

SPECIFIC RETENTION VOLUMES FOR C₅-C₁₂ ALKANE SOLUTES IN THE SERIES OF HOMOLOGOUS *n*-ALKANES, *n*-C₂₈, *n*-C₃₂ AND *n*-C₃₆ AND SQUALANE

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INTRODUCTION

Although the major emphasis in gas-liquid chromatography (GLC) is on quantitative and qualitative analysis, increasing use is being made of the technique for physico-chemical studies, particularly solution thermodynamics¹⁻¹¹.

Frequently the choice of a suitable stationary phase in GLC depends on the activity coefficients of the compounds to be separated, the best separation of compounds having similar boiling points being achieved with a stationary phase which makes the relative activity coefficients as far removed from unity as possible.

It would be an advantage, therefore, if stationary phases could be selected to carry out a required separation without recourse to excessive experimental trial and error. A promising approach to such stationary phase selection is by the study of solution thermodynamics^{4,7,10}. However, before such a procedure can become reliable, data must be obtained for a wide variety of systems, so that relationships between stationary phase properties and performance can be used with confidence.

As a first step in studying the solution thermodynamics of systems encountered in GLC, several workers^{4-7,9} have determined specific retention volumes. The present work sets out to obtain specific retention volume data for aliphatic hydrocarbons in the carbon number range C₅ to C₁₂, on the hydrocarbon stationary phases, squalane, *n*-C₂₈, *n*-C₃₂ and *n*-C₃₆, over the temperature range, 80° to 120°C.

The data obtained are compared with those determined by other workers when available, and the degree of reproducibility between different workers examined.

Few earlier references have included a closely related series of *n*-alkane solvents and frequently single temperatures have limited the usefulness of the results. In addition, the inclusion of a range of *n*-alkane solutes, *n*-C₅ to *n*-C₁₂, permits application of the retention index system of Kováts.

THEORETICAL

The specific retention volume, V_g , is obtained from experimental quantities by the equation:

$$V_g = \frac{F_{cl}}{w} \frac{(p_0 - p_{H_2O})}{p_0} \cdot j \cdot \frac{273}{T_m} \quad (1)$$

where

- F_c = corrected gas flow rate measured at ambient temperature, T_m °K
 t = time between "air" and sample peak maxima
 w = weight of stationary phase in column
 j = compressibility factor,

$$\frac{3}{2} \left[\frac{\left(\frac{p_i}{p_o}\right)^2 - 1}{\left(\frac{p_i}{p_o}\right)^3 - 1} \right]$$

p_i = inlet pressure

p_o = outlet pressure

$$\left(\frac{p_o - p_{H_2O}}{p_o}\right) = \text{correction for partial pressure of water vapour in flowmeter at } T_m \text{ °K.}$$

The specific retention volume is related to the partition coefficient K , defined as the ratio of the weight of solute per unit volume in the liquid phase to that in the gas phase, at infinite dilution, by the equation:

$$V_g = \frac{273 K}{T \rho} \quad (2)$$

where

ρ = density of stationary phase at the column temperature, T °K

The solution thermodynamic data which may be derived from specific retention volumes (paper pending) may be outlined as follows:

The partition coefficient may be related to the activity coefficient, γ^∞ , of the solute in the solvent at infinite dilution, taking the pure solute liquid as the standard state, by the expression:

$$K = \rho \frac{RT}{M \gamma^\infty p^\circ} \quad (3)$$

where

M = molecular weight of solvent

p° = vapour pressure of the solute at the column temperature, T °K

R = gas constant

This expression assumes ideal behaviour in the gas phase.

Since

$$K = \frac{V_g T \rho}{273} \quad (4)$$

$$V_g = \frac{273 R}{M \gamma^\infty p^\circ}$$

Thus the activity coefficient may be determined from the specific retention volume without a knowledge of the density of the stationary phase at the operating

temperature. For non-ideal behaviour in the gas phase, p° may be replaced by the fugacity. However, where fugacities are not available corrections may be made to γ^{∞} by using second virial coefficients.

A number of workers have discussed¹²⁻¹⁴ and used^{1,3,8} this method.

The activity coefficient may be expressed in terms of excess partial molar heat, ΔH^E , entropy, ΔS^E , and free energy, ΔG^E , of solution, by the equations:

$$\Delta G^E = \Delta H^E - T\Delta S^E \quad (5)$$

$$\Delta G^E = RT \ln \gamma^{\infty}_f \quad (6)$$

$$\frac{d \ln \gamma^{\infty}_f}{dT} = \frac{-\Delta H^E}{RT^2}$$

where

γ^{∞}_f = the activity coefficient corrected for gas phase imperfection.

The excess partial molar heat of solution can therefore be obtained at infinite dilution from the gradient of a plot of $\log \gamma^{\infty}_f$ against $1/T$. Inserting ΔH^E and γ^{∞}_f in eqn. 5, ΔS^E can be obtained readily for any value of T .

The heat of solution, ΔH_s , may be obtained from the gradient of the plot of $\log K$ against $1/T$, since

$$\log K = \frac{-\Delta H_s}{2.3RT} + C \quad (7)$$

The activity coefficient data may also be analysed in terms of Miller-Guggenheim's, or Flory-Huggins' theory as followed by ASHWORTH AND EVERETT¹⁵ and MARTIRE^{5,9}.

EXPERIMENTAL

The apparatus used for this study was constructed in the laboratory (Fig. 1). The salient features of the apparatus are given below.

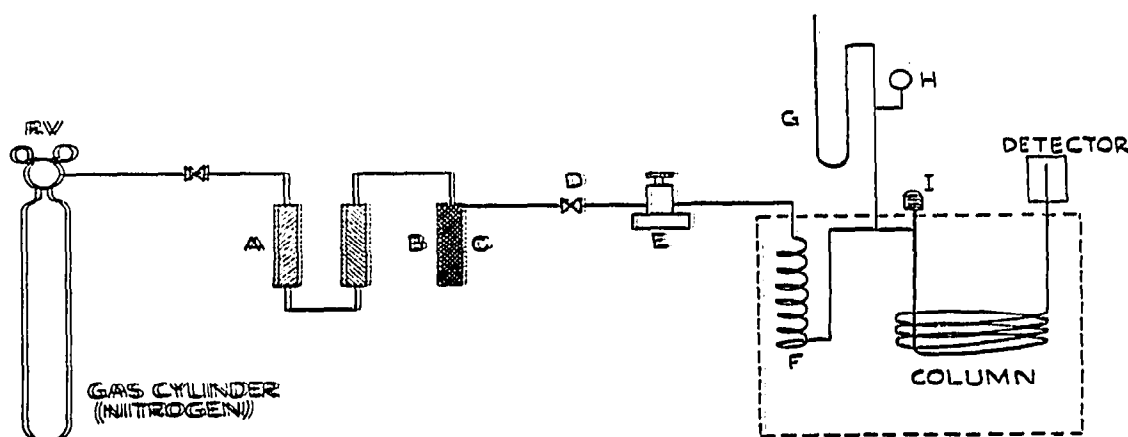


Fig. 1. Carrier gas flow diagram. (A) Brass cylinder, I.D. 1 in., wall 1/16 in., length 2 ft., packing 20-30 mesh calcium sulphate. (B) Brass cylinder (similar dimensions to A), packing 30 mesh activated charcoal. (C) Brass cylinder (same diameter as A & B but length 1 ft.), packing 1/8 in. diameter stainless steel, 80 mesh, gauze rings. (D) On/off valve. (E) Negretti & Zambra precision control valve, Type R 182. (F) Copper spiral, length 6 ft. (G) Mercury manometer. (H) 0-30 p.s.i. Foxboro pressure gauge. (I) Injection port. (RV) Reduction valve of gas cylinder.

Carrier gas

Dry, oxygen-free, nitrogen was controlled by a Negretti and Zambra precision pressure regulator and needle valves. The pressure difference across the column was determined with a mercury manometer and the gas flow measured by a thermostated soap-film meter. The outlet pressure was atmospheric at all times. The pressure differential was measured to ± 0.1 mm and over a period of 4-5 h remained constant to within ± 0.5 mm. The flow rate was found to vary by less than 1% over a similar period, and the error in a particular flow rate, which was determined before and after each sample injection, was 0.2%.

Thermostat

The thermostat was an electrically heated oil bath, the oil being circulated from a Colora Ultrathermostat. The temperature of the columns was determined by mercury in glass thermometers, which had been calibrated at the National Physical Laboratory. Fluctuations in temperature of the order of $\pm 0.01^\circ\text{C}$ were observed as short-term effects over a period of 4 to 5 min.

Stationary phases and preparation of packing

The stationary phases used were *n*-octacosane (*n*-C₂₈), squalane, *n*-dotriacontane (*n*-C₃₂) and *n*-hexatriacontane (*n*-C₃₆). *n*-C₂₈, *n*-C₃₂ and *n*-C₃₆ were obtained from the Aldrich Chemical Co. Ltd. and squalane from the British Petroleum Co. Ltd. The *n*-alkanes were purified by recrystallization from ethyl acetate and isooctane. Purities were determined by high-temperature GLC. Table I contains purities, densities, and density temperature coefficients for the stationary phases.

TABLE I
STATIONARY PHASES

<i>Alkane</i>	<i>Purity</i> (% <i>wl.</i>)	<i>M.p.</i> ($^\circ\text{C}$)	<i>Density</i> (ρ) (g/ml)	$d\rho/dt$ (g/ml/ $^\circ\text{C}$)
<i>n</i> -C ₂₈	>99.5	61.5-61.9	0.7796 (61.6 $^\circ$)	-0.000615 (60 $^\circ$ to 100 $^\circ$)
Squalane	>99.5	—	0.7710 (80.0 $^\circ$)	-0.000649 (80.0 $^\circ$ to 120 $^\circ$)
<i>n</i> -C ₃₂	>99.9	69.5-69.7	0.7816 (70.3 $^\circ$)	-0.0006224 (70.3 $^\circ$ to 140 $^\circ$)
<i>n</i> -C ₃₆	>99.0	75.8-76.2	0.7819 (75 $^\circ$)	-0.000613 (74.6 $^\circ$ to 100 $^\circ$)

The support used throughout was 70-80 mesh non-acid washed Chromasorb G* (Johns-Manville Co. Ltd.). Before use the support was dried under vacuum at 150 $^\circ$ for 5 h. The stationary phases were spread on the support by the technique of dissolving a weighed amount of material in a volatile solvent and forming a slurry with the support, followed by evaporation with gentle rotation. The solvent used was redistilled spectroscopic grade cyclohexane. The amount of stationary phase on the support was

* J.J.'s M support has similar properties.

determined by triplicate soxhlet extractions with cyclohexane. The liquid loadings in all cases was 6.3 to 6.4 % wt.

Columns

Columns were constructed from stainless steel tubing 0.42 cm I.D., 160 cm long, which had been thoroughly cleaned. Connections were made with standard compression fittings. The columns were packed by pouring in the packing while vibrating the tube and the weight of packing accurately determined. The column was then wound into a spiral 13 cm diam. and 3 cm deep. Peak efficiencies were about 2,000 plates.

Sample injection and sample size

The sample to be run was drawn into a 10 μ l Hamilton syringe up to the 5 μ l mark and then the syringe barrel emptied, 5 μ l of methane were then drawn into the syringe. The barrel of the syringe now contained solute vapour and methane. By injecting small samples of this mixture, 1 to 2 μ l, extremely small samples of solute, plus an internal "air" peak marker, could be introduced on to the column. Injections were made through a self-sealing silicone rubber septum. Sample sizes injected by this method were in the range 1.0 to 0.1 $\cdot 10^{-3}$ μ l.

Detector

A hydrogen flame ionisation detector was employed. The outlet of the column was led directly to the tip of the detector jet by small bore, 0.01 in. I.D., tubing. By this means the column effluent passed to the detector rapidly and with a minimum of diffusion taking place. The detector standing current was of the order of $2 \cdot 10^{-12}$ A, this value rising to $6 \cdot 10^{-12}$ A as the temperature of the column was raised to 120°.

The detector was connected to a Vibron Portable Electrometer Type 37B, the input of which "floated" above earth at a polarizing potential of 120 V. The amplifier output was fed to a Leeds and Northrup, 0-5 mV, recorder, time for full-scale deflection being 0.25 sec.

Errors due to chart shrinkage and non-synchronous movement of the chart drive were found to be negligible.

Solutes

The solutes used were obtained from the British Petroleum Co. Ltd., and are listed in Table II with their purities.

EXPERIMENTAL PROCEDURE

To establish whether methane gave reliable values of apparatus hold up volume in the temperature range 80°-120°C, corrected retention volumes, V_R° , for methane were determined at two flow rates, at 80°, 100° and 120°C. Table III contains the results, which show that V_R° for methane is essentially independent of flow rate and temperature, indicating that sorption of methane by the column packing is negligibly small.

To minimise errors arising from loss of stationary phase from the column, the following procedure was adopted: The column temperature was set at 80°C and a

TABLE II

HYDROCARBON SOLUTES AND PURITY IN MOLES %

<i>Solute</i>	<i>Purity</i>	<i>Solute</i>	<i>Purity</i>
<i>n</i> -Pentane	99.99	<i>n</i> -Nonane	99.91
<i>n</i> -Hexane	99.99	2,2-Dimethylheptane	99.85
2-Methylpentane	99.97	2,2,5-Trimethylhexane	98.9
3-Methylpentane	99.8	2,2-Dimethyl-3-ethylpentane	99.87
2,2-Dimethylbutane	99.99	2,2,3,3-Tetramethylpentane	99.94
2,3-Dimethylbutane	99.97	<i>n</i> -Decane	98.4
<i>n</i> -Heptane	99.83	2,3-Dimethyloctane	98.0
2-Methylhexane	99.88	<i>n</i> -Undecane	99.99
3-Methylhexane	97.8	<i>n</i> -Dodecane	99.97
3-Ethylpentane	99.87		
2,2-Dimethylpentane	99.72		
2,3-Dimethylpentane	98.0		
2,4-Dimethylpentane	99.4		
3,3-Dimethylpentane	99.96		
2,2,3-Trimethylbutane	99.99		
<i>n</i> -Octane	99.98		
2-Methylheptane	99.0		
3-Methylheptane	98.0		
3-Ethylhexane	98.0		
2,3-Dimethylhexane	99.8		
2,5-Dimethylhexane	99.95		
2-Methyl-3-ethylpentane	99.0		
2,2,4-Trimethylpentane	99.96		
2,2,3-Trimethylpentane	99.3		
2,3,3-Trimethylpentane	99.3		
2,3,4-Trimethylpentane	99.77		
2,2,3,3-Tetramethylbutane	99.9		

TABLE III

CORRECTED RETENTION VOLUMES FOR METHANE

<i>Corrected flow rate (ml/min)</i>	<i>V_R^o (ml)</i>	<i>Temperature (°C)</i>
25.00	14.52	80
31.54	14.56	
25.29	14.42	100
31.51	14.68	
28.87	14.50	120
35.29	14.37	

sample containing *n*-pentane, *n*-hexane, *n*-heptane and *n*-octane run on the column at three different flow rates, three to four separate injections being made at each flow rate. The column temperature was then raised to 100°C and a similar procedure followed, except that the sample also contained *n*-nonane. Finally, the column temperature was increased to 120°C and the procedure repeated with the sample now containing *n*-decane as well as *n*-nonane. By this method, nine to twelve accurate

TABLE IV

SPECIFIC RETENTION VOLUMES FOR *n*-NONANE ON *n*-DOTRIACONTANE AT 120°C

Corrected flow rate (ml/min)	V_g (ml/g)
28.87	172.74
	172.44
	172.44
35.29	172.47
	172.29
	171.80
44.97	172.12
	171.90
	171.59
Mean 172.20	

values of the specific retention volume were obtained for the normal alkanes up to *n*-decane at 120°C.

The specific retention volumes of other solutes were then determined by obtaining relative retention data using the normal alkanes as internal standards. The specific retention volumes were calculated from the mean of three values of the relative retention determined separately, and the mean of the nine to twelve values of specific retention volume for the standards.

Table IV contains specific retention volume data determined by this procedure for *n*-nonane on *n*-dotriacontane at 120°C, where the maximum variation from the mean is 0.3 %.

RESULTS

The specific retention data are contained in Tables V–VIII. The partition coefficient, K , may be derived from the equation:

$$K = \frac{V_g T \rho}{273.16} = V_g Q$$

The value of Q is given at the bottom of each column of data, such that the partition coefficient for any of the solute–solvent systems studied may be readily obtained. Also at the bottom of each column of data are values of b , *i.e.* the slope of the plot $\log V_g$ against solute carbon number, for the *n*-alkanes. The slope b may then be used to compute retention indices, I , from the equation:

$$I = 100 \left[\frac{\log \frac{V_{gx}}{V_{gN}} + N}{b} \right]$$

where V_{gx} is the specific retention volume of a solute and V_{gN} the specific retention volume of the reference *n*-alkane solute, containing N carbon atoms, and

$$V_{gN} \geq V_{gx} \geq V_{gN-1}$$

TABLE V

SPECIFIC RETENTION VOLUMES—*n*-OCTACOSANE AS STATIONARY PHASE

Hydrocarbon	80.0°C	100.0°C	120.0°C
<i>n</i> -Pentane	25.19	16.41	11.16
2,2-Dimethylbutane	35.14	22.83	—
2,3-Dimethylbutane	45.68	28.68	18.39
2-Methylpentane	46.11	28.68	18.49
3-Methylpentane	51.46	32.57	—
<i>n</i> -Hexane	60.67	36.18	22.92
2,2-Dimethylpentane	76.00	45.07	28.41
2,4-Dimethylpentane	78.55	—	—
2,2,3-Trimethylbutane	86.79	53.35	34.97
3,3-Dimethylpentane	102.9	62.29	40.03
2,3-Dimethylpentane	114.8	65.14	39.68
2-Methylhexane	106.5	60.83	37.44
3-Methylhexane	116.6	66.03	40.14
3-Ethylpentane	127.1	—	46.76
<i>n</i> -Heptane	142.4	78.70	46.45
2,2,4-Trimethylpentane	132.6	75.59	46.08
2,2,3,3-Tetramethylbutane	185.3	103.6	61.45
2,5-Dimethylhexane	178.3	—	—
2,2,3-Trimethylpentane	200.9	—	—
2,3,4-Trimethylpentane	226.9	—	—
2,3,3-Trimethylpentane	245.1	133.3	77.54
2-Methyl-3-ethylpentane	243.0	—	—
2,3-Dimethylhexane	239.5	127.3	72.36
2-Methylheptane	245.1	130.2	73.54
3-Ethylhexane	263.9	—	—
3-Methylheptane	261.2	138.1	78.25
<i>n</i> -Octane	330.9	168.5	93.04
2,2,5-Trimethylhexane	—	145.3	81.59
2,2-Dimethylheptane	—	191.4	—
2,2-Dimethyl-3-ethylpentane	416	—	—
2,2,3,3-Tetramethylpentane	540	273.9	—
<i>n</i> -Nonane	—	357.1	183.8
2,3-Dimethyloctane	—	551	280.2
<i>n</i> -Decane	—	758	363.6
<i>n</i> -Undecane	—	—	720
<i>n</i> -Dodecane	—	—	1427
Conversion factor <i>Q</i>	0.9916	1.0310	1.0686
<i>b</i> value	0.373	0.337	0.307

TABLE VI
SPECIFIC RETENTION VOLUMES—SQUALANE AS STATIONARY PHASE

Hydrocarbon	80.0°C	100.0°C	120.0°C
<i>n</i> -Pentane	25.73	116.31	111.02
2,2-Dimethylbutane	35.38	—	—
2-Methylpentane	46.93	29.45	—
3-Methylpentane	53.71	33.95	—
<i>n</i> -Hexane	61.28	35.93	22.60
2,2,3-Trimethylbutane	90.57	—	—
2,3-Dimethylpentane	116.99	64.38	—
2-Methylhexane	107.8	61.41	—
3-Methylhexane	117.5	66.53	—
<i>n</i> -Heptane	142.9	77.17	45.17
2,2,4-Trimethylpentane	135.4	—	—
2,2,3,3-Tetramethylbutane	189.1	—	—
2,5-Dimethylhexane	185.3	—	—
2,3-Dimethylhexane	243.6	126.5	—
2-Methylheptane	246.8	129.2	—
3-Methylheptane	263.3	137.2	—
<i>n</i> -Octane	330.2	165.3	90.59
<i>n</i> -Nonane	—	350	178.4
2,3-Dimethyloctane	—	528	—
<i>n</i> -Decane	—	735	361
<i>n</i> -Undecane	—	—	725
<i>n</i> -Dodecane	—	—	1449
Conversion factor <i>Q</i>	0.9969	1.0357	1.0725
<i>b</i> value	0.3680	0.3307	0.3023

DISCUSSION

The specific retention volumes of hydrocarbons in squalane have been determined over a range of temperatures by various workers, and a comparison between these data and the data obtained in this work may be made where the temperatures employed correspond. Table IX contains data for aliphatic compounds in the carbon number range C₅ to C₈ at 80°C. The data due to BURNETT¹⁸ were not obtained directly by GLC, but by an entrainment technique where GLC was used to analyse the entraining gas stream. The data of DESTY AND SWANTON⁴ are not strictly comparable with the other data since the temperature in their case was 81°C.

Although the sample of results is small, statistical analysis has been carried out using the data for the *n*-alkanes. Table X contains 95% confidence limits for the mean

TABLE VII
 SPECIFIC RETENTION VOLUMES—*n*-DOTRIACONTANE AS STATIONARY PHASE

Hydrocarbon	80.0°C	100.0°C	120.0°C
<i>n</i> -Pentane	23.58	15.42	10.83
2,2-Dimethylbutane	32.44	21.16	—
2,3-Dimethylbutane	42.79	26.50	—
2-Methylpentane	42.12	27.28	17.85
3-Methylpentane	49.38	30.41	19.97
<i>n</i> -Hexane	56.89	34.04	22.41
2,2-Dimethylpentane	70.57	42.02	—
2,4-Dimethylpentane	—	42.64	—
2,2,3-Trimethylbutane	81.37	47.82	—
3,3-Dimethylpentane	95.89	—	—
2,3-Dimethylpentane	105.7	60.67	—
2-Methylhexane	108.9	57.07	34.60
3-Methylhexane	108.6	61.46	37.50
3-Ethylpentane	118.6	66.79	—
<i>n</i> -Heptane	132.8	73.52	43.55
2,2,4-Trimethylpentane	122.4	69.61	—
2,2,3,3-Tetramethylbutane	170.6	96.31	56.77
2,5-Dimethylhexane	165.9	90.14	52.31
2,2,3-Trimethylpentane	—	102.1	—
2,3,4-Trimethylpentane	210.7	—	—
2,3,3-Trimethylpentane	228.7	123.5	71.30
2-Methyl-3-ethylpentane	—	120.3	68.61
2,3-Dimethylhexane	220.3	118.0	66.94
2-Methylheptane	228.3	119.6	68.07
3-Ethylhexane	245.2	128.8	72.14
3-Methylheptane	242.9	127.3	72.29
<i>n</i> -Octane	308.1	156.8	87.22
2,2-Dimethylheptane	346	—	97.66
2,2-Dimethyl-3-ethylpentane	—	197.2	—
2,2,3,3-Tetramethylpentane	219.7	254.4	—
<i>n</i> -Nonane	—	331	172.2
<i>n</i> -Decane	—	696	335
<i>n</i> -Undecane	—	—	657
<i>n</i> -Dodecane	—	—	1281
Conversion factor <i>Q</i>	1.0026	1.0424	1.0804
<i>b</i> value	0.372	0.336	0.295

TABLE VIII

SPECIFIC RETENTION VOLUMES—*n*-HEXA TRIACONTANE AS STATIONARY PHASE

Hydrocarbon	80.0°C	100.0°C	120.0°C
<i>n</i> -Pentane	21.97	14.54	10.04
2,2-Dimethylbutane	30.48	19.64	—
2,3-Dimethylbutane	39.57	25.07	16.59
2-Methylpentane	40.15	25.10	—
3-Methylpentane	45.58	28.72	18.89
<i>n</i> -Hexane	53.13	31.99	20.36
2,2-Dimethylpentane	65.52	39.12	—
2,4-Dimethylpentane	66.69	39.75	—
2,2,3-Trimethylbutane	75.16	45.27	—
3,3-Dimethylpentane	88.85	52.86	—
2,3-Dimethylpentane	98.08	56.58	35.26
3-Methylhexane	100.6	—	35.55
3-Ethylpentane	109.8	—	38.03
<i>n</i> -Heptane	124.6	69.18	41.03
2,2,4-Trimethylpentane	114.2	64.90	—
2,2,3,3-Tetramethylbutane	159.5	—	52.83
2,5-Dimethylhexane	153.4	84.62	47.71
2,2,3-Trimethylpentane	173.1	95.72	—
2,3,4-Trimethylpentane	196.8	108.9	—
2,3,3-Trimethylpentane	213.7	116.2	66.23
2-Methyl-3-ethylpentane	210.2	112.9	63.32
2,3-Dimethylhexane	206.0	110.4	61.95
2-Methylheptane	211.4	111.8	—
3-Ethylhexane	227.9	122.3	66.33
3-Methylheptane	225.5	119.7	65.60
<i>n</i> -Octane	289.8	148.6	81.93
2,2,5-Trimethylhexane	—	—	70.46
2,2-Dimethylheptane	—	—	92.79
2,2-Dimethyl-3-ethylpentane	357	185.1	105.6
2,2,3,3-Tetramethylpentane	752	239.3	136.2
<i>n</i> -Nonane	—	310	162.1
<i>n</i> -Decane	—	—	319
<i>n</i> -Undecane	—	—	630
<i>n</i> -Dodecane	—	—	1253
Conversion factor <i>Q</i>	1.0069	1.0474	1.0859
<i>b</i> value	0.374	0.337	0.304

TABLE IX

COMPARISON OF SPECIFIC RETENTION VOLUMES OBTAINED BY VARIOUS WORKERS
Squalane stationary phase at 80°C.

<i>Solute</i>	<i>This work</i>	<i>Ref. 16</i>	<i>Ref. 2</i>	<i>Ref. 17</i>	<i>Ref. 18</i>	<i>Ref. 4</i>	<i>Ref. 19</i>
<i>n</i> -Pentane	25.73	26.0	24	25.1	27.3	24.7	25.1
2,2-Dimethylbutane	35.38	36.2					36.1
2-Methylpentane	46.93	49.8					
3-Methylpentane	53.71	56.6					
<i>n</i> -Hexane	61.28	63.9	62.5	60.7	64.1	61.7	60.7
3-Methylhexane	117.5	123					
<i>n</i> -Heptane	142.9	150	145	145	148	144	144.4
3-Methylheptane	263.3	278					
<i>n</i> -Octane	330.2	347	330	339	334	334	339
Year in which data were published	1966	1963	1960	1960	1963	1961	1958

TABLE X

95% CONFIDENCE LIMITS AND PRECISION

<i>Solute</i>	<i>95% C.L. for mean</i>	<i>Precision</i>
<i>n</i> -C ₅	25.33 ± 1.06	1.13
<i>n</i> -C ₆	62.13 ± 1.32	2.78
<i>n</i> -C ₇	145.6 ± 2.3	6.5
<i>n</i> -C ₈	335.9 ± 5.5	15.0

values. Analysis of variance indicates, at a 5% level of significance, that there is a real difference between the means of results for different laboratories. However, by inspection of data in Table IX it seems probable that the results of LITTLEWOOD¹⁶ and BURNETT¹⁸ are causing this by giving, on average, higher values than the others.

From the residual mean square, an overall estimate of precision has been calculated, *i.e.*, the value which would be exceeded in only one case in 20, by the difference between results from two laboratories for any one sample. This was found to be 0.0447 *m*, where *m* is the mean of the data for a particular *n*-alkane solute. Table X contains the separate precisions.

The above analysis indicates that there is a substantial measure of agreement between workers, which is encouraging when account is taken of such factors as varying origin of solutes and solvents, the probable differences in sample sizes and the different apparatus employed.

A similar comparison for the *n*-alkane solvents cannot be made since there is insufficient data in the literature, but a comparable order of precision could be anticipated.

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SUMMARY

Attention continues to be drawn to the need for reliable physico-chemical solution data to be derived by gas-liquid chromatography (GLC), for comparison with those derived from classical (static) procedures, to assist in the establishment of a more useful solution theory and, more immediately, to assess accurately the selectivity of GLC stationary phases.

A procedure based on a specially constructed gas chromatograph is used to determine specific retention volumes for thirty-five pure *n*-alkane solutes (C_5 - C_{12}) in pure *n*-octacosane, *n*-dotriacontane, *n*-hexatriacontane and squalane at 80.0, 100.0 and 120.0°C. Comparisons are made with earlier work, where there is an overlap (squalane), in order to assess the reliability of the data.

Data for the conversion of the specific retention volumes to partition coefficients and to Kováts' retention indices are provided.

REFERENCES

- 1 E. R. ADLARD, M. A. KHAN AND B. T. WHITHAM, in R. P. W. SCOTT (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, p. 251.
- 2 S. EVERED AND F. H. POLLARD, *J. Chromatog.*, 4 (1960) 451.
- 3 D. H. EVERETT AND C. T. H. STODDART, *Trans. Faraday Soc.*, 57 (1961) 746.
- 4 D. H. DESTY AND W. T. SWANTON, *J. Phys. Chem.*, 65 (1961) 766.
- 5 D. E. MARTIRE, in L. FOWLER (Editor), *Intern. Symp. Gas Chromatog., Instr. Soc. America, 4th, 1963*, p. 33.
- 6 S. H. LANGER AND J. H. PURNELL, *J. Phys. Chem.*, 67 (1963) 263.
- 7 D. E. MARTIRE AND L. Z. POLLARA, *Chem. Eng. Data*, 10 (1965) 40.
- 8 A. J. B. CRUIKSHANK, D. H. EVERETT AND M. T. WESTAWAY, *Trans. Faraday Soc.*, 61 (1965) 235.
- 9 D. E. MARTIRE, in A. B. LITTLEWOOD (Editor), *Gas Chromatography 1966*, Inst. Petroleum, London, 1967, p. 21.
- 10 R. E. PECSAR AND J. J. MARTIN, *Anal. Chem.*, 38 (1966) 1661.
- 11 N. PETSOV AND C. DIMITROV, *J. Chromatog.*, 23 (1966) 382.
- 12 D. H. DESTY, A. GOLDFUP, G. R. LUCKURST AND W. T. SWANTON, in M. VAN SWAAY (Editor), *Gas Chromatography 1962*, Butterworths, London, 1962, p. 67.
- 13 D. H. EVERETT, *Trans. Faraday Soc.*, 61 (1965) 1637.
- 14 G. R. LUCKURST, *J. Chromatog.*, 16 (1964) 543.
- 15 A. J. ASHWORTH AND D. H. EVERETT, *Trans. Faraday Soc.*, 56 (1960) 1609.
- 16 A. B. LITTLEWOOD, *J. Gas Chromatog.*, 1 (1963) 6.
- 17 T. HOFSTEE, A. KWANTES AND G. W. A. RIJNDERS, *Proc. Int. Symp. Dist., Brighton, 1960*, p. 105.
- 18 M. R. BURNETT, *Anal. Chem.*, 35 (1963) 1567.
- 19 A. KWANTES AND G. W. A. RIJNDERS, in D. H. DESTY (Editor), *Gas Chromatography 1958*, Butterworths, London, 1959, p. 125.