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INFLUENCE OF VAPOUR PRESSURE, ACTIVITY COEFFICIENT AND STRUCTURE ON THE RETENTION VOLUMES OF BRANCHED-CHAIN NONANES

GIANRICO CASTELLO and GIUSEPPINA D'AMATO

Istituto di Chimica Industriale, Università di Genova, Via Pastore 3, 16132 Genova (Italy)

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SUMMARY

The specific retention volumes, V_g , of all of the isomers of nonane have been measured on a 20% SF-96 column at 80°C, and the vapour pressures, p_0 , at the same temperature have been calculated by three methods and extrapolated from the values for the light isomers. There is a satisfactory agreement between the values of p_0 obtained from an Antoine-type equation, by a method based on the entropy of vaporization, and from extrapolation, and this permits the calculation of p_0 for the heavier isomers. The values of the activity coefficient, γ , which indicate the effect of the solute-solvent interaction on the gas chromatographic behaviour of the compounds, have been calculated and correlated with the molecular structure, the number of quaternary, tertiary, secondary, and primary carbon atoms and the "secondary" methyl groups of the compounds.

INTRODUCTION

In a previous study¹ the specific retention volumes, V_g , of all of the branched-chain hexanes, heptanes and octanes were measured on a 20% SF-96 column at 80, 100 and 120°C, and the vapour pressures, p_0 , at the same temperatures were calculated. Narrow-grid graphs of $\log V_g$ as a function of $\log p_0$ showed a fine structure depending on the molecular branching, and a positive curvature due 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 (GC) 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). The extrapolation of these parameters can permit the calculation of the retention values of higher compounds of the homologous series when authentic reference samples are not available, and therefore the identification of complex mixtures of branched paraffins, obtained on radiolysis²⁻⁴ or on other decomposition or synthetic processes.

In order to check the precision of the results obtained with this technique, and to expand the possibilities of the method to homologous groups of branched

alkanes with more complex structure, the retention volumes of the branched nonanes have been measured, and their p_0 and γ values calculated and correlated with those of smaller paraffins previously studied and with the molecular structure.

EXPERIMENTAL AND RESULTS

Determination of V_g

All of the isomers of nonane were analyzed on a column (4 m \times 0.25 in. O.D.) filled with 20% (w/w) SF-96 methylsilicone on Chromosorb P (DMCS), 60–80 mesh, using a Varian Aerograph 1520 gas chromatograph with a thermal-conductivity detector and proportional temperature control. The carrier gas (helium) flow-rate was 43 ml/min. The choice of SF-96 as liquid phase instead of squalane has been previously discussed¹ and is mainly due to its higher temperature limit and to its wide use for the analysis of heavy hydrocarbons with temperature programming. The specific retention volumes were calculated by the method of Littlewood *et al.*⁵

The analyses were made at 80 (\pm 0.2) $^\circ$ C because of the better resolution of most isomers at this temperature. As previously seen⁶, the different temperature dependences of the retention values cause an inversion of the elution order of some isomers at different temperatures and a coincidence of peaks at intermediate temperatures. The temperature of 80 $^\circ$ C gave the lowest number of corresponding V_g values for different isomers. A better resolution should be achieved with longer packed or open tubular columns, but the separation obtained was satisfactory. The values of V_g for the nonanes at 80 $^\circ$ are shown in Table I.

Calculation of p_0

The values of the saturation vapour pressure, p_0 , of the solute at the analysis temperature can be calculated in different ways. The previous comparison of the results¹ showed that the interpolation of vapour-pressure values by Stull^{7,8} and the use of Schlessinger's equation⁹ give high values. The use of an Antoine-type equation¹⁰

$$\log p_0 = A - [B/(C + t)] \quad (1)$$

where t is the temperature in $^\circ$ C and A , B and C are constants taken from A.P.I. tables¹¹, gave the best approximation, as demonstrated by plotting p_0 as a function of $\log V_g$ and of n for various homologous series. Unfortunately the constants A , B and C are not available for paraffins higher than decanes and for other homologous series, and do not allow the calculation of V_g from vapour-pressure data.

The method of Hass and Newton¹² permits the calculation of p_0 at any temperature, starting from the boiling point at standard or reduced pressure, and using the formula

$$\log p_0 = 2.8808 - \frac{\varphi \Delta t}{T - 0.15 \Delta t} \quad (2)$$

where T is the analysis temperature in $^\circ$ K, Δt is the difference between the boiling point at standard pressure and T , and φ is the entropy of vaporization at 760 torr. The entropies of vaporization are plotted for different homologous series and permit the calculation of p_0 for compounds other than hydrocarbons. An application of this

TABLE I

SPECIFIC RETENTION VOLUMES, V_g , AND VAPOUR PRESSURES, p_0 (CALCULATED FROM EQNS. 1 AND 2) FOR NONANES AT 80 °C

Column (4 m × 0.25 in. O.D.) packed with 20% SF-96 on Chromosorb P (60-80 mesh).

No.		V_g	p_0	
			Eqn. 1	Eqn. 2
1	<i>n</i> -Nonane	297.2	72.7	75.5
2	2-Methyloctane	241.3	95.9	98.3
3	3-Methyloctane	250.5	93.8	95.1
4	4-Methyloctane	239.6	100.2	100.1
5	3-Ethylheptane	246.8	99.0	99.3
6	4-Ethylheptane	224.0	105.9	105.9
7	2,2-Dimethylheptane	166.3	141.1	140.1
8	2,3-Dimethylheptane	224.0	109.6	108.4
9	2,4-Dimethylheptane	170.1	138.3	148.8
10	2,5-Dimethylheptane	191.6	125.2	126.2
11	2,6-Dimethylheptane	183.3	127.4	129.5
12	3,3-Dimethylheptane	197.4	124.4	121.6
13	3,4-Dimethylheptane	229.1	109.6	107.6
14	3,5-Dimethylheptane	191.6	125.5	125.7
15	4,4-Dimethylheptane	183.3	132.5	129.5
16	3-Ethyl-2-methylhexane	211.1	119.3	117.7
17	4-Ethyl-2-methylhexane	176.6	136.6	135.6
18	3-Ethyl-3-methylhexane	224.0	112.3	108.3
19	4-Ethyl-3-methylhexane	224.0	110.5	108.3
20	2,2,3-Trimethylhexane	171.4	140.7	136.0
21	2,2,4-Trimethylhexane	131.1	176.5	172.1
22	2,2,5-Trimethylhexane	127.3	191.1	183.2
23	2,3,3-Trimethylhexane	203.4	124.8	118.9
24	2,3,4-Trimethylhexane	217.5	118.3	113.9
25	2,3,5-Trimethylhexane	159.1	148.9	147.0
26	2,4,4-Trimethylhexane	156.7	157.3	150.4
27	3,3,4-Trimethylhexane	222.4	114.6	108.2
28	3,3-Diethylpentane	265.9	96.1	88.9
29	3-Ethyl-2,2-dimethylpentane	176.6	140.3	135.6
30	3-Ethyl-2,3-dimethylpentane	252.4	101.2	93.9
31	3-Ethyl-2,4-dimethylpentane	197.4	127.8	122.9
32	2,2,3,3-Tetramethylpentane	217.5	117.7	108.8
33	2,2,3,4-Tetramethylpentane	159.1	148.0	139.2
34	2,2,4,4-Tetramethylpentane	126.3	209.7	197.4
35	2,3,3,4-Tetramethylpentane	227.4	112.2	104.3

method to the calculation of the boiling points of alkyl iodides gave satisfactory results¹⁵. In the case of branched nonanes the availability of the A.P.I. constants for the Antoine equation permits a comparison of the two methods whose results are reported in Table I. The values from eqn. 2 are higher for strongly branched alkanes (trimethylhexanes, etc.), but the values of p_0 obtained by the two equations are similar and from these results one can argue that the use of eqn. 2 will give almost satisfactory results when the constants of eqn. 1 are not available.

An extrapolation method can also be used in order to calculate values of p_0 for higher homologues when the vapour pressures of the first terms of the series are

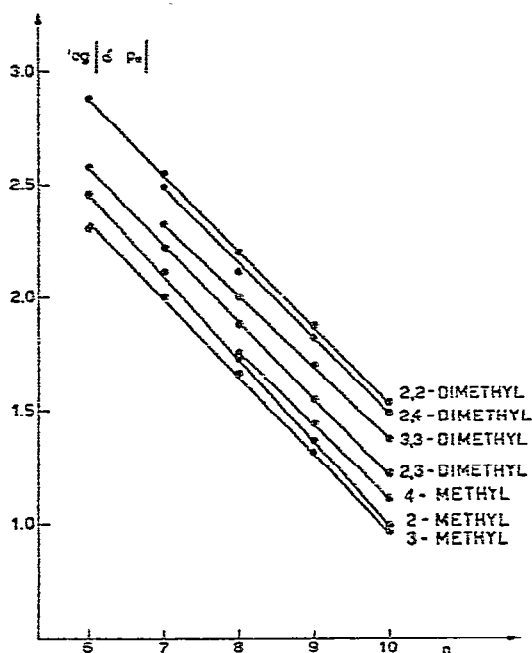


Fig. 1. Linear dependence of $\log |\delta p_0|$ on the number of carbon atoms, n , for various homologous series of branched-chain alkanes.

known. On plotting $\log |\delta p_0|$ (where δ is the difference between the value of any parameter for the branched-chain and the linear isomers) as a function of the number of carbon atoms, n , straight lines were obtained for various homologous series (Fig. 1). The corresponding gradients, g_1 , are in Table II.

$$\log |\delta p_0| = g_0 + g_1 n \quad (3)$$

Similar values can be calculated for other homologous series, with a confidence limit depending on the number of light isomers whose values of p_0 are known from the A.P.I. tables or from other sources.

TABLE II

GRADIENTS, g_1 , OF EQN. 3 FOR VARIOUS HOMOLOGOUS SERIES OF BRANCHED-CHAIN ALKANES AT 80°C

Homologous series	g_1
2-Methylalkanes	-0.363
3-Methylalkanes	-0.331
4-Methylalkanes	-0.318
2,2-Dimethylalkanes	-0.347
2,3-Dimethylalkanes	-0.340
2,4-Dimethylalkanes	-0.340
3,3-Dimethylalkanes	-0.315

Calculation of γ

The activity coefficients, γ , correlated with the solute-solvent interaction¹⁴⁻¹⁷, were calculated from V_g and p_0 values (Table I) and normalized as previously¹ for the "ideal" case by multiplying the Ambrose expression of V_g ^{18,19} by the ratio of solvent/solute molecular weights. For analysis of isomeric compounds on the same liquid phase this ratio is a constant, and changes in the values of γ depend therefore on differences of solute-solvent interactions due to the structure of the solute. In the first column of Table III are the values of γ obtained by using the measured V_g values and p_0 calculated from eqn. 1.

TABLE III

ACTIVITY COEFFICIENTS, γ , CALCULATED FROM THE VALUES OF p_0 (TABLE I, EQN. 1), CODE NUMBERS AND THE NUMBER OF SECONDARY METHYL GROUPS, M , OF NONANES

No.		γ	Code	M
1	<i>n</i> -Nonane	6.14	2700	2
2	2-Methyloctane	5.73	3510	1
3	3-Methyloctane	5.64	3510	2
4	4-Methyloctane	5.53	3510	2
5	3-Ethylheptane	5.43	3510	3
6	4-Ethylheptane	5.59	3510	3
7	2,2-Dimethylheptane	5.65	4401	1
8	2,3-Dimethylheptane	5.40	4320	1
9	2,4-Dimethylheptane	5.64	4320	1
10	2,5-Dimethylheptane	5.53	4320	1
11	2,6-Dimethylheptane	5.68	4320	0
12	3,3-Dimethylheptane	5.40	4401	2
13	3,4-Dimethylheptane	5.28	4320	2
14	3,5-Dimethylheptane	5.52	4320	2
15	4,4-Dimethylheptane	5.47	4401	2
16	3-Ethyl-2-methylhexane	5.27	4320	1
17	4-Ethyl-2-methylhexane	5.54	4320	2
18	3-Ethyl-3-methylhexane	5.28	4401	3
19	4-Ethyl-3-methylhexane	5.36	4320	3
20	2,2,3-Trimethylhexane	5.50	5211	1
21	2,2,4-Trimethylhexane	5.73	5211	1
22	2,2,5-Trimethylhexane	5.46	5211	0
23	2,3,3-Trimethylhexane	5.23	5211	1
24	2,3,4-Trimethylhexane	5.16	5130	1
25	2,3,5-Trimethylhexane	5.60	5130	0
26	2,4,4-Trimethylhexane	5.38	5211	1
27	3,3,4-Trimethylhexane	5.21	5211	2
28	3,3-Diethylpentane	5.19	4401	4
29	3-Ethyl-2,2-dimethylpentane	5.36	5211	2
30	3-Ethyl-2,3-dimethylpentane	5.19	5211	2
31	3-Ethyl-2,4-dimethylpentane	5.26	5130	1
32	2,2,3,3-Tetramethylpentane	5.19	6102	1
33	2,2,3,4-Tetramethylpentane	5.64	6021	0
34	2,2,4,4-Tetramethylpentane	5.01	6102	1
35	2,3,3,4-Tetramethylpentane	5.20	6201	0

DISCUSSION

The lower the solute-solvent interaction, the higher is the value of γ , which therefore decreases with the degree of branching of the compound¹. When isocodal groups are considered²⁰, and isomers having the same number of primary, secondary, tertiary and quaternary carbon atoms and an increasing number of "secondary" methyl groups are compared, a regular trend in γ values is found. In Table III are the code numbers and the number of secondary methyl groups, M , for each compound.

Some observations on the most populated isocodal groups can be made. The code number 3510 is common to methyloctanes and ethylheptanes. The assumption that the retention index of isocodal isomers increases with increasing M is not verified for different structures having the same code number. In fact, the value for 4-ethylheptane ($M = 3$) is in the range of those of the methyloctanes ($M = 2$). The γ values for the methyloctanes decrease with decreasing distance of the methyl group from the centre of the compound. This is a general behaviour for internal branching. The higher value of γ for 4-ethylheptane than for 3-ethylheptane may be surprising, therefore, but 3-ethylheptane has two ethyl groups which may cause a stronger interaction. This effect of the ethyl group is confirmed by some other isocodal pairs having the same values of M : 3,3- and 4,4-dimethylheptane; and 2,4- and 2,5-dimethylheptane.

The 4401 group shows a regular decrease on γ with increasing M , and 3,3- and 4,4-dimethylheptane, having the same M value, exhibit the above effect due to the ethyl group. The 4320 group contains all of the dimethylheptanes which do not possess quaternary carbon atoms (last digit of the code equal to zero), and 4-ethyl-3-methylhexane. The γ values decrease with increasing M and when the tertiary carbon atoms are near to each other and to the centre of the chain. Trimethylhexanes having a tertiary and a quaternary carbon atom belong to the 5311 group and (except for 3,3,4- and 2,2,5-trimethylhexane) have $M = 1$. Their γ values decrease when the quaternary and tertiary carbon atoms are near to the middle of the chain and when they are adjacent.

Table IV shows the effects of structure on isocodal trimethylhexanes. The anomalous position of 2,2,5-trimethylhexane which, with $M = 0$, should have the highest γ value, *i.e.*, the lowest solute-solvent interaction²⁰, may be due to the absence of characteristic groups other than external quaternary and tertiary carbon atoms. The effectiveness of groups in reducing the solute-solvent interaction actually decreases in the order external quaternary, internal quaternary, internal tertiary, external tertiary, secondary carbon atom between tertiary and quaternary and adjacent tertiary and quaternary carbon atoms, and the effects are additive²¹. The greatest effect of an external quaternary carbon atom is shown by the 5211 group, with $M = 2$, where 3-ethyl-2,2-dimethylpentane has the highest value of γ (Table III). The γ values for the 5130 group increase with M , and the terminal ethyl group explains the low value for 2,3,4-trimethylhexane. The 6102 group contains only two isomers, but the dependence of γ on M is also verified. As previously observed¹, the use of retention-index values²⁰ instead of γ does not permit this regular behaviour as a function of structure to be observed for all groups. The V_g values, and therefore the retention-index values, depend on γ and p_0 , and the effect of structural changes on these two parameters is not the same.

TABLE IV

NUMBER OF SECONDARY METHYL GROUPS, ACTIVITY COEFFICIENTS AND STRUCTURE FOR 5211 CODED TRIMETHYLHEXANES

Compound	M	γ	Characteristic groups*
2,2,4-Trimethylhexane	1	5.73	EQ + IT + JO
2,2,3-Trimethylhexane	1	5.50	EQ + IT + TQ
2,2,5-Trimethylhexane	0	5.46	EQ + ET
2,4,4-Trimethylhexane	1	5.38	IQ + ET + JO
2,3,3-Trimethylhexane	1	5.23	IQ + ET + TQ
3,3,4-Trimethylhexane	2	5.21	IQ + IT + TQ

* E = External; I = internal; Q or T = quaternary or tertiary carbon atom; TQ = adjacent tertiary and quaternary and JO = secondary carbon atom between tertiary and quaternary atoms (joint)^{6,21}.

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