CHROM. 9556

THE CORRELATION BETWEEN THE PHYSICAL PROPERTIES AND STRUCTURE OF ALCOHOLS AND THEIR GAS CHROMATOGRAPHIC BEHAVIOUR ON POLAR AND NON-POLAR STATIONARY PHASES

I. C₁–C₈ STRAIGHT-CHAIN ALCOHOLS

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(Received June 28th, 1976)

SUMMARY

Primary and secondary straight-chain alcohols with one to eight carbon atoms have been analysed by gas chromatography at 100° on 3-m columns packed with 20 % of squalane and Carbowax 400, 1000 and 20M, on chlorodimethylsilane-treated Chromosorb W (60–80 mesh), using thermal-conductivity and flame-ionization detectors. The specific retention volumes, V_g, and the retention indices relative to normal alcohols, have been determined for all of the compounds, and the effects of the positions of the hydroxyl groups have been investigated. Boiling points, vapour pressures and molecular volumes have been correlated with the measured retention values. The activity coefficients at infinite dilution and the normalized activity coefficients have been calculated, and their influence on the separation is discussed.

INTRODUCTION

The dependence of the retention values of linear and branched-chain halogenoalkanes on their physical properties was examined in previous papers[1,2]. The influence of the position of methyl groups and of halogen atoms in these compounds on the gas chromatographic (GC) separation has been studied.

In this work the effect of the position of the hydroxyl group in primary and secondary straight-chain alcohols has been investigated. Boiling point, vapour pressure, molecular volume and structure have been correlated with the retention volume measured on columns filled with squalane and with different grades of Carbowax.

MATERIALS AND METHODS

Samples and instruments

The alcohols analysed are listed in Table I, together with their main physical constants. Linear alkanes were also analysed for comparison purposes. The analyses were carried out at 100° by use of a Varian Aerograph Model 1520 gas chromatograph

TABLE I

PHYSICAL CONSTANTS OF THE ALCOHOLS ANALYSED

Values of the T_b and density were obtained from ref. 12.

Alcohol	Molecular weight, M_l	T_b (°C) at 760 Torr	Density at 20° (g/cm³)	Molecular volume (cm³)
Methanol	32.04	65	0.7914	40.49
Ethanol	46.07	78.5	0.7893	58.37
1-Propanol	60.11	97.4	0.8035	74.81
1-Butanol	74.12	117.71	0.8098	91.53
1-Pentanol	88.15	138	0.8144	108.24
1-Hexanol	102.18	157.2	0.8136	125.59
1-Heptanol	116.21	176	0.8219	141.39
1-Octanol	130.23	195	0.8270	157.47
1-Nonanol	144.25	213.5	0.8273	174.36
2-Propanol	60.11	82.4	0.7855	76.52
2-Butanol	74.12	100	0.8080	91.73
2-Pentanol	88.15	119.28	0.8103	108.79
2-Hexanol	102.18	140	0.8104	126.09
2-Heptanol	116.21	160.4	0.8190	141.89
2-Octanol	130.23	178.5	0.8216	158.51
3-Pentanol	88.15	115.6	0.8212	107.34
3-Hexanol	102.18	135	0.8213	124.41
3-Heptanol	116.21	157	0.8227	141.25
3-Octanol	130.23	173	0.8258	157.70
4-Heptanol	116.21	155.4	0.8183	142.01

equipped with proportional temperature control. The temperature was measured by means of precision thermometers installed in different positions in the column oven. Both thermal-conductivity (TCD) and flame-ionization (FID) detectors were used. Pure helium was used as the carrier gas; the inlet pressure was monitored directly at the injector septum by using a mercury manometer connected by means of a hypo- dermic needle. In order to take into account the detector backpressure, the outlet pressure was measured with the same manometer connected to a T-piece installed between the end of the column and the detector inlet. The T-connector was removed during the analyses to avoid a dead volume between the column and detector. The flow of carrier gas was measured at the detector outlet by use of a bubble flow-meter, and was corrected to standard pressure and temperature. Stainless-steel columns (3 m × 1/8 in.), filled with 20% w/w of the liquid phase on chlorodimethylsilane (CDMS)- treated Chromosorb W (60–80 mesh), were used. The stationary phase was screened before and after impregnation in order to ensure a constant mesh size. In order to ascertain whether tailing effects were due to the stainless steel, and if the column ma- terial influenced the retention, some analyses were also accomplished by using glass columns of the same dimensions. No appreciable difference was found between the retention volumes obtained on stainless-steel or glass columns.

Decreasing amounts of the alcohols were injected into the columns, by means of Hamilton microsyringes, in order to determine, by extrapolation, the retention time at zero concentration. For the calculation of γ_l^{max} (see below), another series of anal- yses was made by injecting different volumes of each alcohol, depending on the den-

sity, in order to have a constant factor of 10^{-3} between the weight of injected compound and the weight of liquid phase in the column. The specific retention volumes were calculated by the method of Littlewood *et al.*[3,6].

Liquid phases

Squalane (Varian Aerograph, Walnut Creek, Calif., U.S.A.) and Carbowax (CW) 400, 1000 and 20M (Union Carbide, New York, N.Y., U.S.A.) were used as liquid phases. Squalane is generally considered to be the standard non-polar liquid phase[4,5]. Due to its low-temperature limit (100°), the use of this phase is now decreasing in practical GC, being replaced by silicon-based polymers. Its use in the present work is mainly due to its well defined chemical nature (2,6,10,15,19,23-hexamethyltetracosane) which permits the molecular weight of the liquid phase, M_L, to be exactly known[7,21-23] for the calculation of the activity coefficient at infinite dilution, γ^∞. Unfortunately, the molecular weights of the polyethylene glycols (PEGs) are neither constant nor exactly known for the different grades. Ranges of effective molecular weights up to $\pm 30\%$ of the nominal value are reported by the manufacturers. This results in a large uncertainty in the calculation of the activity coefficient and therefore we have attempted to establish as exactly as possible the M_L value of the used Carbowax. In Table II are given the ranges of molecular weights supplied by the manufacturers and the values determined experimentally by various workers. Values for Carbowax 4000 and 6000 are also reported.

In our measurements we used Carbowax 1000, whose properties seem to be fairly constant, Carbowax 20M, in order to determine the behaviour of a high-molecular-weight PEG, and Carbowax 400, which has an M_L value similar to that of squalane. The molecular weight of CW 400 was measured by vapour-pressure osmometry, by use of a Mechrolab Model 302 instrument, at 65°, with toluene as solvent. An M_L value of 425 $\pm$ 3 % was obtained, corresponding to the mean of nine monomeric units in the polymer chain. While CW 400 and 1000 had a narrow molecular-weight distribution, as shown by gel-permeation chromatography on a 16-ft. Styragel column with tetrahydrofuran as solvent and a pressure of 120 p.s.i. (Waters Assoc., Milford, Mass., U.S.A.), CW 20M clearly showed a bimodal distribution, more or less enhanced, depending on the commercial source of the polymer. The results reported below were obtained by use of CW 20M having an $\bar{M}_v$ (viscosimetric) value of *ca.* 19500 and the narrowest available dispersion.

Calculation of vapour pressure

Several methods were tested in order to calculate the saturation vapour pressure, p_i^0, of the analysed compounds (solutes) at the analysis temperature. The best results, as demonstrated by the correspondence with some values found in the literature, were obtained by using the method reported by Hass and Newton[12] for alcohols and an Antoine-type equation with constants taken from API tables[13] for linear alkanes.

RESULTS AND DISCUSSION

The specific retention volumes, V_g, at 100°, and the retention indices relative to linear 1-alcohols (I_{OH}), are reported in Table III for squalane and CW 400, 1000

TABLE II

MOLECULAR WEIGHTS OF SOME POLYETHYLENE GLYCOLS, AS SUPPLIED BY THE MANUFACTURER AND AS MEASURED BY VARIOUS WORKERS

$\bar{M}_v$ = Viscosimetric, $\bar{M}_w$ = weight average and $\bar{M}_n$ = number-average molecular weights.

Nominal M_L	Given interval (Union Carbide)	$\bar{M}_v$ (ref. 8)	$\bar{M}_w$				$\bar{M}_n$			
			ref. 8	ref. 9	ref. 10	ref. 11	ref. 8	ref. 9	ref. 10	ref. 11
400	380–420	—	—	407–422	—	—	—	400–422	—	—
1000	950–1050	1250	1000	1020	—	—	1030	—	1030	—
4000	3000–3700	2650	2870	4200–4350	2940	—	—	3200	—	—
6000	6000–7500	7410	7110	6700–7700	—	5750	—	6500–6800	—	5350
20 000	15 000–20 000	17 500	—	—	—	21 500	17 500	—	—	17 000

TABLE III

SPECIFIC RETENTION VOLUMES, V_g, AND RETENTION INDICES RELATIVE TO LINEAR 1-ALCOHOLS, I_{OH}, AT 100°

Alcohol	Squalane		CW 400		CW 1000		CW 20M	
	V_g	I_{OH}	V_g	I_{OH}	V_g	I_{OH}	V_g	I_{OH}
Methanol	2.77	100	36.1	100	28.7	100	22.8	100
Ethanol	5.80	200	44.6	200	35.6	200	27.9	200
1-Propanol	14.86	300	79.9	300	64.7	300	53.3	300
1-Butanol	36.38	400	147.1	400	123.7	400	100.2	400
1-Pentanol	85.4	500	269.2	500	231.8	500	186	500
1-Hexanol	190.7	600	485.7	600	427	600	341	600
1-Heptanol	402	700	862.6	700	765	700	621.7	700
1-Octanol	804.2	800	1514	800	1360	800	1123	800
1-Nonanol	1550	900	2630	900	2336	900	2012	900
2-Propanol	9.62	254	40.9	187	32.7	186	26.1	190
2-Butanol	23.13	349	72	282	59	285	48.4	285
2-Pentanol	54.9	448	125.8	374.5	106.2	376	86.6	377
2-Hexanol	119	541	220	468	189	467.5	154.5	470
2-Heptanol	251	637	386	561	336	561	273	563
2-Octanol	504	732.6	674	657	594	657	482	658
3-Pentanol	53.6	445	112.3	356	95	359	79.5	363
3-Hexanol	116	538	196	447	170	451	138.3	452
3-Heptanol	242	632.1	339	539	300	542	243	544
3-Octanol	505	732.9	600	637	539	640	440	642
4-Heptanol	241	631.6	308	523	274	528	232	536

and 20M, respectively. The I_{OH} values allow a direct comparison between the behaviour of the secondary compounds and that of the primary ones, as previously shown for halogenoalkanes[1,2,14]. Where comparison is possible, the values of V_g are close to those reported by McReynolds[6] at 100° and, by extrapolation, agree with the V_g values of C_1–C_5 alcohols measured at various temperatures on Carbowax 400 by Bighi et al.[15]. For linear alcohols, the general behaviour of log V_g as a function of n showed a slight negative curvature. This curvature was greater for squalane, the Δlog V_g values (the differences between the values for two consecutive members of a homologous series) decreasing with the number of carbon atoms in the chain, n, more quickly than for Carbowax-type liquid phases (see Table IV). Methanol showed a higher V_g value than expected on polar phases; this behaviour has been discussed by Takacs[16].

The effect of the position of the hydroxyl group in the chain and of the polarity of the liquid phase is demonstrated by the behaviour of the I_{OH} values (Fig. 1). The first secondary alcohols to be eluted were those in which the hydroxyl group is near to the centre of the chain[17]; the 1-alcohols were eluted considerably later. This behaviour is similar to that observed for linear halogenoalkanes[1] on non-polar liquid phases, while the difference between primary and secondary alcohols is greater than these between the corresponding halogenoalkanes on polar phases. The differences between the I_{OH} values of the linear primary and secondary alcohols, δI_{OH}, also depended on the grade of Carbowax. The dependence of δI_{OH} values on n was approximately linear, within the limits of the experimental error, and therefore the I_{OH} values of higher secondary alcohols can be calculated by extrapolation of the available values.

TABLE IV

Δ log V_z VALUES OF LINEAR ALCOHOLS ON SQUALANE, CARBOWAX 400, 1000 AND 20M

	Δ log V_g			
	Squalane	CW 400	CW 1000	CW 20M
1-Alcohols				
C_2-C_1	0.321	0.092	0.094	0.088
C_3-C_2	0.409	0.253	0.259	0.281
C_4-C_3	0.389	0.265	0.281	0.274
C_5-C_4	0.371	0.262	0.273	0.269
C_6-C_5	0.349	0.256	0.265	0.264
C_7-C_6	0.324	0.249	0.254	0.260
C_8-C_7	0.301	0.244	0.250	0.257
C_9-C_8	0.285	0.240	0.235	0.253
2-Alcohols				
C_4-C_3	0.381	0.246	0.256	0.268
C_5-C_4	0.375	0.242	0.255	0.253
C_6-C_5	0.336	0.242	0.253	0.251
C_7-C_6	0.324	0.238	0.250	0.247
C_8-C_7	0.303	0.242	0.247	0.246
3-Alcohols				
C_6-C_5	0.335	0.221	0.237	0.240
C_7-C_6	0.319	0.258	0.262	0.245
C_8-C_7	0.319	0.248	0.254	0.257

The "retarding effect" due to substitution of a hydrogen atom at various points in the chain by a hydroxyl group can be measured by the equivalent methylenes' number[1], M_e, for the I_{OH} values, or by the functional retention index, FRI, calculated after Swoboda[18], by subtracting the Kováts' retention index of the parent n-paraffin from the retention index of the alcohol. The ratio between the FRI value and the M_e (I_{OH}) value of the same compound on both polar and non-polar liquid
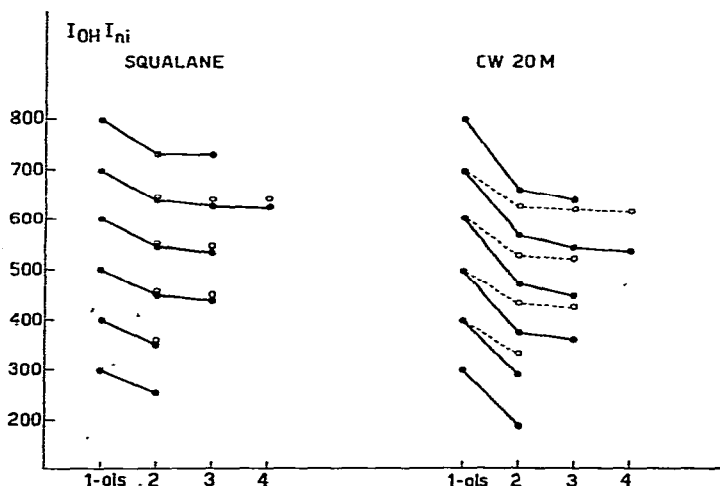
Fig. 1. I_{OH} and I_{ni} at 100° for straight-chain alcohols (●) and alkyl iodides (○).

phases is *ca.* 100. Therefore, the M_e (I_{OH}) values can be obtained from the FRI values when the direct calculation is not possible due to the short retention times of light alkanes on very polar liquid phases. While the FRI value can only be calculated for retention, the M_e concept can be applied to other physical properties, such as boiling point, T_b, molecular volume, V_m, etc., thus allowing a comparison of the effects of the substituent group on various properties.

In Table V are reported the M_e (I_{OH}), the M_e (T_b) and the M_e (V_m) values for linear alkanols. The negative sign of the M_e (V_m) values indicates that on replacing an H atom by an –OH group the V_m decreases, an indication of the strong hydrogen bonding[19]. This effect was higher for terminal –OH groups than for internal substitution, and slightly increased with n and with decreasing molecular weight of the Carbowax. The importance of association phenomena and hydrogen bonding in the retention is shown by the difference between the M_e (I_{OH}) values on polar and non-polar liquid phases. A comparison between the behaviour of alcohols and of halogen-substituted compounds is shown in Table VI, where the values of M_e for the sixth terms of every homologous series are reported. The data for halogenoalkanes in non-polar solvents refer to Apiezon L (ref. 1), as some tests showed that the retention indices on this liquid phase differ from the corresponding values on squalane by a few units, and the M_e (I_{ni}) values (I_{ni} is the retention index relative to linear 1-iodoalkanes[1]) are very close for both phases. The effect of hydrogen bonding in the pure liquid on V_m and T_b is clearly seen, taking into account the molecular-weight variation due to the substituents (ratios of weights: $OH/CH_2 = 1.14$; $Cl/CH_2 = 2.46$; $Br/CH_2 = 5.62$; $I/CH_2 = 8.97$).

During the GC separation, the hydrogen bonding influences the alcohol–PEG interaction both via the intramolecular ether linkages (acceptor groups) and via the

TABLE V

EQUIVALENT METHYLENES, NUMBERS FOR I_{OH}, T_b AND V_m

Alcohol	M_e (I_{OH})				M_e (T_b)	M_e (V_m)
	Squalane	CW 400	CW 1000	CW 20M		
Methanol	1.81	8.94	8.21	7.70	3.04	—
Ethanol	1.94	8.30	7.57	7.01	3.59	—
1-Propanol	2.10	8.36	7.58	7.05	3.35	—
1-Butanol	2.22	8.44	7.70	7.15	3.23	−0.58
1-Pentanol	2.32	8.47	7.81	7.23	3.12	−0.46
1-Hexanol	2.43	8.53	7.90	7.32	3.01	−0.31
1-Heptanol	2.41	8.54	8.00	7.39	2.83	−0.32
1-Octanol	2.39	8.54	8.09	7.45	2.76	−0.33
1-Nonanol	2.36	—	8.11	7.50	2.69	−0.26
2-Propanol	1.56	7.16	5.75	5.91	2.99	−0.97
2-Butanol	1.64	7.16	6.42	5.89	2.74	−0.56
2-Pentanol	1.74	7.16	6.44	5.89	2.54	−0.42
2-Hexanol	1.78	7.18	6.44	5.90	2.42	−0.28
2-Heptanol	1.75	7.16	6.47	5.96	2.26	−0.28
2-Octanol	1.70	7.15	6.51	6.02	2.10	−0.27
3-Pentanol	1.71	6.95	6.24	5.74	2.44	−0.52
3-Hexanol	1.74	6.88	6.19	5.72	2.25	−0.39
3-Heptanol	1.69	6.97	6.27	5.71	2.37	−0.32
3-Octanol	1.70	6.85	6.33	5.81	1.88	−0.32
4-Heptanol	1.69	6.81	6.11	5.63	2.28	−0.30

TABLE VI

VALUES OF EQUIVALENT METHYLENES, NUMBERS FOR VARIOUS PARAMETERS FOR THE SIXTH TERMS OF VARIOUS HOMOLOGOUS SERIES

Parameter	Position of substituent	Substituent			
		−Cl	−Br	−I	−OH
M_e (T_b)	1	2.20	2.92	3.65	3.01
	2	1.81	2.53	3.26	2.42
	3	1.83	2.56	3.31	2.25
M_e (V_m)	1	0.41	0.60	1.05	−0.31
	2	0.50	0.68	1.13	−0.28
	3	0.49	0.58	0.98	−0.39
M_e (I_{nl}) or M_e $(I_{OH})^*$	1	2.48	3.42	4.47	2.36
	2	2.06	2.90	3.95	1.74
	3	2.06	2.93	3.92	1.71
M_e (I_{nl}) or M_e $(I_{OH})^{**}$	1	4.51	5.86	6.83	7.32
	2	3.71	4.96	6.12	5.90
	3	3.79	4.93	6.09	5.72

* Non-polar liquid phase: Apiezon for halogenoalkanes, squalane for alcohols.
** Polar liquid phase: Carbowax 20M.

terminal hydroxyls (donor–acceptor groups). The ratio O/OH of internal ether linkages to terminal hydroxyl groups increases with M_L. The different value of this ratio may have an effect on the decrease in V_g and M_e (I_{OH}) values with increasing grade of the Carbowax. From Table II the following approximate values of O/OH result: CW 400, ca. 4; CW 1000, 10–11; CW 20M, 170–225. Experimental determinations of the hydroxyl groups of various Carbowaxes, however, showed that CW 20M has a hydroxyl content very close to that of CW 6000, due to the method of preparation of CW 20M, made by the reaction of CW 6000 with a diepoxide to yield a product of higher molecular weight[20]. Two secondary hydroxyl groups therefore remain at each connection point between two CW 6000 molecules, and the O/OH ratio is between 67 and 84. Fig. 2 shows, on a log–log scale, the dependence of the V_g values of 1-alkanols on the O/OH ratio and, respectively, on $M_L/100$ (for direct comparison). The linear behaviour of log V_g as a function of log O/OH clearly shows the influence of this ratio with respect to the effect of the molecular weight of the solvent. The length of the aliphatic chain of the alkanol also has a small effect. Straight-chain 2- and 3-alcohols exhibit the same behaviour.

Correlations between retention and vapour pressure

In a previous study on halogenoalkanes[2] an almost constant value of the ratio $I_{nh}/T_b V_m$ (I_{nh} is the retention index of a branched-chain halogenoalkane relative to the series of linear homologues with the same halogen) was found for linear compounds, while a regular "fine structure" in this ratio in the case of branched molecules permits the calculation of the I_{nh} values of some compounds by graphical interpolation. The behaviour of $I_{OH}/T_b V_m$ for straight-chain alcohols is shown in Fig. 3. The values for all of the Carbowaxes correspond within ± 1%. The values for various n are more scattered than for halogenoalkanes, but their behaviour clearly shows the effect of V_m on the retention, while the ratio $\delta I_{OH}/\delta T_b$ increases with n on all of the polar and non-polar liquid phases.
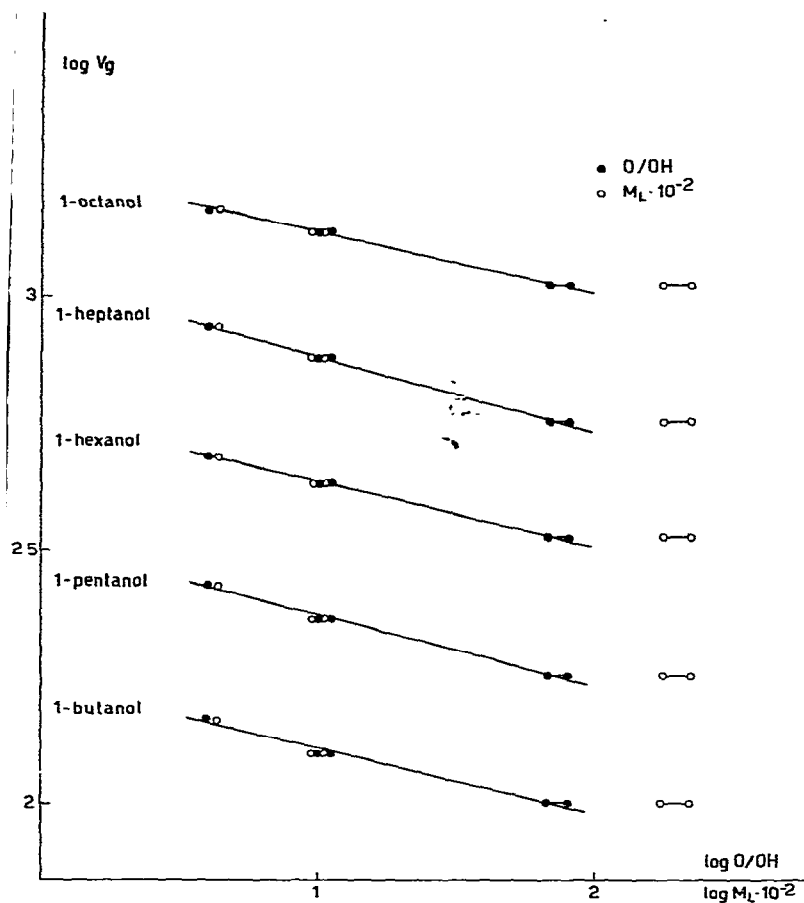
Fig. 2. Log V_g of 1-alcohols as a function of log $M_L \cdot 10^{-2}$ ($\bigcirc$) and log O/OH ($\bullet$).

The correlation between the GC behaviour and the vapour pressure of the various compounds is better investigated by using the values of the vapour pressure p_i^0, of solute 1 at the analysis temperature instead of the boiling point, T_b, at standard pressure. A useful relation between p_i^0 and V_g is given by eqn. 1, reported by Purnell[21] and Brown[22]:

$$V_g = \frac{273\ R}{p_i^0\ M_L\ \gamma^\infty} \tag{1}$$

where M_L is the molecular weight of the liquid phase L (solvent) and γ^∞ is the activity coefficient at infinite dilution. For ideal solutions, $\gamma^\infty = 1$ and V_g is inversely proportional to the vapour pressure of the compound. However, the molecular-size difference between l and L causes a negative deviation from Raoult's law due to entropy effects, even when l and L have the same chemical structure[22]. Therefore, V_g is controlled by p_i^0 and γ^∞.

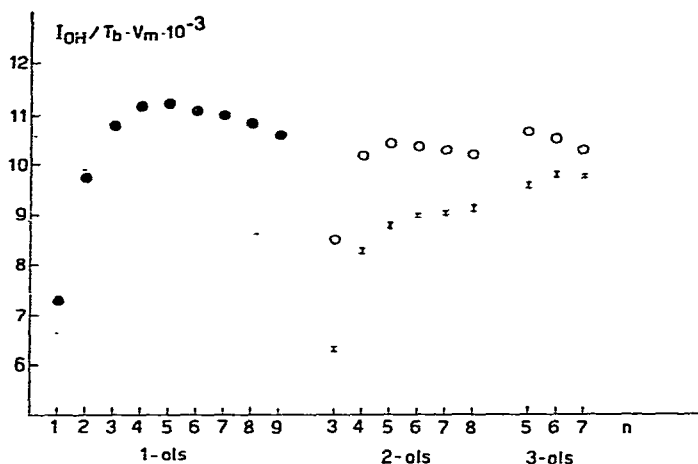The use of eqn. 1 for the calculation of γ^∞ yields incorrect values if some fac-

Fig. 3. Ratio $I_{OH}/T_b V_m$ (T_b in °K) for straight-chain alcohols: (●) squalane and Carbowaxes; (○) squalane; (I) Carbowaxes.

tors are not taken into account. First, eqn. 1 has been deduced by starting from the hypothesis that the solute vapour is ideal and that the number of moles of solute in solution, N_i^s, is much smaller than the number of moles of solvent in the column, N_L. When low-molecular-weight solutes are analysed by using polymeric liquid phases of very high molecular weight, the approximation $(N_L + N_i^s) = N_L$ loses its validity; therefore, the following relation must be applied:

$$C_i^g RT = p_i^0 \gamma_i \cdot \frac{N_i^s}{N_L + N_i^s} \qquad (2)$$

C_i^g being the molar concentration of the solute in the gas phase. If V is the total volume of the solvent plus dissolved solute, $C_i^s = N_i^s/V$ is the molar concentration of l in the solution, $C_i^s/C_i^g = K = V_R/V_L$, K being the partition coefficient and V_R the corrected retention volume, W_L is the weight of the solvent in the column, W_i^s is the weight of the solute dissolved and M_l is the molecular weight of the solute, the following equation results:

$$V_R = \frac{RT}{p_i^0 \gamma_l} \cdot \frac{V_L}{V} \cdot \left(\frac{W_L}{M_L} + \frac{W_i^s}{M_l} \right) \qquad (3)$$

As the retention volume per gram of solvent at the column temperature is given by $V_g^T = V_R/W_L$, and the specific retention volume, after Ambrose et al.[7], is $V_g = 273 V_g^T/T$, a general equation can be deduced:

$$V_g = \frac{273R}{p_i^0 \gamma_i} \cdot \frac{V_L}{V} \cdot \left(\frac{1}{M_L} + \frac{W_i^s}{W_L} \cdot \frac{1}{M_l} \right) \qquad (4)$$

Eqn. 4 is equivalent to eqn. 1 when $V_L = V$ and $M_l/M_L \gg W_i^s/W_L$. While the first condition is likely to be satisfied, the latter is no longer true for high-molecular-weight solvents and when the V_g values are not extrapolated to zero injected volume.

The use of experimental "finite volume" V_g values for calculation of the activity coefficient by use of eqn. 1 causes errors whose importance mainly depends on the ratio M_i/M_L. The following equation (obtained by applying the condition $V_L = V$) can therefore be used to calculate γ_i:

$$\gamma_i = \frac{273\,R}{p_i^0\,V_g\,M_i} \cdot \left(\frac{M_i}{M_L} + \frac{W_i^s}{W_L} \right) \tag{5}$$

The term W_i^s/W_L depends on K and does not correspond exactly to the ratio of the injected weight to the weight of the liquid phase; therefore the use of eqn. 5 with the condition W_i^s = injected weight will give the upper limit to the γ_i values (γ_i^{max}). The difference between the values of the activity coefficient obtained by using eqn. 1 or 5 may be very large, depending on the ratio M_L/M_i. As an example, for Carbowax 300 the difference is *ca.* 2% for methanol and 0.2% for 1-octanol, while for Carbowax 20M the difference can be as high as 58 and 16% respectively.

While this discrepancy can be removed by using V_g values extrapolated to zero injected volume, at the price of much more experimental work, or by using other and more complex equations for the calculation of the activity coefficient[23–25], especially in studies of solution equilibria at infinite dilution, another difficulty in the use of both eqn. 1 and eqn. 5 arises when polymeric liquid phases are used as solvents. The molecular weights of polymeric phases are generally unknown, making it impossible to use equations that depend on a knowledge of M_L. In the case of PEGs a nominal M_L value is supplied by the manufacturers but, as pointed out above (see Table II), the uncertainty in these values results in a large scatter in the calculated γ^∞ or γ_i values ($\pm$ 5% for Carbowax 400 and 1000; $\geqslant$ 25% for Carbowax 20M). The direct measurement of M_L and of the polydispersion cannot generally be accomplished by all GC workers, and therefore the use of γ^∞ or γ_i as a measure of the solute–solvent interaction would not be suitable for identification purposes or for liquid-phase characterization.

When different solutes are analysed on the same liquid phase, the M_L value is a constant; by injecting a constant weight, W_i, the ratio W_i^s/W_L has a very small variation. Therefore, it is possible to include all of the approximately known terms in a unique coefficient, obtained from eqn. 6:

$$\gamma = \frac{\gamma_i}{\left(\dfrac{M_i}{M_L} + \dfrac{W_i^s}{W_L} \right)} \tag{6}$$

Therefore, γ can be calculated on the basis of known values as follows:

$$\gamma = \frac{273\,R}{p_i^0\,M_i\,V_g} \tag{7}$$

As the value of γ^∞ is equal to γ_i when the ratio W_i^s/W_L tends to zero (zero injected volume, or infinite dilution), the following relation can thus be written:

$$\gamma = \gamma^\infty \cdot \frac{M_L}{M_i} \tag{8}$$

TABLE VII

VALUES OF γ^∞, γ AND C FOR SQUALANE (SQ) AND VARIOUS CARBOWAXES AT 100°

M_L (squalane) = 422.8; M_L (CW 400) = 425 ± 3%.

Alcohol	γ^∞		γ				C			
	SQ	CW 400	SQ	CW 400	CW 1000	CW 20M	SQ	CW 400	CW 1000	CW 20M
Methanol	5.21	0.39– 0.41	68.77	5.28	6.64	8.35	0.014	0.189	0.151	0.120
Ethanol	4.11	0.52– 0.55	37.71	4.95	6.14	7.84	0.026	0.202	0.163	0.128
1-Propanol	3.21	0.58– 0.61	22.58	4.20	5.18	6.29	0.044	0.238	0.193	0.159
1-Butanol	2.87	0.69– 0.73	16.38	4.05	4.82	5.95	0.061	0.247	0.207	0.168
1-Pentanol	2.72	0.83– 0.89	13.07	4.15	4.81	6.00	0.076	0.241	0.208	0.167
1-Hexanol	2.67	1.01– 1.07	11.04	4.34	4.93	6.17	0.090	0.231	0.203	0.162
1-Heptanol	2.78	1.25– 1.33	10.11	4.71	5.31	6.54	0.099	0.212	0.188	0.153
1-Octanol	3.17	1.63– 1.73	10.30	5.47	6.09	7.37	0.097		0.164	0.136
1-Nonanol	3.58		10.50		7.30					
2-Propanol	2.85	0.65– 0.69	20.03	4.71	5.89	7.38	0.050	0.212	0.170	0.135
2-Butanol	2.38	0.71– 0.75	13.58	4.20	5.13	6.25	0.074	0.238	0.195	0.160
2-Pentanol	2.06	0.87– 0.92	9.87	4.30	5.09	6.27	0.101	0.233	0.196	0.159
2-Hexanol	2.13	1.11– 1.17	8.80	4.74	5.53	6.76	0.114	0.211	0.181	0.148
2-Heptanol	2.29	1.44– 1.53	8.34	5.43	6.23	7.67	0.120	0.184	0.160	0.130
2-Octanol	2.46	1.77– 1.88	7.99	5.97	6.78	8.35	0.125		0.147	0.120
3-Pentanol	1.80	0.83– 0.88	8.63	4.12	5.07	5.82	0.116	0.243	0.197	0.172
3-Hexanol	1.78	1.02– 1.08	7.35	4.36	5.02	6.19	0.136	0.229	0.199	0.162
3-Heptanol	2.09	1.44– 1.53	7.61	5.44	6.15	7.59	0.131	0.184	0.163	0.132
4-Heptanol	1.96	1.49– 1.58	7.15	5.61	7.89	7.45	0.140	0.178	0.127	0.134
Ethane	0.43	1.38– 1.46	6.04	20.13			0.166	0.050		
Butane	0.59	3.49– 3.71	4.32	26.38			0.231	0.038		
Hexane	0.71	6.59– 6.99	3.49	33.52			0.286	0.030		
Octane	0.79	9.38– 9.96	2.93	36.02			0.341	0.028		
Decane	0.87	14.59–15.44	2.60	44.80			0.384	0.022		
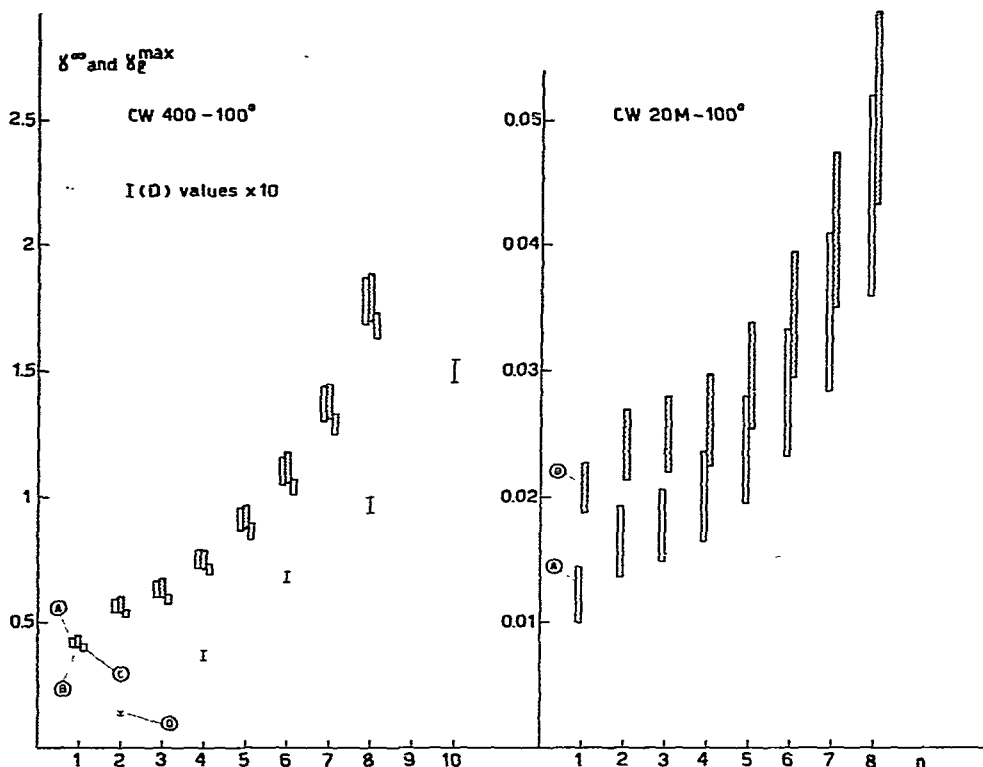
Fig. 4. Ranges of γ^∞ (A) and γ_i^{max} (B) for 1-alcohols on polar phases calculated from M_L values taken from literature; γ^∞ for 1-alcohols (C) and paraffins (D) were also calculated using the experimental M_L value of CW 400. Values for paraffins have been multiplied by 10.

The normalized coefficient γ can therefore be calculated from experimental data by using eqn. 7, independently of a knowledge of the true value of M_L, thus allowing a comparison of the retention-volume–vapour-pressure correlation for different solutes.

When isomeric compounds are analysed on the same liquid phase, the ratio M_i/M_L is a constant and, since the effect of p_i^0 is taken into account by eqn. 7, the values of γ are correlated only with the structure of the solute and with the solute–solvent interactions. When M_L is known, γ_i or γ^∞ can be calculated from γ if the W_i/W_L ratios of the V_g values at infinite dilution are available. As γ, γ^∞ and γ_i are inversely proportional to V_g, a decrease in their values is connected with an increase in the solute–solvent interaction (at constant p_i^0). In order to obtain a direct proportionality, useful for the immediate evaluation of the behaviour of different isomers, an interaction coefficient, $C = 1/\gamma$, may be used. Its value can be directly calculated from p_i^0, M_i and V_g. In Table VII are given values of γ^∞ on squalane and on CT 400 ($M_L = 425 \pm 3\%$), values of γ and values of the interaction constant C on squalane and CW 400, 1000 and 20M at 100°.

Fig. 4 shows, as a function of n on CW 400 and 20M, the values of γ^∞ and γ_i^{max}, calculated by using M_L intervals taken from the literature and reported in Table II (plots A and B) and, for CW 400, by using the measured value of $425 \pm 3\%$. The

deviations in Fig. 4 are relatively small for CW 400, but for CW 20M the differences due to the uncertainty in M_L are unacceptably high. Intermediate grade of Carbowax showed a behaviour which depended on the uncertainty in the M_L values, and 2- and 3-alkanols yielded similar plots. The values of γ, γ^∞ and C were also calculated for some linear alkanes on squalane and CW 400 at 100°. The results are reported in Table VII, and the γ^∞ values calculated from the experimentally measured M_L of CW 400 are plotted in Fig. 4 (D).

The values of γ and γ^∞ of alkanols and alkanes on squalane are shown in Fig. 5 as a function of n, where it can be seen that both coefficients exhibit a regular, but not simple, behaviour. On PEGs, γ^∞ values of both alcohols and linear alkanes increased with n and γ^∞ values of alcohols showed a minimum. Minima were also shown by the γ values of alcohols on both polar and non-polar liquid phases, their positions and values depending on the polarity and grade of the solvent. γ^∞ differed from unity even when hydrocarbons were analysed on squalane, but its value would probably tend to 1 when M_i approached M_L. γ and γ^∞ values for secondary alkanols were lower than those for 1-alcohols on squalane, higher on Carbowaxes.

The values of the interaction coefficient, C (Table VII), were higher when the chemical structure of the solute was similar to that of the solvent; therefore a low interaction is shown by alcohol–squalane and alkane–PEG systems. The highest values of C for secondary alcohols on squalane may be explained by the interaction of the
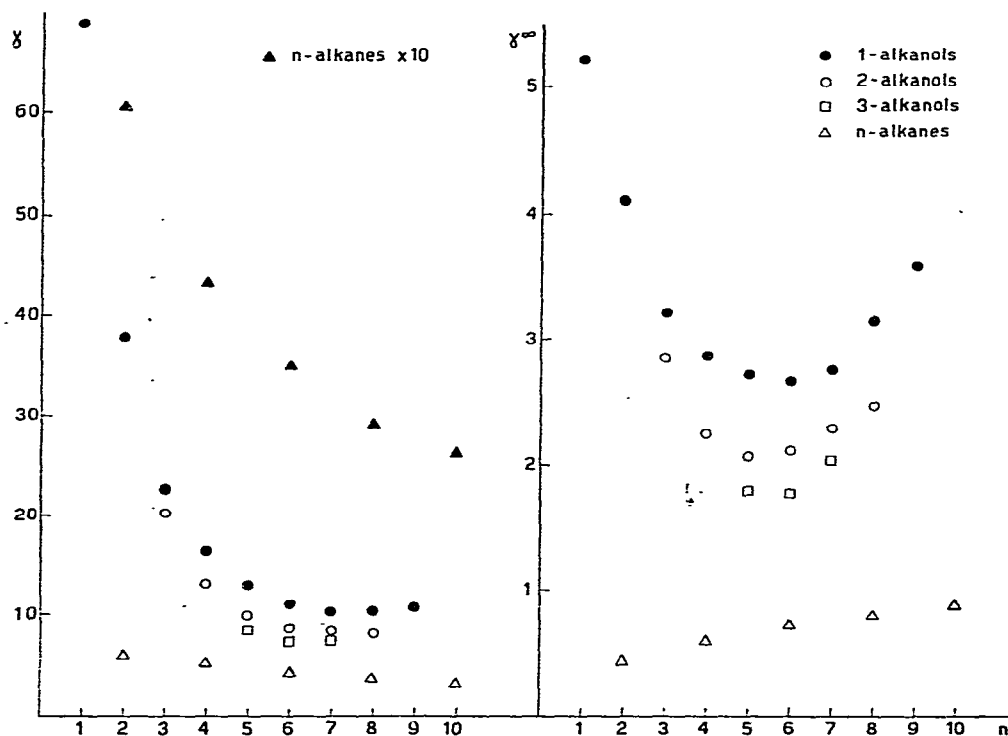

Fig. 5. Values of γ and γ^∞ for alcohols on squalane at 100°.

two terminal methyl groups with the methyls of the squalane molecule[26]; in 1-alcohols, only one methyl group is available for this interaction. On the other hand, because of steric-hindrance effects, the position of the hydroxyl group at the end of the chain probably increases the alcohol–PEG interaction which depends on hydrogen bonds.

Measurements of V_g values of branched-chain alcohols on polar and non-polar liquid phases are now in progress in order to ascertain the effect on the GC behaviour of alcohols.

REFERENCES

1 G. Castello and G. D'Amato, *J. Chromatogr.*, 76 (1973) 293.
2 G. Castello and G. D'Amato, *J. Chromatogr.*, 79 (1973) 33.
3 A. B. Littlewood, C. S. G. Phillips and D. F. Price, *J. Chem. Soc., London*, (1955) 1480.
4 L. Rohrschneider, *J. Chromatogr.*, 22 (1966) 6.
5 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
6 W. O. McReynolds, *Gas Chromatographic Retention Data*, Preston Technical Abstracts Co., Evanston, Ill., 1966.
7 D. Ambrose, A. I. M. Keulemans and J. H. Purnell, *Anal. Chem.*, 30 (1958) 1582.
8 A. Teramoto and H. Fujita, *Makromol. Chem.*, 85 (1965) 261.
9 H. G. Elias and H. Lys, *Makromol. Chem.*, 92 (1966) 1.
10 J. P. Arlic, P. A. Spegt and A. E. Skoulios, *Makromol. Chem.*, 99 (1966) 160.
11 P. Spegt, *Makromol. Chem.*, 140 (1970) 167.
12 H. B. Hass and R. F. Newton, in *Handbook of Chemistry and Physics*, 51st ed., Chemical Rubber Co., Cleveland, Ohio, 1970–1971.
13 B. J. Zwalinski and R. C. Wilhoit, *Vapor Pressure and Heats of Vaporization of Hydrocarbons and related Compounds*, API 44-TRC, No. 101, 1941.
14 G. Castello, G. D'Amato and E. Biagini, *J. Chromatogr.*, 41 (1969) 313.
15 C. Bighi, A. Betti, F. Dondi and R. Francesconi, *J. Chromatogr.*, 42 (1969) 176.
16 J. M. Takacs, *J. Chromatogr. Sci.*, 11 (1973) 211.
17 M. Šingliar, *J. Chromatogr.*, 65 (1972) 311.
18 P. A. T. Swoboda, in M. van Swaay (Editor), *Gas Chromatography*, Butterworths, London, 1962, p. 273.
19 S. N. Vinogradov and R. H. Linnell, *Hydrogen Bonding*, Van Nostrand–Reinhold, Princeton, N.J., 1971.
20 D. G. Bush, L. J. Kunzelsaver and S. H. Merrill, *Anal. Chem.*, 35 (1963) 1250.
21 H. Purnell, *Gas Chromatography*, Wiley, New York, London, 1962, p. 206.
22 I. Brown, *J. Chromatogr.*, 10 (1963) 284.
23 D. H. Desty and W. T. Swanton, *J. Phys. Chem.*, 65 (1961) 766.
24 D. H. Everett and C. T. H. Stoddard, *Trans. Farad. Soc.*, 57 (1961) 746.
25 P. Alessi, I. Kikic and G. Torriano. *J. Chromatogr.*, 105 (1975) 257.
26 A. C. W. van Kemenade and H. Groenendijk, *Chromatographia*, 2 (1969) 316.