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INFLUENCE OF VAPOUR PRESSURE AND ACTIVITY COEFFICIENTS ON THE RETENTION VOLUMES OF BRANCHED-CHAIN ALKANES*

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SUMMARY

The specific retention volumes, V_g , of all of the C_6 - C_8 branched-chain alkanes were measured on a 20% SF-96 column at 80°, 100° and 120°, and the vapour pressures, p_0 , at the same temperatures were calculated by three methods. A better agreement of the Antoine-type equation was found.

Narrow grid plots of $\log V_g$ as a function of $\log p_0$ showed a fine structure depending on molecular branching, and a positive curvature owing to the influence of the activity coefficient, γ .

The values of γ , which indicate the effect of the solute-solvent interactions on the gas chromatographic behaviour of the compounds, were calculated and correlated with the molecular structure and with some physical properties (molecular volume, density, surface tension and latent heat of vaporization).

INTRODUCTION

The gas chromatographic (GC) separation of most isomeric hydrocarbons can be easily accomplished by using efficient columns, but their complete identification in a complex mixture is still difficult, even if a GC-MS instrument is available, because at present the mass spectra of all hydrocarbon isomers heavier than nonane have not been tabulated. An identification based on the GC behaviour is therefore very attractive.

In a previous paper¹, a method was given for the identification of branched-chain alkanes by calculation of their retention indices² on the basis of molecular structure. Additive terms were calculated that are correlated with different structural groups of the molecule, and permit the theoretical calculation of the retention indices of any branched-chain isomer containing some of these groups. A deviation of a few index units was found between the calculated and experimental values for C_5 - C_9 branched-chain hydrocarbons.

The method can also be applied to retention data available in the literature,

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even if the analytical conditions are not exactly the same. An extrapolation of the additive rules to hydrocarbons heavier than nonane, formed by gamma-radiolysis^{3,4} and analysed on an SF-96 methylsilicone column, was made by using additive terms calculated from experimental values measured on the same liquid phase¹, and from literature data for retention indices on SE-30 methylsilicone⁵, Apiezon L⁶ and squalane⁷.

The synthesis and the identification on the basis of the radiolytic mechanism of the formation of the products confirmed the results of the additive method, and showed that the retention indices of heavier branched-chain alkanes on many non-polar phases, or the elution order of the isomers, can be predicted by using the data obtained using similar stationary phases. The results are more accurate when the McReynolds constants⁸ of the liquid phases involved are very similar, and the best fit is obviously obtained when the retention values of the basic compounds for the application of the method are measured on the same column and with the same analytical parameters of the compounds to be identified.

Unfortunately, extrapolation to heavier hydrocarbons with very complex structures cannot easily be made with the few data available in the literature, owing to the mutual effect of many tertiary and quaternary carbon atoms in the same molecule, which modify the basic additive terms calculated empirically by using the retention indices of less complex light hydrocarbons.

In order to overcome this difficulty and to make the retention behaviour of the branched-chain heavy alkanes more predictable, a better knowledge of the influence of the molecular shape on the physical properties and on the solute-solvent interactions is necessary.

For the determination of precise correlations, however, the use of the retention indices is not completely satisfactory when the results obtained on different stationary phases have to be compared. In fact, while the use of the retention index is very rapid and convenient (and with completely non-polar phases is also fully justified, from the theoretical point of view, when the polarity of the stationary phase increases), the use of linear alkanes as the reference series causes an arbitrary shift of the retention indices of the more retained polar compounds, poorly correlated with the true retention volumes and with the physical properties of the compounds.

For the analysis of alkanes, the ideal and less polar liquid phases are, of course, heavy alkanes. Squalane is considered to be an almost ideal alkane stationary phase, and is used as the reference compound in both the Rohrschneider⁹ and McReynolds⁷ systems of characterization of liquid phases, but when both the solute (the compound to be analyzed) and the solvent (the liquid phase) are alkanes, "selectivity" rather than "polarity" effects still occur within the group of aliphatic hydrocarbons which are usually classified as non-polar, and valuable differences in the retention indices for branched-chain alkanes can be seen when alkanes that have different numbers of methyl groups in the molecule are used as stationary phases^{10,11}. Squalane, with eight methyl groups, retains the branched-chain slightly more than the linear alkanes, and the resulting retention indices are higher than those obtained by using linear alkanes as stationary phases^{9,10}.

Therefore, an "absolute" value such as the specific retention volume, V_r , should be used when the correlation between structure and retention is investigated, notwithstanding the difficulty involved in its calculation. An additional advantage of the

use of V_g is that its expression, due to Ambrose *et al.*¹² and Purnell¹³, in the logarithmic form

$$\log V_g = \log \left(\frac{273 R}{M_l} \right) - \log p_0 - \log \gamma \quad (1)$$

where $273 R = 1.702 \cdot 10^7$, M_l is the molecular weight of the solute, p_0 is the saturation vapour pressure of the solute at the temperature of analysis and γ is the activity coefficient, allows the separation of the effects of the parameters that depend on the solute only (M_l , p_0) from those that depend on the solute-solvent interaction, expressed by γ (refs. 14 and 15).

$\log (273 R/M_l)$ is a constant when isomeric compounds are considered, and the value of V_g therefore depends on p_0 and γ .

As previously observed^{16,17}, the value of γ differs from unity, as postulated in the case of "ideal" solute-solvent pairs, even if alkanes are analyzed on alkane liquid phases. The influence of the activity coefficient on the correlations between relative retention data (retention indices) and boiling point for the same hydrocarbons has also been shown^{18,19}. Pierotti *et al.*¹⁴, whose expression of $\log \gamma$ differs somewhat from eqn. 1, but is practically equivalent to it, found that for some alkanes, cycloalkanes, alcohols and ketones the structural changes which are important to p_0 are in some instances different from those which are important to γ .

In order to elucidate the effect of these factors on the GC behaviour of branched-chain alkanes, we measured the V_g values of many alkanes on a non-polar liquid phase, calculated the p_0 and the γ values and correlated these parameters with the structure of the molecules and other physical properties such as the molecular volume, density and surface tension.

EXPERIMENTAL AND RESULTS

Determination of V_g

All of the C₆-C₈ isomers of alkanes were analysed on a column 4 m long and 1/4 in. O.D., filled with 20% (w/w) SF-96 methylsilicone on Chromosorb P (DMCS), 60-80 mesh, by using a Varian Aerograph 1530 gas chromatograph with a thermal conductivity detector and proportional temperature control. A constant flow-rate of helium carrier gas of 43 ml/min was maintained by appropriate adjustment at every temperature, in order to compensate for the variation in the viscosity of the carrier gas and of the liquid phase¹⁶.

A silicon-based liquid phase was used, instead of the "standard non-polar" squalane, because its higher temperature limit (300° compared with 100°) makes it the best phase for the analysis of heavy hydrocarbons. It therefore seemed more convenient to study the behaviour of relatively light alkanes under the same conditions that can be applied to the higher homologues, in order to allow extrapolation or valid comparison with experimental data that may be available in the future.

The specific retention volumes were calculated by the method of Littlewood *et al.*²⁰. When comparison was possible, *i.e.*, for linear alkanes and 2,3-dimethylbutane at 120°, the values corresponded to the V_g values given by McReynolds⁵ for SE-30

TABLE I

VALUES OF THE SPECIFIC RETENTION VOLUME, V_o , MEASURED ON AN SF-96 COLUMN AT 80°, 100° AND 120°

Alkane	Temperature (°C)		
	80	100	120
<i>n</i> -Hexane	31.86	18.82	11.91
2-Methylpentane	25.28	15.33	9.83
3-Methylpentane	28.52	17.08	10.99
2,2-Dimethylbutane	20.36	12.71	8.42
2,3-Dimethylbutane	25.09	15.41	10.01
<i>n</i> -Heptane	67.09	36.85	21.85
2-Methylhexane	53.00	29.93	18.20
3-Methylhexane	56.67	31.90	19.32
3-Ethylpentane	60.0	33.57	20.2
2,2-Dimethylpentane	40.38	23.60	14.76
2,3-Dimethylpentane	54.65	31.13	19.03
2,4-Dimethylpentane	40.56	23.54	14.59
3,3-Dimethylpentane	50.03	28.98	17.96
2,2,3-Trimethylbutane	43.61	25.66	16.20
<i>n</i> -Octane	141.2	72.11	40.10
2-Methylheptane	109.7	57.70	32.91
3-Methylheptane	116.7	61.01	34.70
4-Methylheptane	111.3	58.60	33.52
3-Ethylhexane	117.3	61.54	34.93
2,2-Dimethylhexane	80.07	43.81	25.86
2,3-Dimethylhexane	105.9	56.50	32.75
2,4-Dimethylhexane	87.75	47.35	27.67
2,5-Dimethylhexane	85.79	46.48	27.22
3,3-Dimethylhexane	96.43	52.59	30.51
3,4-Dimethylhexane	117.3	61.96	35.91
2-Methyl-3-ethylpentane	115.5	60.97	35.08
3-Methyl-3-ethylpentane	117.3	62.46	35.94
2,2,3-Trimethylpentane	92.4	50.52	30.29
2,2,4-Trimethylpentane	65.12	36.53	22.06
2,3,3-Trimethylpentane	104.8	56.83	33.35
2,3,4-Trimethylpentane	93.79	51.20	30.14
2,2,3,3-Tetramethylbutane	82.15	46.07	27.72

methylsilicone, as can be expected owing to the close values of the McReynolds constants for the two phases⁸.

Therefore, the V_o values reported in Table I can be used, with the above McReynolds tables, to aid in the rapid distinction of branched-chain alkanes from other compounds.

Calculation of p_0 and γ

By using eqn. 1, the values of the activity coefficient, γ , can be calculated if V_o and p_0 at the temperature of analysis are known. p_0 , which is purely a solute property, affects the GC separation through its effect on the magnitude of the partition coefficient and on relative volatilities. Its values at 80°, 100° and 120° can be calculated:

(a) by using an Antoine-type equation²¹:

$$\log p_0 = A - [B/(C + t)] \quad (2)$$

where t is the temperature in °C and A , B and C are constants taken from A.P.I. tables²²;

(b) by interpolation of the vapour pressures at various temperatures, published by Stull²³ and reported in Perry's Chemical Engineer's Handbook²⁴;

(c) by using the equation reported by Schlessinger²⁵:

$$\log p_0 = (-0.2185 A/K) + B \quad (3)$$

TABLE II

VALUES OF p_0 (torr) AT 80°, 100° AND 120° CALCULATED BY (A) THE ANTOINE EQUATION, (B) THE INTERPOLATION OF STULL'S DATA AND (C) THE SCHLESSINGER EQUATION

Alkane	A			B			C		
	80°	100°	120°	80°	100°	120°	80°	100°	120°
<i>n</i> -Hexane	1068	1845	2991	1113	1932	3111	991	1800	2995
2-Methylpentane	1366	2308	3656				1559	2843	4747
3-Methylpentane	1250	2119	3382				1424	2611	4380
2,2-Dimethylbutane	1819	2965	4570				2191	3871	6290
2,3-Dimethylbutane	1448	2414	3794	1457	2592	3782	1345	2349	3778
<i>n</i> -Heptane	427.8	795.7	1375	435.2	806.0	1382	381.1	736.2	1393
2-Methylhexane	558.3	1012	1710	589.2			588.9	1129	2032
3-Methylhexane	526.9	957.8	1623	549.0			555.1	1088	1932
3-Ethylpentane	502.7	917.1	1559	522.9			528.7	1040	1852
2,2-Dimethylpentane	778.3	1361	2230				848.2	1600	2749
2,3-Dimethylpentane	564.8	1016	1707	587.0			593.2	1144	2004
2,4-Dimethylpentane	748.4	1318	2175	751.0			805.3	1526	2633
3,3-Dimethylpentane	634.4	1121	1855	653.4			671.8	1271	2190
2,2,3-Trimethylbutane	740.8	1289	2105	744.2			764.0	1403	2357
<i>n</i> -Octane	175.0	351.2	747.6	212.0	360.8	265.5	153.5	316.0	585.0
2-Methylheptane	230.9	450.5	811.4	272.0	464.2		228.7	476.0	889.5
3-Methylheptane	221.7	433.9	783.0	262.7	464.5		219.3	458.9	861.4
4-Methylheptane	230.5	449.8	810.0	271.4	461.3		228.6	477.3	894.5
3-Ethylhexane	225.2	439.6	791.5		450.3		223.1	466.4	874.6
2,2-Dimethylhexane	331.8	623.6	1087	355.1	644.5		335.9	675.7	1227
2,3-Dimethylhexane	250.0	481.5	857.5	289.0	498.9		248.8	512.3	948.4
2,4-Dimethylhexane	305.0	577.8	1044	334.6	600.4		308.5	628.3	1153
2,5-Dimethylhexane	307.2	582.9	1024	336.6	605.5		311.1	634.8	1166
3,3-Dimethylhexane	284.5	538.4	944.6	317.8	560.1		286.8	583.2	1068
3,4-Dimethylhexane	234.0	452.5	809.0	274.7	466.4		232.2	478.5	886.9
2-Methyl-3-ethylpentane	251.1	482.0	856.0	290.4	500.1		249.9	510.8	940.1
3-Methyl-3-ethylpentane	235.4	449.9	796.5	275.7	461.9		233.7	473.8	865.9
2,2,3-Trimethylpentane	306.4	573.9	998.1	257.5	596.7		309.4	619.1	1119
2,2,4-Trimethylpentane	425.9	776.6	1320	434.0			440.2	859.5	1521
2,3,3-Trimethylpentane	264.4	499.1	874.5	302.1	518.9		265.5	535.4	973.9
2,3,4-Trimethylpentane	271.6	515.5	907.2	307.8	536.0		271.3	548.3	999.2
2,2,3,3-Tetramethylbutane	344.7	636.3	1094	260.0	640.3		297.4	668.9	1336

TABLE III
VALUES OF THE ACTIVITY COEFFICIENT γ

Alkane	Temperature ($^{\circ}\text{C}$)		
	80	100	120
<i>n</i> -Hexane	5.80	5.68	5.55
2-Methylpentane	5.72	5.59	5.50
3-Methylpentane	5.54	5.45	5.30
2,2-Dimethylbutane	5.33	5.24	5.13
2,3-Dimethylbutane	5.43	5.31	5.20
<i>n</i> -Heptane	5.92	5.79	5.65
2-Methylhexane	5.74	5.61	5.45
3-Methylhexane	5.69	5.56	5.42
3-Ethylpentane	5.63	5.52	5.39
2,2-Dimethylpentane	5.40	5.29	5.16
2,3-Dimethylpentane	5.50	5.37	5.23
2,4-Dimethylpentane	5.59	5.47	5.35
3,3-Dimethylpentane	5.35	5.22	5.09
2,2,3-Trimethylbutane	5.26	5.13	4.98
<i>n</i> -Octane	6.04	5.88	5.72
2-Methylheptane	5.89	5.73	5.57
3-Methylheptane	5.76	5.64	5.48
4-Methylheptane	5.81	5.65	5.50
3-Ethylhexane	5.64	5.50	5.38
2,2-Dimethylhexane	5.61	5.45	5.301
2,3-Dimethylhexane	5.64	5.48	5.306
2,4-Dimethylhexane	5.57	5.45	5.309
2,5-Dimethylhexane	5.65	5.50	5.34
3,3-Dimethylhexane	5.431	5.26	5.17
3,4-Dimethylhexane	5.433	5.31	5.13
2-Methyl-3-ethylpentane	5.13	5.07	4.96
3-Methyl-3-ethylpentane	5.40	5.30	5.22
2,2,3-Trimethylpentane	5.26	5.14	5.04
2,2,4-Trimethylpentane	5.37	5.253	5.12
2,3,3-Trimethylpentane	5.39	5.253	5.11
2,3,4-Trimethylpentane	5.85	5.64	5.45
2,2,3,3-Tetramethylbutane	5.26	5.08	4.91

where K is the temperature in $^{\circ}\text{K}$, A is the molar heat of vaporization in calories per gram-mole and B is a constant. Both A and B , which differ from the constant in the Antoine-type equation, were taken from the CRC Handbook of Chemistry and Physics²⁵.

The p_0 values obtained with the three methods, reported in Table II, show that, especially for branched-chain alkanes, the results differ, generally increasing in the order method (a) < (b) < (c). As the values of γ calculated by eqn. 1 depend on p_0 , the choice of the most reliable method is essential for a correct evaluation of the activity coefficient. By plotting the values of $\log p_0$ and of $\log \gamma$ given by the three methods as a function of $\log V_g$ and of n (number of carbon atoms) for various homologous series (n -alkanes and 2-methyl-, 3-methyl-, 2,2-dimethyl-, 2,3-dimethyl-, 2,4-dimethyl- and 3,3-dimethylalkanes), at 80° , 100° and 120° , and taking into

account that $\Delta \log p_0^*$ is approximately constant and corresponds to the increment of free energy of vaporization per methylene group added to the structure, the smallest scattering is given by the values calculated by using the Antoine equation (eqn. 2), which, in the considered temperature interval, gives the best approximation.

Therefore, the values of p_0 calculated by method (a), and the corresponding values of the activity coefficient, γ , which are listed in Table III, were used.

DISCUSSION

In the considered interval of n , the plots of the $\log V_g$ values for the homologous series (2-methyl-, 3-methyl-, etc.) are nearly linear with respect to n , showing the "classical" dependence of $\log V_g$ on n (ref. 26), which, as previously found¹⁷ is no longer true when a large range of values of n is considered. Notwithstanding this, by using the values of the slope d_1 of the equation

$$\log V_g \approx d_0 + d_1 n \quad (4)$$

which are reported in Table IV, the V_g values of homologous compounds that have 10–12 carbon atoms can be calculated with an approximation better than 3%. The relatively narrow linearity range of the plot makes the values of the extrapolated intercepts, d_0 , of little significance from the practical point of view, and therefore it appears to be more convenient to use the equation

$$\log V_g (C_{n+m}) = \log V_g (C_n) + m d_1 \quad (5)$$

where C_n is the branched-chain alkane with n carbon atoms whose V_g value is reported in Table I, and C_{n+m} is the higher homologue whose V_g value has to be calculated.

TABLE IV

SLOPES, d_1 , OF EQUATION 4 FOR VARIOUS HOMOLOGOUS SERIES OF BRANCHED-CHAIN ALKANES AT 80°, 100° AND 120°

Homologous series	Column temperature (°C)		
	80	100	120
<i>n</i> -Alkanes	0.326	0.297	0.271
2-Methylalkanes	0.322	0.288	0.263
3-Methylalkanes	0.315	0.276	0.250
4-Methylalkanes	0.339	—	—
2,2-Dimethylalkanes	0.304	0.269	0.243
2,3-Dimethylalkanes	0.317	0.282	0.257
2,4-Dimethylalkanes	0.335	0.303	0.278
3,3-Dimethylalkanes	0.298	0.259	0.230

* Δ is the difference between the value of any parameter for two consecutive members of a homologous series, while δ is the difference between the value for the branched-chain and linear isomers.

The dependence of d_1 on the reciprocal of the absolute temperature is linear for n -alkanes, whereas it shows a small positive curvature for the branched-chain isomers, according to their higher values of $\Delta T/^\circ\text{C}$, as previously observed^{10,27}.

Dependence of V_σ on p_0

As expressed by eqn. 1, the values of V_σ at every temperature are inversely proportional to p_0 , and depend on the activity coefficient, γ . The general behaviour is shown in Fig. 1, where the family of dashed lines represents "ideal" values of V_σ of the linear alkanes at three temperatures if γ were constant and equal to unity for all compounds ("ideal" solute-solvent pair).

By connecting the points with respect to the temperature of analysis and to the number of carbon atoms (the latter lines are not reported owing to the small scale of the figure), a very narrow grid plot^{13,28} is obtained for every homologous series. In fact, while the term $\log(273 R/M_1)$ of eqn. 1 depends only on the molecular weight and is therefore constant for all isomers, the values of $\log p_0$ are higher for branched-chain compounds and cause a small systematic displacement of the corresponding lines, giving a fine structure to the plot. This effect is enhanced by the influence of $-\log \gamma$, as the values of γ also depend on the structure and degree of branching.

The experimental values of $\log V_\sigma$ for linear alkanes reported with full lines in Fig. 1 are systematically lower than the "ideal" values, and the influence of γ sometimes increases and sometimes decreases the distance between the lines, as the effect of structural changes on p_0 and γ is not the same (see Tables II and III).

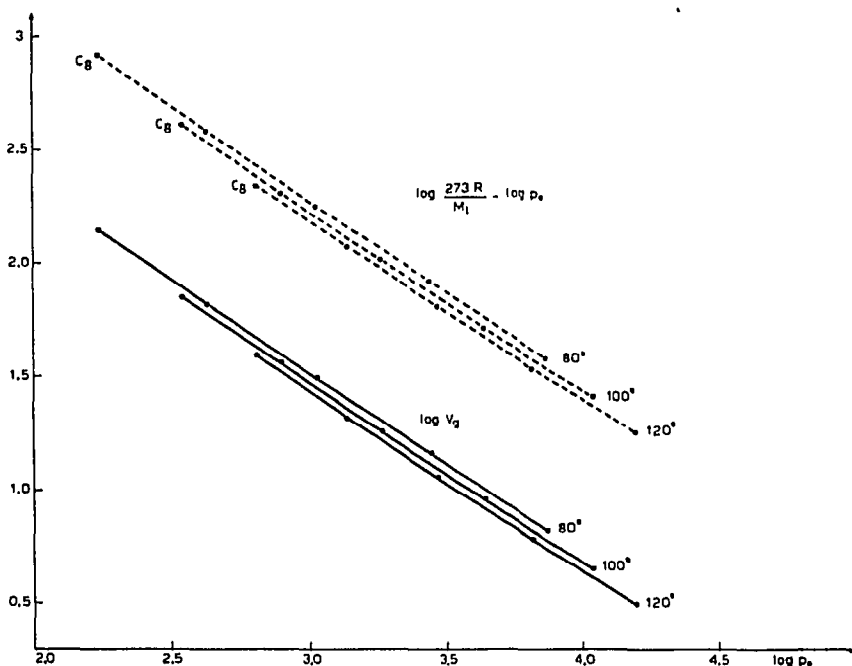


Fig. 1. "Ideal" (above) and experimental (below) values of $\log V_\sigma$ as a function of $\log p_0$ for linear alkanes at various temperatures.

The isotherms and the lines connecting the points that represent the same compound at different temperatures in Fig. 1 show a positive curvature, owing to the decrease of $\log(273 R/M_i)$ when M_i increases for both "ideal" and experimental V_g values, and to the variation of γ with the number of carbon atoms for the experimental lines.

This is shown by the data reported in Table V, where the variation of $\log V_g$ and $\log p_0$ with temperature and the ratios of these values are listed for *n*-, methyl- and dimethylalkanes. The behaviour, common to all isomers, can be summarized by the following expressions:

$$\log V_g^{100} - \log V_g^{120} < \log V_g^{80} - \log V_g^{100}, \text{ i.e., } \frac{V_g^{100}}{V_g^{120}} < \frac{V_g^{80}}{V_g^{100}} \quad (6)$$

$$\log p_0^{120} - \log p_0^{100} < \log p_0^{100} - \log p_0^{80}, \text{ i.e., } \frac{p_0^{120}}{p_0^{100}} < \frac{p_0^{100}}{p_0^{80}} \quad (7)$$

$$\frac{\log V_g^{100} - \log V_g^{120}}{\log p_0^{120} - \log p_0^{100}} < \frac{\log V_g^{80} - \log V_g^{100}}{\log p_0^{100} - \log p_0^{80}} \quad (8)$$

showing that the distance between the isotherms in Fig. 1 decreases as the temperature increases, and that the isotherms are slightly divergent when *n* increases.

The regularity of data reported in Table V seems to suggest a "hyperfine" structure of the grid plot, which cannot be correctly evaluated here owing to the limited range of *n* and temperature, but which may help in the identification of higher isomers by extrapolation.

TABLE V

VARIATION OF $\log V_g$ AND $\log p_0$ WITH TEMPERATURE (*D*), AND RATIOS OF THE DIFFERENCES FOR ALKANES WITH DIFFERENT DEGREES OF BRANCHING

Alkane	<i>D</i> log V_g		<i>D</i> log p_0 (A.P.I.)		<i>D</i> log V_g / <i>D</i> log p_0	
	100°–120°	80°–100°	100°–120°	80°–100°	100°–120°	80°–100°
<i>n</i> -Hexane	0.199	0.228	–0.210	–0.237	–0.950	–0.962
<i>n</i> -Heptane	0.227	0.260	–0.237	–0.269	–0.956	–0.965
<i>n</i> -Octane	0.255	0.292	–0.266	–0.302	–0.958	–0.965
2-Methylpentane	0.193	0.217	–0.201	–0.227	–0.962	–0.958
2-Methylhexane	0.216	0.248	–0.228	–0.258	–0.948	–0.961
2-Methylhexane	0.245	0.282	–0.255	–0.290	–0.959	–0.970
3-Methylpentane	0.192	0.222	–0.203	–0.229	–0.944	–0.969
3-Methylhexane	0.218	0.249	–0.229	–0.259	–0.951	–0.961
3-Methylheptane	0.245	0.282	–0.256	–0.291	–0.956	–0.966
2,2-Dimethylbutane	0.179	0.204	–0.188	–0.212	–0.951	–0.963
2,2-Dimethylpentane	0.204	0.229	–0.214	–0.243	–0.950	–0.944
2,2-Dimethylhexane	0.229	0.262	–0.241	–0.274	–0.948	–0.956
2,3-Dimethylbutane	0.187	0.212	–0.196	–0.222	–0.954	–0.954
2,3-Dimethylpentane	0.214	0.244	–0.255	–0.255	–0.949	–0.958
2,3-Dimethylhexane	0.237	0.273	–0.251	–0.285	–0.944	–0.959

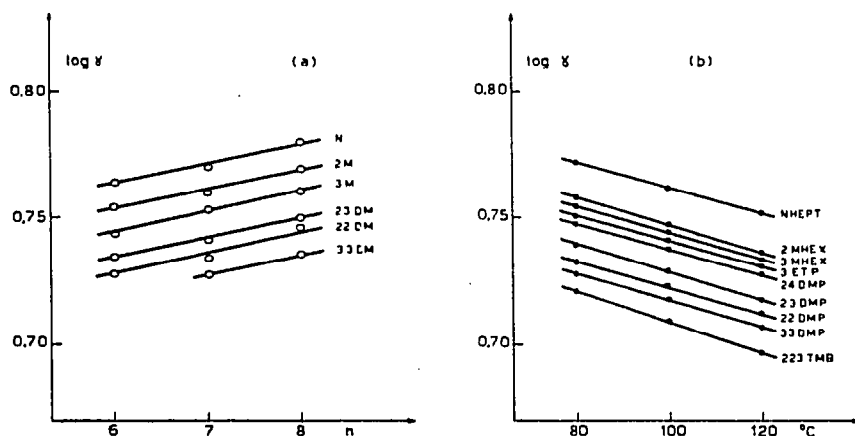


Fig. 2. (a) $\log \gamma$ of homologous branched-chain alkanes as a function of n ; (b) $\log \gamma$ of some isomeric alkanes as a function of temperature. N, Normal; M, methyl; ET, ethyl; B, butane; P, pentane; HEX, hexane; HEPT, heptane; D, di; T, tri.

Dependence of γ on n , T and structure

As seen above, the fine structure of the $\log V_a$ versus $\log p_0$ plots is influenced by the behaviour of γ , which generally increases with n and decreases with temperature. Therefore, the temperature dependence of the ratio of activity coefficients, used to calculate δI (ref. 19) should never be neglected. The dependence of γ on n and T

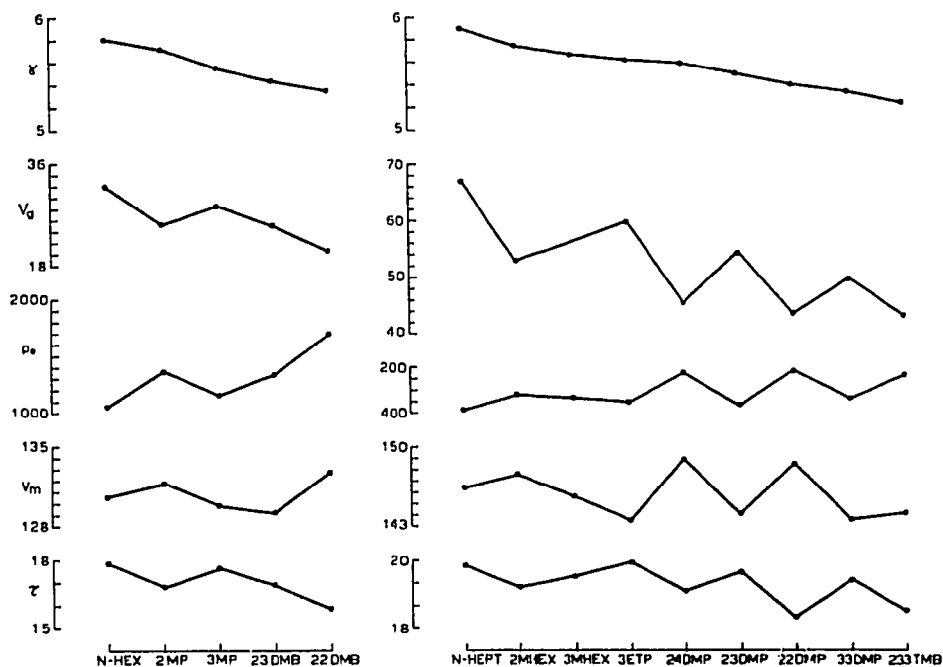


Fig. 3. Comparison of γ_0 and other physical properties of hexanes and heptanes as a function of structure. γ , V_a and p_0 at 80°; V_m and τ at 25° (liquid).

is reported in Fig. 2, which shows good linearity, especially as a function of temperature, and allows extrapolation of values to higher n and T , even if $\log \gamma$ is obtained as a small difference between large values and therefore depends greatly on experimental error.

The dependence of γ on the molecular structure and its comparison with other parameters is shown in Fig. 3, where the values are plotted in order of decreasing γ . At higher temperature, the behaviour is the same with a greater difference between the values for isomers and those for linear alkanes. Octanes are not reported, but their behaviour is similar and can be deduced from data in Tables I, II and III. While higher homologues of the compounds reported in Fig. 3 follow the same sequence (n -alkane, 2-methyl-, 3-methyl-, etc.), other isomers interpolate the sequence with some inversion at different temperatures. This may be due to the close values of γ , which emphasizes the effect of experimental fluctuations. The behaviour as a function of structure seen in Fig. 3 is expressed numerically by the values of δV_a , δp_0 and $\delta \gamma$ reported in Table VI.

Fig. 3 shows how p_0 affects the V_a values, being partially compensated for γ .

TABLE VI
 δV_a , δp_0 AND $\delta \gamma$ AT 80°, 100° AND 120°

Alkane	δV_a			δp_0			$\delta \gamma$		
	80°	100°	120°	80°	100°	120°	80°	100°	120°
2-Methylpentane	-6.58	-3.49	-2.08	288	463	665	-0.09	-0.08	-0.05
3-Methylpentane	-3.34	-1.74	-0.98	182	274	341	-0.26	-0.22	-0.25
2,2-Dimethylbutane	-11.50	-6.11	-3.49	751	1120	1579	-0.47	-0.44	-0.42
2,3-Dimethylbutane	-6.77	-3.40	-1.90	380	569	803	-0.37	-0.37	-0.35
2-Methylhexane	-14.1	-6.9	-3.6	130	216	335	-0.179	-0.185	-0.198
3-Methylhexane	-10.4	-4.9	-2.5	99	162	248	-0.229	-0.234	-0.236
3-Ethylpentane	-7.1	-3.3	-1.6	75	121	184	-0.29	-0.27	-0.26
2,2-Dimethylpentane	-28.8	-13.2	-7.1	350	563	855	-0.51	-0.50	-0.49
2,3-Dimethylpentane	-12.4	-5.7	-2.8	137	220	332	-0.41	-0.42	-0.42
2,4-Dimethylpentane	-26.5	-13.3	-7.3	321	522	800	-0.32	-0.32	-0.30
3,3-Dimethylpentane	-17.1	-7.9	-3.9	207	325	480	-0.57	-0.57	-0.56
2,2,3-Trimethylbutane	-23.5	-11.2	-5.6	313	493	730	-0.66	-0.66	-0.67
2-Methylheptane	-31.5	-14.4	-7.2	55.9	99.3	164	-0.151	-0.152	-0.150
3-Methylheptane	-24.5	-11.1	-5.4	47	83	135	-0.28	-0.245	-0.241
4-Methylheptane	-29.9	-13.5	-6.6	55.5	98.6	162	-0.229	-0.231	-0.227
3-Ethylhexane	-23.9	-10.6	-5.2	50	88	144	-0.39	-0.38	-0.34
2,2-Dimethylhexane	-61.1	-28.3	-14.2	157	272	439	-0.43	-0.43	-0.424
2,3-Dimethylhexane	-35.3	-15.6	-7.3	75	130	210	-0.40	-0.41	-0.419
2,4-Dimethylhexane	-53.4	-24.8	-12.4	130	227	366	-0.47	-0.44	-0.416
2,5-Dimethylhexane	-55.4	-25.6	-12.9	132	232	376	-0.38	-0.38	-0.38
3,3-Dimethylhexane	-44.8	-19.5	-9.6	109	187	297	-0.60	-0.62	-0.55
3,4-Dimethylhexane	-23.9	-10.1	-4.2	59	101	161	-0.60	-0.57	-0.59
2-Methyl-3-ethylpentane	-25.7	-11.9	-5.1	76	131	208	-0.90	-0.81	-0.76
3-Methyl-3-ethylpentane	-23.9	-9.6	-5.0	60	98.7	149	-0.64	-0.58	-0.50
2,2,3-Trimethylpentane	-48.8	-21.6	-9.8	131	223	350	-0.77	-0.74	-0.68
2,2,4-Trimethylpentane	-76.1	-35.6	-18.0	251	425	672	-0.66	-0.63	-0.60
2,3,3-Trimethylpentane	-36.4	-15.3	-6.7	89	148	227	-0.65	-0.63	-0.62
2,3,4-Trimethylheptane	-47.4	-20.9	-10.0	97	164	260	-0.19	-0.24	-0.28
2,2,3,3-Tetramethylbutane	-59.0	-26.0	-12.4	170	285	446	-0.77	-0.80	-0.81

The vertical scales are the same, showing that relatively small p_0 fluctuations cause larger variations in V_g for heptanes than for hexanes.

Other physical properties were also examined. The molecular volume, V_m , which is proportional to the reciprocal of density, changes with structure in the opposite direction to V_g for each isomers group, but its effect is hardly distinguishable from that of p_0 . The ratio $1/T_b \cdot V_m$, connected to structure and position of the substituent in halogenated alkanes²⁹, shows very similar behaviour to p_0 .

The surface tension, τ , behaves as the heat of vaporization, C_{vap} , (inversely proportional to p_0). As these parameters are both correlated with solute-solute interactions, their behaviour, which is similar to that of the V_g , shows that the interactions between hydrocarbon molecules and the liquid phase are of the same type as those which exist in the pure hydrocarbon, and that highly branched molecules (2,2-DMB*; 2,4-DMP; 2,2-DMP, etc.) with a low density, a high V_m and a smaller reciprocal attraction therefore need a smaller energy to be driven away by mechanical (τ) or thermal (C_{vap}) energy.

A measure of the "selectivity" of the liquid phase is given by γ , the values of which are lower in the case of strong solute-solvent interactions, which increase V_g with respect to compounds that have the same vapour pressure at the temperature of analysis. The interaction increases with the degree of branching of the molecule, depending on:

(a) Tertiary and quaternary carbon atoms (2,2-DMB; 2,2,3-TMB; 2,2,4,4-TMB); γ is generally lower for internal than for external branching¹.

(b) Length of the linear part of the molecule (2-methyl-, 3-methyl-, etc.); when the number of connected methylenes is the same, the compounds that have them in the middle of the molecule have higher values of γ (2,5-DMHEX; 2,3-DMHEX).

(c) Number of methyl groups and their nature. It has been shown previously¹⁰ that the retention index of isocodal isomers (*i.e.*, compounds that, having the same number of primary, secondary, tertiary and quaternary carbon atoms, are identified by the same four-digit code) increases with increasing number of methyl groups connected to a methylene ("secondary" methyl) group, and this behaviour was explained by the assumption that a Van der Waals bond is possible between a methyl group of the stationary phase and a methyl group of the solute when their rotational frequencies correspond.

This rule is completely satisfied by the γ values in Table III, which decrease regularly with increasing number of "secondary" methyl groups, while the retention indices values show some exceptions. When isocodal compounds have the same number of secondary methyl groups, the values of γ differ according to points (a) and (b) reported above (3-MHEPT and 4-MHEPT; 2,3-DMHEX and 2,4-DMHEX).

A quantitative measure of the importance of the above structural parameters is given approximately by the values of δ (Table VI), which change regularly with n , T and structure. Their extrapolation allows the corresponding parameter of higher homologues to be calculated directly or checked when available from literature sources. By using eqn. 1, each of the missing values (V_g , p_0 or γ) can be calculated.

The use of GC retention data for the determination of vapour pressure at various temperatures helps in finding the best conditions for the preparative separation

* For compound abbreviations, see the legend to Fig. 2.

of pure isomers, and the knowledge of V_o versus p_o correlations allows simulated distillation techniques to be applied to the characterization of complex hydrocarbon mixtures.

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