

THE APPLICATION OF GAS CHROMATOGRAPHY TO
THE DETERMINATION OF RETENTION DATA AND ACTIVITY
COEFFICIENTS OF SOME ALKANES, ALKYL NITRATES,
NITROALKANES AND ALCOHOLS ON SELECTED
STATIONARY PHASES

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It has been realised for some time that gas chromatography can be applied to the determination of some physical constants of some compounds, and its use in the analytical field is ever widening. Activity coefficients at infinite dilution for a number of alkanes and other substances on polar and non-polar solvents have been calculated by KWANTES AND RIJNDERS¹, and for a number of halogenated hydrocarbons in dinonyl phthalate (DNP) and Silicone oil 702² from the data of POLLARD AND HARDY³.

Little work on the gas chromatography of the simple alkyl nitrates has been reported^{4, 5}. GRAY AND PRATT⁶ have calculated the latent heats of vaporisation of methyl, ethyl, *n*- and iso-propyl, *n*- and iso-butyl nitrates by normal physical methods.

The activity coefficients from gas chromatographic measurements are here determined for the series ethyl to *n*-octyl nitrate, nitromethane to 1-nitrobutane and *n*-pentane to *n*-nonane on squalane and DNP as solvents. The selectivity of diglycerol was such that reproduceable results were only obtained for the series of nitroalkanes and a series of normal alcohols.

The expression used here for the activity coefficients at infinite dilution is that derived by PORTER, DEAL AND STROSS⁷ and KWANTES AND RIJNDERS¹, who have outlined the assumptions underlying its derivation. The expression is:

$$\gamma_p^0 = \frac{N_s RT}{k p_0}$$

where: N_s = the number of moles of solvent per unit volume at the column temperature $T^\circ\text{K}$.

R = the gas constant.

p_0 = the vapour pressure of the pure solute at $T^\circ\text{K}$.

k = the partition coefficient of the solute between the liquid and gas phases, given by:

$$V_R = V_m + kV_l$$

where: V_R = the retention volume, corrected for column pressure drop and temperature.

V_m = the dead volume of the column.

V_l = the volume of the solvent at $T^\circ\text{K}$.

The retention volume, measured at room temperature, has to be corrected to column temperature, thus bringing about the replacement of column temperature by ambient temperature in the top of the expression.

EXPERIMENTAL

The apparatus closely followed SCOTT's design for routine analysis^{8,9}. The column, of length 1 m, was heated by a vapour jacket containing successively boiling benzene, toluene and xylene, giving column temperatures of 80° , 111° and 139° respectively. The carrier gas was a 3:1 mixture of hydrogen and nitrogen whose flow, about 35 ml/min, was measured by a capillary flowmeter. The hydrogen flame detector was completely enclosed in the vapour jacket and so, to facilitate burning of the carrier gas at the jet, oxygen was introduced at about 110 ml/min. Inlet pressures were about 1.5 atmospheres.

The Pt-Ir/Rh-Au thermocouple, held 3 mm above the microflame, was maintained at column temperature; the thermo-e.m.f., balanced against a 4 V accumulator, was recorded on a 10 mV Elliot recorder.

The injection system was of SCOTT's design also, the capillary introducing samples of up to $1\ \mu\text{l}$. This is small enough to be within 1% of the limiting case of zero sample size.

The solid support was 60-80 mesh ground firebrick, holding 20% weight for weight of liquid phase. More than 15% has been found necessary to ensure the independence of γ_p^0 from the amount of solvent present.

Samples of ethyl nitrate and *n*-butyl to *n*-nonyl nitrates were kindly supplied by the Shell Petroleum Co., Ltd., and 1-nitropropane by the Ministry of Supply Research Establishment, Waltham Abbey. 1-Nitrobutane was prepared from *n*-butyl bromide and silver nitrite, and after redistillation, gave only one peak on the chromatogram.

RESULTS

The specific retention volume, V_g , is defined as V_R^0 , the retention volume fully corrected for dead volume, pressure drop across the column and measured at the column temperature, divided by the weight of the solvent.

Specific retention volumes and activity coefficients are shown in Tables I and II respectively, for the alkanes, alkyl nitrates and nitroalkanes on squalane and DNP. Specific retention volumes and activity coefficients of the alcohols and nitroalkanes on diglycerol are given in Table III.

TABLE I
SPECIFIC RETENTION VOLUMES ON SQUALANE AND DNP

<i>Solvent</i>	<i>Squalane</i>			<i>DNP</i>		
	<i>Temp.</i>	80°	111°	139°	80°	111°
Pentane		24	—	—	15.5	—
Hexane		62.5	26.5	14	35.5	16.7
Heptane		145	54.5	27	80.5	34
Octane		330	115	49.5	147	71
Nonane		750	233	99	397	138
Ethyl nitrate		40	20.5	12	102	42
<i>n</i> -Propyl nitrate		105	42.5	22	215	80.5
<i>n</i> -Butyl nitrate		263	93	41.5	512	166
<i>n</i> -Amyl nitrate		610	194	88	1145	340
<i>n</i> -Hexyl nitrate		—	400	151	—	678
<i>n</i> -Heptyl nitrate		—	—	288	—	—
<i>n</i> -Octyl nitrate		—	—	550	—	—
Nitromethane		22.5	11.5	6.6	100	42.5
Nitroethane		48.5	23	13	193	71.5
1-Nitropropane		110	47	23.5	362	128
1-Nitrobutane		240	98	45.5	810	255

TABLE II
ACTIVITY COEFFICIENTS ON SQUALANE AND DNP

<i>Solvent</i>	<i>Squalane</i>			<i>DNP</i>		
	<i>Temp.</i>	80°	111°	139°	80°	111°
Pentane		0.66	—	—	1.0	—
Hexane		0.65	0.70	0.66	1.1	1.1
Heptane		0.67	0.69	0.68	1.2	1.2
Octane		0.70	0.71	0.72	1.6	1.2
Nonane		0.77	0.78	0.80	1.4	1.3
Ethyl nitrate		1.9	1.7	1.6	0.74	0.73
<i>n</i> -Propyl nitrate		1.5	1.4	1.4	0.72	0.71
<i>n</i> -Butyl nitrate		1.3	1.2	1.2	0.68	0.68
<i>n</i> -Amyl nitrate		1.3	1.3	1.3	0.72	0.71
<i>n</i> -Hexyl nitrate		—	1.2	1.2	—	0.70
<i>n</i> -Heptyl nitrate		—	—	1.3	—	—
<i>n</i> -Octyl nitrate		—	—	1.3	—	—
Nitromethane		5.7	6.4	5.7	1.0	1.3
Nitroethane		3.7	4.2	3.2	0.90	1.2
1-Nitropropane		2.8	3.2	2.4	0.85	1.1
1-Nitrobutane		2.7	3.0	2.0	0.83	1.1

TABLE III
SPECIFIC RETENTION VOLUMES AND ACTIVITY COEFFICIENTS ON DIGLYCEROL

	80°		111°	
	V_g	γ_p^0	V_g	γ_p^0
Nitromethane	58.5	5.1	—	—
Nitroethane	48.5	9.2	—	—
1-Nitropropane	52	11	—	—
1-Nitrobutane	66	26	—	—
Methanol	74.5	1.1	26.5	1.1
Ethanol	67	2.0	24.5	1.7
<i>n</i> -Propanol	85	3.4	29	3.3
<i>n</i> -Butanol	122	5.4	38.5	4.9
<i>n</i> -Pentanol	176	6.5	51.5	6.4
<i>n</i> -Hexanol	263	12	66	11

DISCUSSION

Figs. 1 and 2 show graphically the relationships of $\log V_g$ and number of carbon atoms (Fig. 1) and $\log V_g$ and reciprocal of column temperature (Fig. 2).

As is to be expected from the theory of gas-liquid chromatography, there is a linear relationship between $\log V_g$ and number of carbon atoms (Fig. 1), from which other members of the same series might be identified. It is interesting to note the order of elution of an alkyl nitrate and the 1-nitroalkane of the same carbon number. For example, on squalane at 80°, ethyl nitrate is eluted before nitroethane, *n*-propyl nitrate before 1-nitropropane, but *n*-butyl nitrate *after* 1-nitrobutane. This is shown in Fig. 1 by the fact that the lines for these two classes of compounds cross between carbon numbers 3 and 4. Again, since the lines for the same two classes of compounds on DNP at 80° converge as the carbon number increases, one can predict that the two compounds of carbon number 7 will be eluted together.

The relative separation efficiencies of the two solvents squalane and DNP are indicated by considering the ratio of the specific retention volumes of two adjacent compounds of an homologous series. Squalane proves to be more efficient than DNP in this respect. For instance, the mean ratio of the specific retention volumes of adjacent straight-chain alkanes is 2.34 on squalane, but 2.27 on DNP at the same temperature, showing that squalane is a slightly better solvent. Corresponding figures for the nitroalkanes are 2.20 and 1.99 respectively, and for the alkyl nitrates 2.48 and 2.25 respectively.

However, for the separation of an alkyl nitrate from the nitroalkane with the same number of carbon atoms, DNP proves to be far more efficient than squalane. Defining the Separation Factor as the ratio of the specific retention volume of a nitroalkane and that of the alkyl nitrate of the same carbon number, we arrive at the following conclusions from results tabulated in Table IV.

From this table, DNP proves to be about 1.6 times more efficient for the three comparisons possible—namely for the ethane, propane and butane nitro- and nitrate

ΔH_s varies from about 6–10 kcal/mole, and the value for an alkyl nitrate is generally approximately the same as that for the nitroalkane of the same carbon number—if anything, slightly higher. This situation is reversed in the case of ethyl nitrate (8.4 kcal/mole) and nitroethane (8.9 kcal/mole).

TABLE V
HEATS OF SOLUTION OF ALKYL NITRATES AND NITROALKANES ON SQUALANE
AND DNP IN KILOCALORIES/MOLE

	Squalane	DNP	ΔH_s
Nitromethane	5.9	7.3	8.2 (ref. ¹⁰)
Nitroethane	6.6	8.9	—
1-Nitropropane	7.5	9.0	—
1-Nitrobutane	8.1	9.9	—
Ethyl nitrate	5.9	7.8	7.92 (ref. ⁶) at b.p.
<i>n</i> -Propyl nitrate	7.6	8.4	8.58 (ref. ⁶) at b.p.
<i>n</i> -Butyl nitrate	9.1	9.9	9.40 (ref. ⁶) at 120°
<i>n</i> -Amyl nitrate	9.6	10.8	—

Vapour pressures

The vapour pressure of the pure solute appears in the expression for γ_p^0 . Vapour pressure-temperature relationships for the alkanes and nitroalkanes were readily available¹⁰. For ethyl, *n*-propyl and *n*-butyl nitrates, the equations derived by GRAY AND PRATT⁶ were used. These are of the form:

$$\log_{10} p(\text{mm Hg}) = A - \frac{B}{t(^{\circ}\text{C}) + D}$$

where *A*, *B* and *D* are constants for a given nitrate. These equations give good straight lines for $\log_{10} p$ against $1/T$ in the range 80–139°. The only information about vapour pressures of the higher nitrates was the following:

Compound	Boiling point (°C)
<i>n</i> -Butyl nitrate	34–36/15 mm Hg
<i>n</i> -Amyl nitrate	61/22 mm Hg
<i>n</i> -Hexyl nitrate	68/15 mm Hg
<i>n</i> -Heptyl nitrate	83–84/15 mm Hg
<i>n</i> -Octyl nitrate	100/13 mm Hg

The boiling points of *n*-amyl and *n*-hexyl nitrates were determined at 760 mm Hg as 157° and 180° respectively. *n*-Heptyl and *n*-octyl nitrates decomposed on heating. Thus two points were available for the *n*-amyl and *n*-hexyl nitrates and only one for the *n*-heptyl and *n*-octyl nitrates. From this information, and coupled with the more comprehensive information for the ethyl, *n*-propyl and *n*-butyl nitrates, the “most likely” lines were drawn for the *n*-heptyl and *n*-octyl nitrates, using the single point available for each nitrate.

Activity coefficients

Tables II and III show the values for γ_p^0 obtained on squalane, DNP and diglycerol. Those for the alkanes on squalane agree substantially with those obtained by KWANTES AND RIJNDERS¹. For example, KWANTES AND RIJNDERS calculate the values of γ^0 for heptane at 80°, 105° and 135° to be 0.68, 0.66 and 0.68 respectively. Our values at 80°, 111° and 139° are 0.67, 0.69 and 0.68 respectively. These results ($\gamma_p^0 < 1$) indicate the system of a non-polar solute in a non-polar solvent. The results for the nitroalkanes on squalane are not very reproducible, and this is probably due to the residual adsorption effects of the solid support on the polar solute. KWANTES AND RIJNDERS found that for all systems of the polar solute on non-polar solvent, skew peaks were given, with tailing, and retention times were dependent on sample size on all types of inorganic support. We observed tailing peaks for the nitroalkanes on squalane, using ground firebrick as support, and γ_p^0 was > 1 , indicating a marked difference in polarity of the solute and the solvent. So it seems clear that the nature of the solid support was influencing the retention time of the solute. This effect might have been nullified by the use of an inert support such as metal helices¹.

For the alkyl nitrates on squalane, γ_p^0 is only just > 1 , and not far greater than the figure for the corresponding alkane of the same carbon number. This would indicate that the molecule $R \cdot O \cdot NO_2$ is considerably less polar than the corresponding nitroalkane $R \cdot NO_2$. Moreover, the values of γ_p^0 for the alkyl nitrates on squalane are quite consistent with temperature, indicating that the effect of the solid support was negligible.

SUMMARY

Retention data are obtained for some normal alkanes, nitroalkanes, alkyl nitrates and alcohols on the stationary phases squalane, dinonyl phthalate and diglycerol. The relative separation efficiencies of the two solvents squalane and dinonyl phthalate with respect to the nitrogen-containing series, and activity coefficients and heats of solution are calculated. The relative polarities of some of the solutes and solvents and the effects of the solid support are also discussed.

REFERENCES

- ¹ A. KWANTES AND G. W. A. RIJNDERS, in D. H. DESTY, *Gas Chromatography*, Butterworth's Sci. Publ., London, 1958, p. 125.
- ² C. J. HARDY, *J. Chromatog.*, 2 (1959) 490.
- ³ F. H. POLLARD AND C. J. HARDY, *Anal. Chim. Acta*, 16 (1957) 135.
- ⁴ F. H. POLLARD AND C. J. HARDY, *Chem. & Ind. (London)*, (1955) 527.
- ⁵ F. H. POLLARD, A. E. PEDLAR AND C. J. HARDY, *Nature*, 174 (1954) 979.
- ⁶ P. GRAY AND M. W. T. PRATT, *J. Chem. Soc.*, (1957) 2163.
- ⁷ P. E. PORTER, C. H. DEAL AND F. H. STROSS, *J. Am. Chem. Soc.*, 78 (1956) 2999.
- ⁸ R. P. W. SCOTT, *Benzole Producers Ltd., Interim Research Report*, 55-11.
- ⁹ R. P. W. SCOTT, *Benzole Producers Ltd., Interim Research Report*, 57-23.
- ¹⁰ *International Critical Tables*, McGraw-Hill Book Co., New York, 1927.