing to their larger content of volatile materials.

The highest grade of polyethylene glycol (Carbowax 20M) has been suggested as a "preferred" liquid phase³ that can be substituted for 19 phases currently in use, as tabulated by McReynolds⁴, who also reported the results of the analysis of many substances on various grades of Carbowax⁵.

In spite of this large amount of data, no systematic evaluation and discussion of the separating characteristics of the PEGs has been made with respect to their molecular weight, to the temperature of analysis and to various homologous series of analyzed compounds.

This paper reports an evaluation of the retention characteristics of eight

TABLE I

PROPERTIES OF CARBOWAXES AND RECOMMENDED MAXIMUM TEMPERATURES FOR USE AS STATIONARY PHASES

<i>Carbowax grade</i>	<i>Molecular weight*</i>	<i>Melting range (°C)</i>	<i>Vapour pressure at 100 °C (torr)*</i>	<i>Max. temp. (°C)**</i>
200	190- 210	< -65	-	80
300	285- 315	-15- -8	2.9×10^{-3}	100
400	380- 420	4- 8	9.0×10^{-5}	125
600	570- 630	20-25	5.2×10^{-6}	125
1000	950- 1050	37-40	3.3×10^{-9}	175
1540	1300- 1600	43-46	2.0×10^{-12}	200
4000	3000- 3700	53-56	$< 2.0 \times 10^{-12}$	200
6000	6000- 7500	60-63	$< 2.0 \times 10^{-12}$	200
20M	15000- 20000	50-55	$< 2.0 \times 10^{-12}$	250

* From Union Carbide.

** From Varian Aerograph.

different grades of Carbowax for various homologous series (*n*-alkanes, 1-alcohols, methyl alkyl ketones and linear chloro-, bromo- and iodoalkanes) and a comparison with the non-polar phase Apiezon L, the behaviour of which has been evaluated previously⁶.

EXPERIMENTAL

The types of Carbowax, weight percentages and temperatures of analysis are reported in Table II, together with the homologous series tested on each column.

TABLE II

HOMOLOGOUS SERIES ANALYZED AND ANALYSIS CONDITIONS

<i>Liquid phase</i>	<i>Liquid phase weight %</i>	<i>Column temperatures (°C)</i>	<i>Reference</i>	<i>Homologous series</i>
Carbowax 300, 400, 600, 1000, 1540	20	100, 120	this work, 5	alkanes, alcohols
Carbowax 4000	23	120, 140	5	alkanes, alcohols
Carbowax 6000	22	120, 140	5	alkanes, alcohols
Carbowax 20M	22	120, 160	5	alkanes, alcohols, ketones
Carbowax 20M	20	100, 120, 140, 160	this work	alkanes, alcohols, chloro-, bromo- and iodoalkanes
Carbowax 20M	15	75, 100, 125	6	alkanes, chloro-, bromo- and iodoalkanes
Apiezon L	20	100, 120	5	alkanes, alcohols, ketones
Apiezon L	20	100, 125, 150	this work	alkanes, alcohols
Apiezon L	15	100, 120, 125	6	alkanes, chloro-, bromo- and iodoalkanes

The analyses were carried out on stainless-steel columns, 3 m \times 1/8 in., filled with 20% w/w of various Carbowaxes on dimethyldichlorosilane-treated Chromosorb W, 60–80 mesh. A Varian Aerograph 1720 gas chromatograph was used; the temperature was controlled by an isothermal proportional temperature control and monitored with precision thermometers.

The retention data on Carbowax 4000 and 6000 have been taken from McReynolds' tables⁵ as the values for other grades correspond satisfactorily (within about 1–3 index units). The data for Apiezon L are reported from a previous paper⁶.

RESULTS AND DISCUSSION

The plots of the logarithm of the specific retention volume, $\log V_g$ (ref. 6), as a function of the number of carbon atoms (n) in the chain for 1-alcohols (from methanol to octanol), appeared to be almost linear, following the well known logarithmic behaviour⁷ represented by the equation

$$\log V_g = d_0 + d_1 n \quad (1)$$

The calculation of the constants in the above equation for different Carbowaxes at various temperatures was performed by using the least-squares method and gave the results reported in Table III. These values of d_0 and d_1 allowed a satisfactory pre-calculation of V_g to be made for terms in the homologous series from propanol to octanol, but gave erratic values when an attempt was made to calculate the intersection points of the various lines.

TABLE III

PARAMETERS OF THE EQUATION $\log V_g = d_0 + d_1 n$ FOR 1-ALCOHOLS ON VARIOUS CARBOWAXES AT FOUR TEMPERATURES

Carbowax grade	d_0				d_1			
	100°	120°	140°	160°	100°	120°	140°	160°
300	1.1661	0.9503			0.2513	0.2306		
400	1.1569	0.9267			0.2537	0.2345		
600	1.1010	0.8645			0.2580	0.2411		
1000	1.0339	0.8184			0.2638	0.2427		
1540	1.0179	0.7958			0.2627	0.2438		
4000	1.0052	0.7760	0.5601		0.2660	0.2475	0.2293	
6000	—	0.7683	0.5582		—	0.2487	0.2297	
20M	0.9750	0.7399	0.5360	0.3749	0.2690	0.2499	0.2320	0.2155

A thorough examination of the experimental data showed that the plots of $\log V_g$ versus n are not exactly linear, and therefore do not strictly follow eqn. 1. A similar behaviour was observed for Apiezon greases and n -alkanes for a wide range of values of n (ref. 6), but it was not clear if the observed deviation was true or due to experimental error. In this case, the accuracy of the data obtained and the very similar behaviour of the values tabulated by McReynolds⁵ confirm the non-linearity of the plots of $\log V_g$ versus n .

TABLE IV
VALUES OF $(\log V_\theta (\text{exp.}) - \log V_\theta (\text{calc.}))$ FOR VARIOUS CARBOWAXES AT 120°

<i>1-Alcohol</i>	<i>Carbowax grade</i>							
	300	400	600	1000	1540	4000	6000	20M
Methanol	0.1475	0.1420	0.1349	0.1376	0.1394	0.1468	0.1503	0.1625
Ethanol	-0.0050	-0.0083	-0.0132	-0.0093	-0.0092	-0.0133	-0.0153	-0.0118
Propanol	-0.0076	-0.0080	-0.0035	-0.0062	-0.0061	-0.0053	-0.0052	0.0018
Butanol	0.0052	0.0069	0.0118	0.0074	0.0086	0.0085	0.0063	0.0087
Pentanol	0.0106	0.0114	0.0164	0.0134	0.0146	0.0118	0.0094	0.0106
Hexanol	0.0065	0.0087	0.0070	0.0087	0.0086	0.0085	0.0090	0.0087
Heptanol	-0.0046	-0.0024	-0.0069	-0.0041	-0.0027	0.0034	0.0013	-0.0063
Octanol	-0.0048	-0.0082	-0.0123	-0.0095	-0.0090	-0.0133	-0.0152	-0.0113

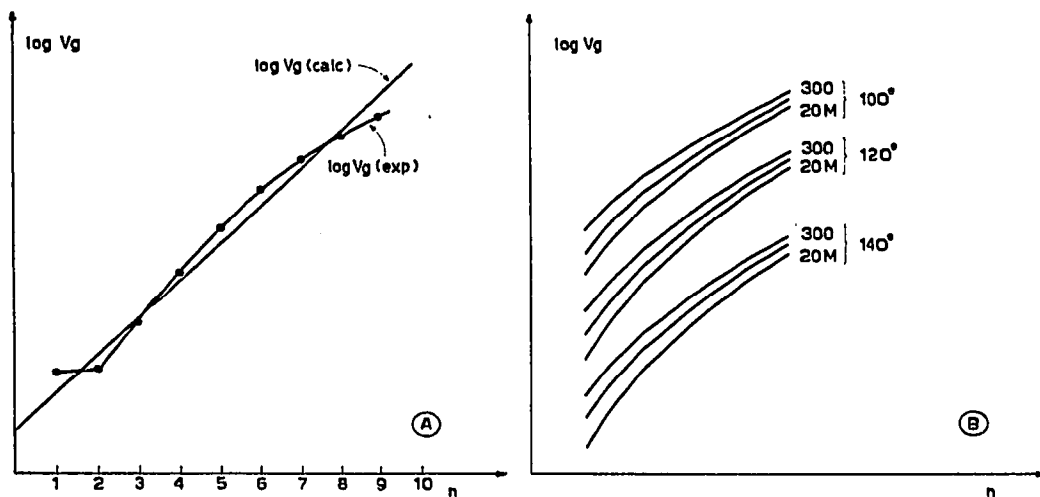


Fig. 1. Behaviour of $\log V_\theta$ of 1-alcohols: A, as function of the number of carbon atoms (n); B, as function of temperature and grade of Carbowax.

After the first terms, whose deviation from linearity has recently been discussed by Takács⁸, the differences between the experimental $\log V_\theta$ values and the $\log V_\theta$ values calculated by means of eqn. 1 and Table III, show a negative-positive-negative behaviour, as shown in Table IV and Fig. 1A. The vertical scale in this figure is expanded in order to emphasize the behaviour.

Fig. 1B shows, again with arbitrary units on the vertical axis, the general behaviour of $\log V_\theta$ as a function of n for different temperatures and various grades of Carbowax. The curvature of these plots, which is sufficiently great to lead to significant errors in the theoretical calculation of V_θ over a large range of values of n , has no practical effect when the nearest neighbours are considered, where the "classical" logarithmic dependence of V_θ on n can still be used.

Effect of the molecular weight of Carbowax

The dependence of the V_{θ} values of 1-alcohols on the molecular weight of the liquid phase (MW) is shown in Fig. 2. Taking into account the above approximation of eqn. 1, a linear relationship is also found between the parameters d_0 and d_1 and the reciprocal of MW (see Figs. 3 and 4).

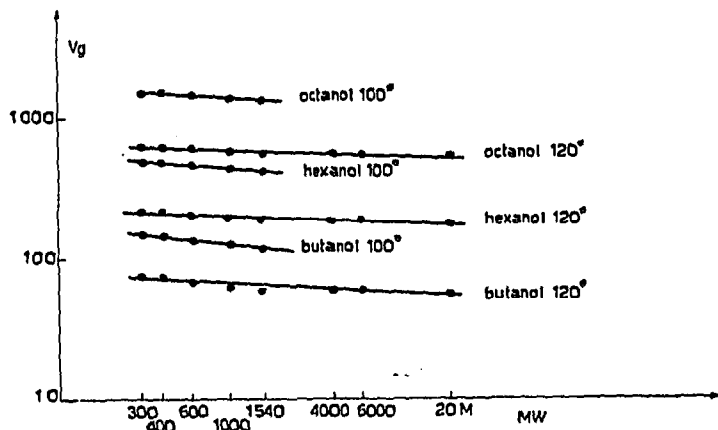


Fig. 2. Dependence of V_{θ} of 1-alcohols on molecular weight of Carbowax and on temperature (logarithmic scale).

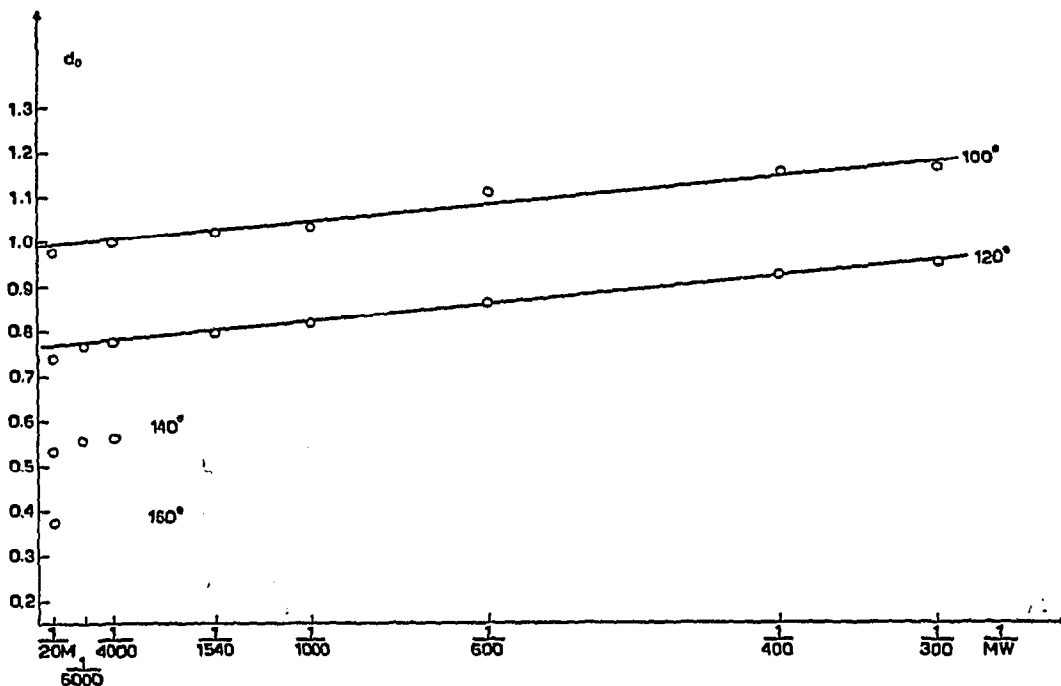


Fig. 3. Linear dependence of the intercept d_0 of eqn. 1 on the reciprocal of the molecular weight of the Carbowax.

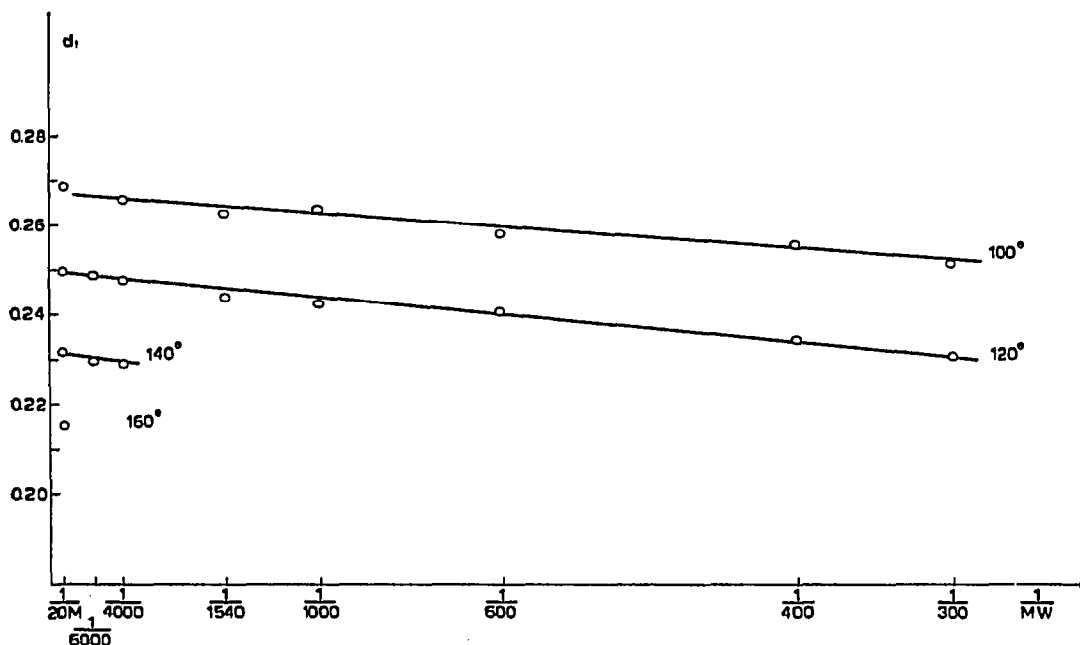


Fig. 4. Linear dependence of the slope d_1 of eqn. 1 on the reciprocal of the molecular weight of the Carbowax.

The following equations can therefore be written:

$$d_0 = f_0 + f_1 \cdot \frac{1}{MW}; \quad d_1 = e_0 + e_1 \cdot \frac{1}{MW} \quad (2)$$

d_0 depends on $1/MW$ about 10 times more than d_1 , as is also emphasized by the different scales of the vertical axes in Figs. 3 and 4.

The plots for lower grades of Carbowax cannot be extrapolated to higher temperature owing to the high vapour pressures of these liquid phases.

Effect of temperature

The dependence of d_0 and d_1 on the reciprocal of the absolute temperature of analysis is linear in the interval studied, as can be seen from Fig. 5. The lines for different grades of Carbowax are parallel and a factor of about 10 is again found between the slope of d_0 and that of d_1 .

Owing to the observed parallel behaviour, the slopes of the equations

$$d_0 = b_0 + b_1 \cdot \frac{1}{T}; \quad d_1 = c_0 + c_1 \cdot \frac{1}{T} \quad (3)$$

are fairly constant for every grade of Carbowax, and have the values $b_1 = 1.68$ and $c_1 = 0.15$.

The intercepts b_0 and c_0 , however, depend on MW (b_0 increases and c_0 decreases) with a complex dependence that cannot be calculated, owing to the

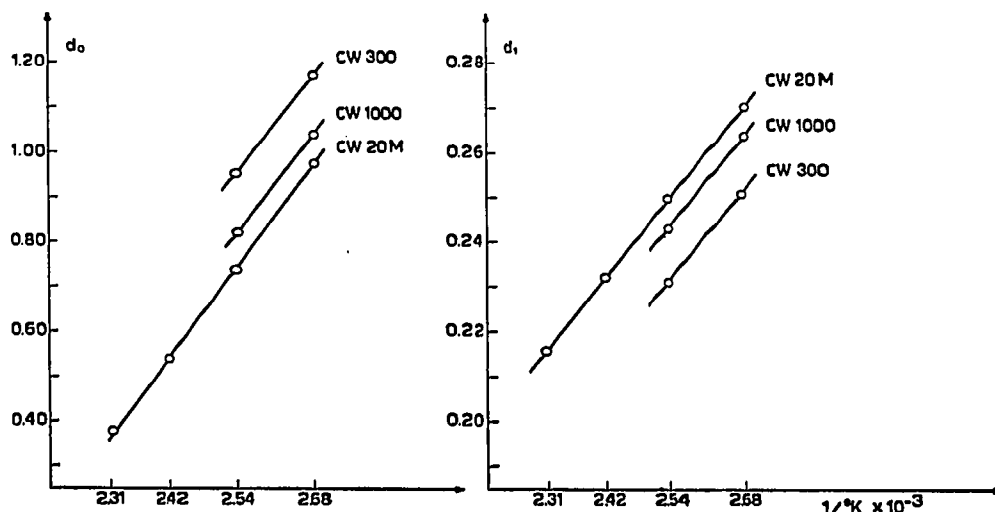


Fig. 5. Linear dependence of d_0 and d_1 on the reciprocal of the absolute temperature of analysis.

lack of experimental data for low-molecular-weight Carbowaxes. An attempt was made to solve the system of eqns. 1, 2 and 3, in order to calculate directly the dependence of V_θ on MW, T and n , but no simple, satisfactory result was obtained. Only the values of e_0 , e_1 , f_0 , f_1 were calculated, and these are reported in Table V as a function of the analysis temperature.

TABLE V

PARAMETERS OF THE EQUATIONS $d_0 = f_0 + f_1 \cdot 1/\text{MW}$ AND $d_1 = e_0 + e_1 \cdot 1/\text{MW}$ AT THREE TEMPERATURES

Column temperature ($^{\circ}\text{C}$)	f_0	f_1	e_0	e_1
100	0.99	56.8	0.268	-3.2
120	0.77	56.8	0.250	-5.7
140	0.55	56.7	0.232	-4.8*

* Slope calculated between 4000 and 20M.

Effect of the position of the hydroxyl group

The retention volumes of secondary aliphatic alcohols are lower than those of the 1-alcohols. Fig. 6 shows a schematic representation of the variations of V_θ as a function of n , of the position of the hydroxyl group, and of the type of Carbowax.

Calculation of the activity coefficient, γ

In a previous paper⁶, the equation, suggested by Ambrose *et al.*⁹ and Purnell¹⁰:

$$\log V_\theta = \log \frac{1.7 \cdot 10^7}{M_l} - \log p_0 - \log \gamma \quad (4)$$

TABLE VI
VALUES OF γ CALCULATED FROM EQN. 4

Alcohol	Carbowax grade															
	300		400		600		1000		1540		4000		6000		20M	
	100°	120°	100°	120°	100°	120°	100°	120°	100°	120°	100°	120°	100°	120°	140°	160°
1-Methanol	5.03	5.05	5.30	5.35	6.04	6.18	6.73	6.81	7.11	7.13	7.27	7.70	7.32	7.60	7.58	7.31
1-Ethanol	4.66	4.36	4.86	4.56	5.42	5.15	6.08	5.65	6.47	5.92	6.15	6.37	6.24	6.30	6.58	6.21
1-Propanol	4.26	3.78	4.37	3.89	4.67	4.25	5.37	4.70	5.60	4.91	5.00	5.06	5.05	5.09	5.26	5.09
1-Butanol	3.96	3.60	3.99	3.65	4.29	3.92	4.77	4.34	5.01	4.51	4.56	4.82	4.62	4.86	4.85	4.58
1-Pentanol	3.81	3.68	3.82	3.70	4.07	3.92	4.49	4.31	4.65	4.47	4.51	4.42	4.55	4.46	4.78	4.17
1-Hexanol	3.90	3.72	3.87	3.71	4.07	3.92	4.46	4.27	4.61	4.41	4.38	4.29	4.38	4.29	4.67	4.14
1-Heptanol	4.21	3.92	4.14	3.87	4.40	4.06	4.72	4.37	4.85	4.50	4.38	4.22	4.39	4.15	4.68	4.13
1-Octanol	4.58	4.14	4.50	4.10	4.75	2.23	5.04	4.53	5.19	4.67	4.62	4.23	4.62	4.25	4.78	4.27
2-Propanol	4.49	3.98	4.69	4.14	5.18	4.61	5.86	5.08	6.14	5.25	5.56	4.09	5.62	4.04	5.90	7.09
2-Butanol	4.06	3.55	4.11	3.63	4.42	3.93	4.97	4.33	5.12	4.49	4.59	4.31	4.61	4.33	4.83	4.00
2-Pentanol	4.18	4.03	4.22	4.04	4.55	4.34	4.99	4.74	5.20	4.89	4.93	4.98	5.22	—	5.22	—
2-Hexanol	4.31	4.13	4.29	4.13	4.56	4.38	4.94	4.72	5.13	4.89	4.89	4.81	4.94	4.87	5.20	—
3-Hexanol	4.17	3.99	4.13	3.96	4.34	4.20	4.68	4.48	4.83	4.59	4.61	—	4.64	—	—	—

TABLE VII

VALUES OF γ CALCULATED FROM EQN. 4 FOR VARIOUS HOMOLOGOUS SERIES ON APIEZON L AND CARBOWAX 20M COLUMNS AT 120°

n	n-Alkanes		1-Chloroalkanes		1-Bromoalkanes		1-Iodoalkanes		1-Alcohols		2-Alcohols		Aldehydes		Ketones		
	APL	CW20	APL	CW20	APL	CW20	APL	CW20	APL	CW20	APL	CW20	APL	CW20	APL	CW20	
1																	
2									53.81	7.58							
3									31.79	6.58				16.10	6.19		
4	5.23	17.80							20.92	5.26	19.27	5.90	12.99	6.30	12.99	5.79	
5									16.06	4.85	12.13	4.83	7.88	5.30			
6	4.32	19.84	2.57	7.21	1.86	4.61	1.67	3.47	13.39	4.78	10.91	5.22			8.11	5.84	
7			2.46	7.58	1.59	4.26	1.48	3.59	10.80	4.61	9.45	5.20			6.85	5.78	
8	3.84	22.57	2.22	7.83	1.57	4.89	1.41	3.99	10.03	4.68					5.78	6.31	
9									9.22	4.78					5.08	5.57	
10	3.34	24.47													4.64	6.13	

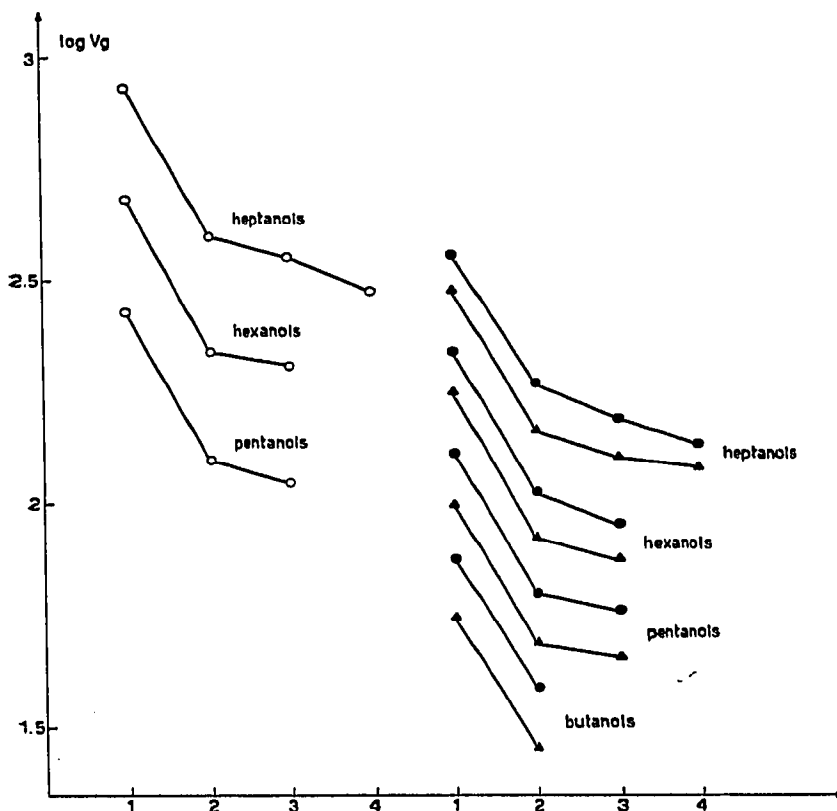


Fig. 6. Effect of the position of the hydroxyl group on the retention volume of alcohols. \circ , Carbowax 300 at 100°; \bullet , Carbowax 300 at 120°; \blacktriangle , Carbowax 20M at 120°.

where M_1 is the molecular weight of the solute, p_0 is the saturation vapour pressure of the solute at the analysis temperature and γ is the activity coefficient, has been discussed for the separation of n -alkanes on Apiezon greases. Notwithstanding the almost ideal solute-solvent pair, values of $\log \gamma$ different from unity have been found.

The values of $\log \gamma$ for different compounds can be taken as a measure of the solute-solvent interaction, as the other terms in eqn. 4 depend only on the solute^{11,12}.

In Table VI, values of γ are reported for many alcohols, analyzed on various grades of Carbowax, from 300 to 20M.

Table VII reports the values of γ for some homologous series on Apiezon L (APL) and Carbowax 20M (CW20) columns at 120°. Many values are lacking, owing to the difficulty of finding reliable values of p_0 in the literature, but the available data (taken from refs. 13 and 14) enable the following general conclusions to be drawn:

- (a) On Apiezon L (non-polar phase), with increasing n the values of γ decrease for every homologous series.

- (b) On Carbowax 20M (polar phase), with increasing n the values of γ increase for n -alkanes, are about constant for aldehydes and ketones, and decrease for alcohols.
- (c) Except for haloalkanes, which have low values of γ on both phases, other homologous series have values of γ that increase on Apiezon L and decrease on Carbowax 20M in accordance with their "polarity", as tabulated by Rohrschneider¹⁵.

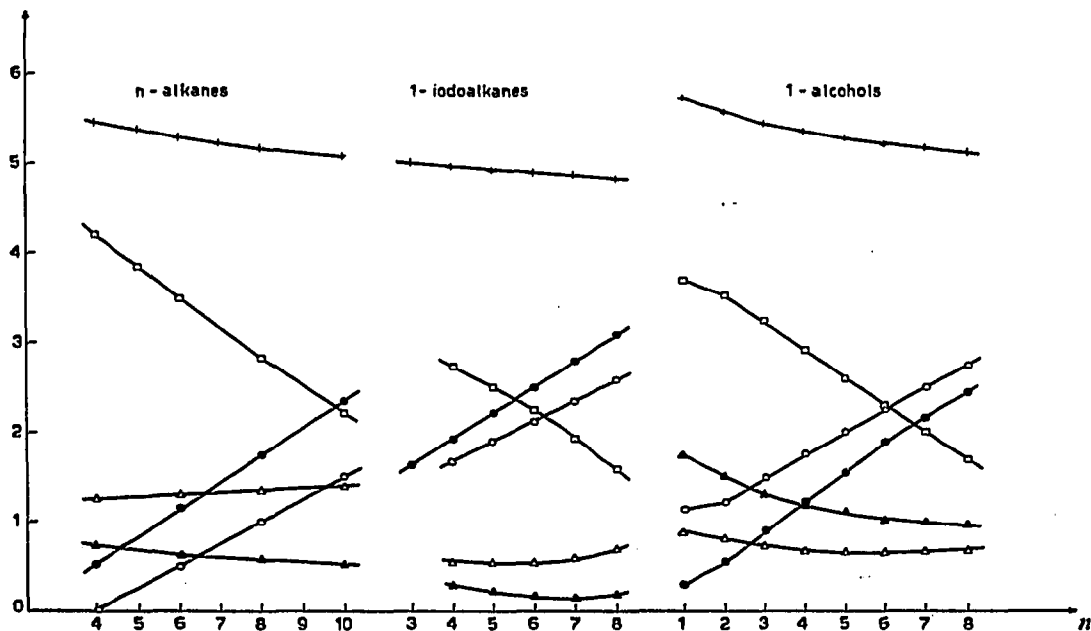


Fig. 7. Contribution of various terms in eqn. 4 to the V_0 values of different homologous series. +, $\log 1.702 \cdot 10^7 / M_i$; □, $\log p_0$; ○, $\log V_0$ (Carbowax 20M); ●, $\log V_0$ (Apiezon L); △, $\log \gamma$ (Carbowax 20M); ▲, $\log \gamma$ (Apiezon L); all plotted against n .

Fig. 7 shows how the terms in eqn. 4 give a different contribution (positive or negative) to the values of $\log V_0$ as a function of n for various homologous series on Apiezon L and Carbowax 20M.

The plots are self-explanatory, but it must be emphasized that the different values of $\log V_0$ for the two phases are due to the different values of $\log \gamma$, and that the slope of $\log V_0$ values is greater on Apiezon L, independent on the absolute value of the retention volumes.

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