

GAS-LIQUID CHROMATOGRAPHY IN QUALITATIVE ANALYSIS  
PART. III. THE CONSTANCY OF  $\Delta Me$  VALUES WITHIN  
HOMOLOGOUS SERIES AND RELATIONS WITHIN THE PERIODIC TABLE

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INTRODUCTION

A preliminary note<sup>1</sup> has suggested the usefulness of a new retention parameter ( $\Delta Me$ ) in gas-liquid chromatography. Extensions of the application of this parameter will be reported in this and subsequent papers.

EXPERIMENTAL

Chromatograms were obtained using an apparatus consisting of glass columns (5 ft. long and 4 mm I.D.) with a modified flame ionisation detector<sup>2</sup>. The carrier gas was a 3:1 (by volume) mixture of hydrogen and nitrogen. The columns were packed with a 20% w/w mixture of dinonyl phthalate (B.D.H.) and acid-washed (1% phosphoric acid) 60-72 mesh celite (J. J's, Ewell, Surrey). The columns were heated by means of vapour jackets, methanol 65°, and water 100°. Samples for analysis (~10  $\gamma$ ) were introduced by means of stainless steel capillary pipettes<sup>3</sup>. All the solutes used were obtained commercially except allyl methyl ether, sulphide and selenide, and di-*n*-butyl sulphide, selenide, and telluride which were kindly prepared by D. T. WOODBRIDGE of these laboratories.

Retention times were measured from the time of injection of the sample to the time of appearance of the peak maxima on the recorded chart and were corrected for the calculated "dead-time"<sup>4</sup> of the apparatus. *n*-Paraffins were used as internal standards to calculate retention ratios in  $R_{x9}$  units<sup>5</sup>.

THEORY

The "effective" molecular weight of the solute ( $Me$ ) has been defined<sup>1</sup> as:

$$Me = 14.026 \frac{\log_{10} R_{x9}}{b} + 128.25$$

where  $R_{x9}$  is the retention ratio relative to *n*-nonane<sup>5</sup> and  $b$  is the slope of the plot of  $\log_{10} R_{N9}$  against carbon number ( $N$ ) for the *n*-paraffins<sup>4</sup>. The former expression is a specific form of the general relation:

$$Me = 14.026 \frac{\log_{10} R_{xN}}{b} + M_N$$

where  $R_{xN}$  is the retention ratio with respect to the  $n$ -paraffin with  $N$  carbon atoms and molecular weight  $M_N$ .

$\Delta Me$  has been defined<sup>1</sup> by the relation:

$$\Delta Me = Me - M$$

where  $M$  is the molecular weight of the solute.

$\Delta Me$  can be regarded as a measure of the extent to which the parts of a molecule (*i.e.* electrons, dipoles, and hydrogen bonding sites etc.) can interact with the stationary phase relative to an  $n$ -paraffin of the same molecular weight. Thus, in general, functional groups having strong interactions with the stationary phase tend towards positive  $\Delta Me$  values whilst groups with screened electrons (*i.e.* subvalency electrons in high atomic weight elements and sterically hindered structures) tend towards negative  $\Delta Me$  values.

$\Delta Me$  should be expected to be constant within a homologous series, provided the interaction energy of the functional group in the solute with the stationary phase is independent of chain length. This is expected to prevail after the first few members of a homologous series.

#### RESULTS AND DISCUSSION

The  $\Delta Me$  values for the members of a number of homologous series at various temperatures are shown in Table I. The first few members of each series depart progressively from a constant value of  $\Delta Me$  as the chain length is reduced but with the exception of cyanides this is less than one  $\Delta Me$  unit. As this trend must in part be due to the high experimental error for rapidly eluted materials precise analyses of trends in this region are somewhat confused. However, from  $n$ -propyl upwards  $\Delta Me$  values are sensibly constant. The mean  $\Delta Me$  values in Table II have been "weighted" according to retention.

Standard statistical procedures suggest that the errors throughout these data could arise from a common cause. It therefore appears justified to take overall standard deviations at the various temperatures which provide a general indication of the reproducibility of the method and its variation with temperature. Thus with the exception of cyanide the overall standard deviation is comparable with or less than the experimental error in measuring retention<sup>4</sup> and shows a steady decrease with temperature.

The small variation of  $\Delta Me$  with temperature can be accurately represented by the expression:  $\Delta Me_\theta = \Delta Me_0 + \mu\theta$  (within the limits set by the standard deviation along a homologous series), where  $\Delta Me_0$  and  $\Delta Me_\theta$  are the values at 0° (calculated) and  $\theta^\circ\text{C}$  respectively and  $\mu$  is a constant. The values of  $\Delta Me_0$  and  $\mu$  in Table III were derived from the data in Table II.

In view of the virtually linear variation of many physico-chemical parameters (*e.g.* molar volume, parachor, spectroscopic frequencies) of a substituent with vertical position in the periodic table, it seemed likely that  $\Delta Me$  values would vary in the same way. In the case of the  $n$ -alkyl halides  $\Delta Me$  values (on 20% w/w DNP/celite) can with reasonable precision be represented by an equation of the form  $\Delta Me = \alpha + P(\beta + \gamma\theta)$  where  $\alpha$ ,  $\beta$  and  $\gamma$  are constants,  $\theta$  the column temperature in degrees centigrade, and  $P$  is the period of the periodic table in which the halide is situated

TABLE I

$R_{x0}$  AND  $Me$  VALUES FOR *n*-ALKYL CHLORIDES, BROMIDES, IODIDES, CYANIDES, THIOLS AND ALK-1-ENES  
(20% w/w dinonyl phthalate on 60-72 mesh celite)

Substance	20°			65°			100°		
	$R_{x0}$	$Me$	$b = \frac{0.490}{\Delta Me}$	$R_{x0}$	$Me$	$b = \frac{0.380}{\Delta Me}$	$R_{x0}$	$Me$	$b = \frac{0.314}{\Delta Me}$
1-Chloropropane	0.033	85.84	+ 7.34	—	—	—	—	—	—
1-Chlorobutane	0.106	100.35	+ 7.78	0.182	100.94	+ 8.37	0.250	101.35	+ 8.78
1-Chloropentane	0.333	114.67	+ 8.07	0.451	115.50	+ 8.90	0.525	115.75	+ 9.15
1-Chlorohexane	—	—	—	1.091	129.64	+ 9.02	1.104	130.17	+ 9.55
1-Chloroheptane	—	—	—	2.643	143.83	+ 9.18	2.310	144.50	+ 9.85
1-Chlorooctane	—	—	—	—	—	—	4.77	158.56	+ 9.89
1-Chlorodecane	—	—	—	—	—	—	20.15	186.50	+ 9.79
Bromoethane	0.027	83.36	— 25.62	0.063	83.93	— 25.05	—	—	—
1-Bromopropane	0.084	97.45	— 25.55	0.156	98.46	— 24.54	—	—	—
1-Bromobutane	0.259	111.45	— 25.58	0.381	112.78	— 24.25	0.470	113.60	— 23.43
1-Bromopentane	—	—	—	0.933	127.14	— 23.92	0.993	128.11	— 22.95
1-Bromohexane	—	—	—	2.233	141.13	— 23.95	2.054	142.21	— 22.87
1-Bromoheptane	—	—	—	5.40	155.29	— 23.82	4.275	156.43	— 22.68
1-Bromooctane	—	—	—	—	—	—	8.80	170.45	— 22.68
Iodomethane	0.027	83.35	— 58.60	0.065	84.43	— 57.52	—	—	—
Iodoethane	0.076	96.22	— 59.76	0.148	97.62	— 58.36	0.222	99.05	— 56.93
1-Iodopropane	0.228	109.90	— 60.11	0.355	111.64	— 58.37	0.463	113.31	— 56.70
1-Iodobutane	0.680	123.46	— 60.57	0.852	125.68	— 58.35	0.957	127.40	— 56.63
1-Iodopentane	—	—	—	2.033	139.62	— 58.44	1.960	141.30	— 56.75
1-Iodohexane	—	—	—	4.81	153.44	— 58.65	4.050	155.39	— 56.70
1-Iodoheptane	—	—	—	—	—	—	8.40	169.55	— 56.56
1-Iodooctane	—	—	—	—	—	—	17.08	183.32	— 56.82
Methyl cyanide	0.048	90.64	+ 49.54	0.098	91.01	+ 49.96	—	—	—
Ethyl cyanide	0.114	101.25	+ 46.17	0.194	101.96	+ 46.88	—	—	—
<i>n</i> -Propyl cyanide	0.316	113.93	+ 44.83	0.426	114.57	+ 45.47	0.506	115.04	+ 45.94
<i>n</i> -Butyl cyanide	0.966	127.82	+ 44.69	1.056	129.12	+ 45.99	1.077	129.69	+ 46.56
<i>n</i> -Pentyl cyanide	—	—	—	2.572	143.40	+ 46.24	2.267	144.13	+ 46.97
<i>n</i> -Hexyl cyanide	—	—	—	—	—	—	4.665	158.13	+ 46.95
Ethanethiol	0.021	80.21	+ 18.08	—	—	—	—	—	—
<i>n</i> -Propanethiol	0.065	94.27	+ 18.12	0.129	95.42	+ 19.27	—	—	—
<i>n</i> -Butanethiol	0.206	108.61	+ 18.43	0.320	109.98	+ 19.80	0.401	110.52	+ 20.34
<i>n</i> -Pentanethiol	0.626	122.43	+ 18.22	0.777	124.20	+ 19.90	0.845	124.98	+ 20.77
<i>n</i> -Hexanethiol	—	—	—	1.863	138.22	+ 19.99	1.759	139.21	+ 20.98
<i>n</i> -Heptanethiol	—	—	—	4.479	142.29	+ 20.03	3.642	153.33	+ 21.07
<i>n</i> -Octanethiol	—	—	—	—	—	—	7.47	167.27	+ 20.98
Pent-1-ene	0.011	72.19	+ 2.06	—	—	—	—	—	—
Hex-1-ene	0.034	86.21	+ 2.05	0.072	86.06	+ 1.90	—	—	—
Hept-1-ene	0.106	100.35	+ 2.17	0.177	100.49	+ 2.31	0.237	100.31	+ 2.13
Oct-1-ene	0.321	114.21	+ 1.91	0.420	114.34	+ 2.13	0.492	114.49	+ 2.28
Dec-1-ene	—	—	—	2.420	142.42	+ 2.16	2.092	142.57	+ 2.31
Dodec-1-ene	—	—	—	—	—	—	8.75	170.34	+ 2.03

TABLE II  
MEAN  $\Delta Me$  VALUES OF FUNCTIONAL GROUPS IN PRIMARY SUBSTITUTED *n*-ALKANES  
(20% w/w dinonyl phthalate on celite)

Class	20°	65°	100°
R·Cl	+ 7.95 (± 0.25)	+ 9.08 (± 0.20)	+ 9.78 (± 0.16)
R·Br	- 25.58 (± 0.02)	- 23.92 (± 0.18)	- 22.84 (± 0.20)
R·I	- 60.36 (± 0.47)	- 58.55 (± 0.16)	- 56.74 (± 0.12)
R·CN	+ 44.99 (± 1.08)	+ 46.23 (± 0.68)	+ 46.85 (± 0.30)
R·SH	+ 18.26 (± 0.11)	+ 19.98 (± 0.13)	+ 20.98 (± 0.14)
R·CH=CH <sub>2</sub>	+ 1.99 (± 0.13)	+ 2.16 (± 0.07)	+ 2.09 (± 0.13)
Mean standard deviation	± 0.50	± 0.31	± 0.19
Mean standard deviation excluding R·CN	± 0.25	± 0.15	± 0.15

± Refers to the "weighted" standard deviation.

TABLE III  
 $\Delta Me_0$  AND  $\mu$  VALUES FOR PRIMARY SUBSTITUTED *n*-ALKANES (SEE TEXT)

Class	$\Delta Me_0$	$\mu \cdot 10^3$	$\sigma$
R·Cl	+ 7.52 (± 0.11)	+ 22.9 (± 1.6)	0.09
R·Br	- 26.23 (± 0.14)	+ 34.4 (± 1.9)	0.11
R·I	- 61.32 (± 0.21)	+ 45.0 (± 3.0)	0.17
R·CN	+ 44.61 (± 0.21)	+ 23.4 (± 3.0)	0.17
R·SH	+ 17.63 (± 0.20)	+ 34.2 (± 2.8)	0.16
R·CH=CH <sub>2</sub>	+ 2.00 (± 0.11)	+ 1.40 (± 1.6)	0.09

± Refers to best estimate of standard deviation of  $\Delta Me_0$  and  $\mu$ .  $\sigma$  is the best estimate of the standard deviation of experimental values of  $\Delta Me$  from those calculated from  $\Delta Me_0 = \Delta Me_0 + \mu\theta$ .

TABLE IV  
VARIATION OF  $\Delta Me$  WITH VERTICAL POSITION IN THE PERIODIC TABLE  
FOR GROUP VI COMPOUNDS (SEE TEXT)  
(20% w/w dinonyl phthalate on celite at 100° ( $b = 0.311$ ))

Compound	$R_{29}$	$\Delta Me$	Shift per period
Di- <i>n</i> -butyl ether	0.994	- 2.09	
Di- <i>n</i> -butyl sulphide	5.26	+ 14.45	+ 16.54
Di- <i>n</i> -butyl selenide	8.05	- 24.10	- 38.55
Di- <i>n</i> -butyl telluride	14.48	- 61.13	- 37.05

(*i.e.*  $P = 2$  for chlorine etc.). Using the least squares method on this expression the best numerical form is:

$$\Delta Me = 76.66 + P (-34.44 + 0.0113 \theta)$$

This gives a standard deviation between observed and calculated values of  $\pm 0.41$  in  $\Delta Me$ , which is comparable with but slightly larger than experimental errors in measuring retention.

It was of interest to see whether this linear relation was confined to the halides or of general application. The data for the Group VI di-*n*-butyl compounds (Table IV) reveal that the change of  $\Delta Me$  between dialkyl sulphides and selenides is very close to the change between selenides and tellurides. Ethers are clearly anomalous. *n*-Alkyl fluorides, also being in the first period might be expected to be anomalous but their intense toxicity<sup>6</sup> precluded investigation.

The change of  $\Delta Me$  per period is somewhat greater for the Group VI compounds,  $-37.8$ , than for the halogens,  $-33.3$ . This is probably a reflection of the different valency states and would be expected to increase progressively with the normal covalency. The slight deviations of the periodic relationship from linearity after the first period are complex and could be due to a number of factors (*i.e.* isotopic composition, van der Waals radii, participation of higher orbitals, screening effects, etc.). The linearity is close enough and seems general enough, however, to be a very useful method of predicting retention data when analogues from the same period are available. The value of the shift per period appears to be relatively independent of the nature of the other groups attached to the functional group. Thus the experimentally determined values of  $\Delta Me$  for allyl methyl sulphide and selenide (at  $20^\circ$ ) are  $17.7$  and  $-19.9$  respectively giving a shift per period of  $-37.6$  which is very close to the value for the di-*n*-butyl analogues at  $100^\circ$  (*viz.*  $-38.6$ ). This independence may break down for sterically hindered structures or structures with strong intramolecular interactions or conjugation or where the pendant groups contain other functional groups which can interact strongly with the stationary phase.

#### SUMMARY

A new retention parameter,  $\Delta Me$ , has been found to be constant within a homologous series with a linear temperature dependence over the limited region studied. Also regular changes in  $\Delta Me$  values have been observed with substituents from the same group of the periodic table. This method should be of general application.

#### REFERENCES

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