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GAS–LIQUID CHROMATOGRAPHIC RETENTION DATA OF SOME ALIPHATIC AND ALICYCLIC SULPHIDES*

VLASTIMIL MARTINŮ AND JAROSLAV JANÁK
Institute of Instrumental Analytical Chemistry, Czechoslovak Academy of Sciences, Brno (Czechoslovakia)

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SUMMARY

Gas chromatographic retention indices of some lower aliphatic and alicyclic sulphides on isodecyl phthalate and Apiezon L columns at 110–150° are given and correlated.

INTRODUCTION

The identification and analysis of sulphur compounds in mixtures with hydrocarbons has been a topical analytical problem in the chemical refining and processing of crude petroleum[1]. The aim of the present work is to utilise the empirical rules with respect to the properties of retention indices[2] for substances that have not yet been investigated experimentally in this way[3].

The retention indices of some lower aliphatic and alicyclic sulphides on two stationary phases of different polarity have been measured and the temperature and structural dependences investigated. KOVÁTS' relationship[2], providing for the logarithmic interpolation of the position of the peak of a substance between two neighbouring *n*-paraffins, was used in the calculation. Provided the logarithmic scale of the reference paraffins is linear beyond the interval investigated as well, it is possible to carry out extrapolations. Over a narrow temperature interval, the temperature dependence of the retention index may be considered as approximately linear, though it has been found to be hyperbolic[4] over a wider interval.

EXPERIMENTAL

A Chrom 2 apparatus (Laboratory Instruments, N.E., Prague, Czechoslovakia), partly modified (injection port, gas flow stabilisation) to fit the character of the work, was used.

Measurements were carried out on 1600 mm long columns of 3 mm I.D., wound

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into helices. Apiezon L (ApL) (Edwards High Vacuum Ltd., Crawley, Great Britain) and isodecyl phthalate (IDP) (Carlo Erba S.p.A., Milan, Italy) were used as stationary phases. As a support, Chromosorb W 80–100 mesh (Johns-Manville, Trenton, N.J., U.S.A.) was employed; it was dried at 120° and coated by 20 wt.% of the stationary phase. The Apiezon L and isodecyl phthalate columns contained 4.3 and 4.1 g of the packings, respectively. The Apiezon L column was conditioned at 160° and the column with isodecyl phthalate at 155°. The separation efficiencies of the columns were 2490 (ApL) and 2680 (IDP) theoretical plates, as measured for a decane peak at 120°.

Each member of the homologous series of sulphides was chromatographed at five different temperatures within the interval of 110–150°; except that with the Apiezon L column a temperature interval of 120–160° was used in the measurement of the thiacyclopentanes. The temperature was stabilised to ± 0.2°. For each sulphide a pair of *n*-paraffins was chosen such that the three-component mixture prepared from them was well resolved by chromatography.

About 0.1 μl of the mixture was injected with a Hamilton syringe, each charge being carried out five times on both columns at all the above temperatures. The column hold-up time was measured by injecting 5 μl of town gas. The measurement was

TABLE I

RETENTION INDICES OF MODEL SULPHIDES

Sulphide	*Isodecyl phthalate*			*Apiezon L*		
	110°	*130°*	*150°*	*110°*	*130°*	*150°*
Me-S-Me	579	585	592	516	523	528
Et-S-Me	—	687[a]	—	—	623[a]	—
Pr-S-Me	783	787	792	718	723	727
Bu-S-Me	—	869[a]	—	—	810[a]	—
sec.-Bu-S-Me	843	849	853	784	790	796
Et-S-Et	759	765	772	694	698	704
Pr-S-Et	—	864[a]	—	—	801[a]	—
Bu-S-Et	957	962	965	896	901	906
sec.-Bu-S-Et	—	898[a]	—	—	841[a]	—
Pr-S-Pr	—	958[a]	—	—	894[a]	—
Bu-S-Pr	1047	1052	1057	986	992	995
sec.-Bu-S-Pr	996	999	1005	940	946	951
iso-Pr-S-*sec.*-Bu	941	946	951	886	890	897
tert.-Bu-S-*tert.*-Bu	968	975	982	913	920	927
sec.-Bu-S-*sec.*-Bu	—	999[a]	—	—	952[a]	—
iso-Bu-S-*iso*-Bu	1048	1052	1060	991	997	1003
Bu-S-Bu	1146	1148	1155	1082	1086	1092
2-Me-thiacyclopentane	—	936[a]	—	—	885[a]	—
2-Et-thiacyclopentane	1026[b]	1031	1039	977[b]	981	994
2-Pr-thiacyclopentane	1120[b]	1125	1139	1071[b]	1077	1088
2-Bu-thiacyclopentane	1217[b]	1221	1228	1168[b]	1174	1182

[a] Correlated value.
[b] Temperature 120°.

carried out with 15 different sulphides and 6 *n*-alkanes (C_7–C_{12}), all being the products of Lachema, Brno, Czechoslovakia. The purity (min. 95%) was satisfactory.

The average values calculated of the retention indices are summarised in Table I. The interval of confidence for the retention indices of the sulphides investigated did not exceed ± 2 units on both columns at 130°.

RESULTS AND DISCUSSION

The fifteen sulphides measured (Table I) were arranged into seven homologous series. In this instance, a series of at least three sulphides is called a homologous series, the retention indices of which are in a mutual relation reflecting a gradual defined change in the structure of the compounds. In each of these series, it is possible to correlate the retention index with the varying structural parameter.

The determination of the retention indices of the sulphides which have not been measured in the individual homologous series are quoted in Fig. 1.

The values of the retention indices of sulphides that were not amenable to direct measurement were determined by interpolation or extrapolation with the aid of the correlation dependence of the retention indices on the carbon numbers of the sulphides measured. The increaments of the symmetrically substituted sulphides represent the

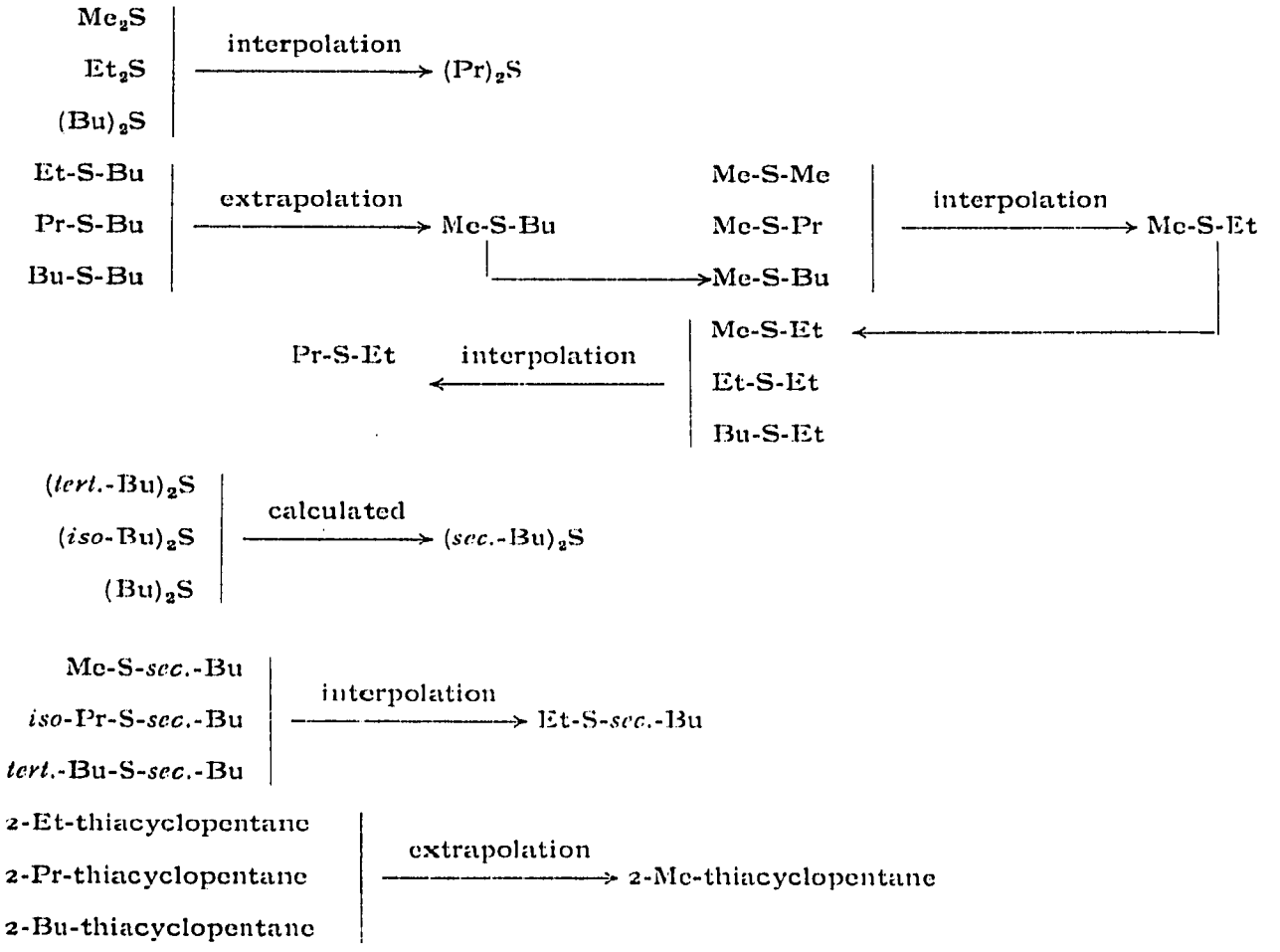

Fig. 1.

structural changes of both substituents in the molecule. The same increaments, from the qualitative viewpoint, with the nonsymmetrical sulphides are due to only one of the substituents while the other one remains unaffected.

The individual homologous series of the sulphides and the values I, ΔI, and $I_0\,(\partial I/\partial T)$ for both columns and for three of the originally employed five temperatures are summarised in the tables. In addition, the intervals of confidence ($i = st/\sqrt{n}$) calculated from five replicate injections of each sample for a confidence level of 0.95 have been quoted for all the retention indices of all the experimentally measured sulphides on both columns, at 130°.

TABLE II

RETENTION INDICES OF HOMOLOGOUS DIALKYL SULPHIDES

Sulphide	*Isodecyl phthalate*			± *i*	*Apiezon L*			± *i*	*ΔI*
	110°	*130°*	*150°*		*110°*	*130°*	*150°*		
Me_2S	579	585	592	0.82	516	523	528	1.17	62
$\partial T/10°$	3	3.5			3.5	2.5			
Et_2S	759	765	772	0.99	694	698	704	1.12	67
$\partial T/10°$	3	3.5			2	3			
$(Pr)_2S$	—	958[a]	—		—	894[a]	—		64
$(Bu)_2S$	1146	1148	1155	0.95	1082	1086	1092	0.71	62
$\partial T/10°$	1	3.5			2	2			

[a] Interpolation.

In compliance with the known findings[2,3] on the temperature dependence of retention indices, it can also be seen that the retention index values of sulphides show approximately linear variations with temperature within a narrow temperature interval (50°). With respect to the retention indices of members of homologous series

TABLE III

RETENTION INDICES OF HOMOLOGOUS ALKYL METHYL SULPHIDES

Sulphide	*Isodecyl phthalate*			± *i*	*Apiezon L*			± *i*	*ΔI*
	110°	*130°*	*150°*		*110°*	*130°*	*150°*		
Me-S-Me	579	585	592	0.82	516	523	528	1.17	62
$\partial T/10°$	3	3.5			3.5	2.5			
Et-S-Me	—	687[b]	—		—	623[b]	—		64
Pr-S-Me	783	787	792	1.12	718	723	727	0.24	64
$\partial T/10°$	2	2.5			2.5	2			
Bu-S-Me	—	869[a]	—		—	810[a]	—		59

[a] Extrapolation.
[b] Interpolation.

TABLE IV

RETENTION INDICES OF HOMOLOGOUS ALKYL ETHYL SULPHIDES

Sulphide	*Isodecyl phthalate*			± *i*	*Apiezon L*			± *i*	*ΔI*
	110°	*130°*	*150°*		*110°*	*130°*	*150°*		
Me-S-Et	—	687[a]	—		—	623[a]	—		64
Et-S-Et	759	765	772	0.99	694	698	704	1.12	67
$\partial T/10°$	3	3.5			2	3			
Pr-S-Et	—	864[a]	—		—	801[a]	—		63
Bu-S-Et	957	962	965	0.34	896	901	906	0.53	61
$\partial T/10°$	2.5	1.5			2.5	2.5			

[a] Interpolation.

TABLE V

RETENTION INDICES OF HOMOLOGOUS ALKYL PROPYL SULPHIDES

Sulphide	*Isodecyl phthalate*			± *i*	*Apiezon L*			± *i*	*ΔI*
	110°	*130°*	*150°*		*110°*	*130°*	*150°*		
Me-S-Pr	783	787	792	1.12	718	723	727	0.24	64
$\partial T/10°$	2	2.5			2.5	2			
Et-S-Pr	—	864[a]	—		—	801[a]	—		63
Pr-S-Pr	—	958[a]	—		—	894[a]	—		64
Bu-S-Pr	1047	1052	1057	0.74	986	992	995	0.80	60
$\partial T/10°$	2.5	2.5			3	1.5			

[a] Interpolation.

TABLE VI

RETENTION INDICES OF HOMOLOGOUS ALKYL BUTYL SULPHIDES

Sulphide	*Isodecyl phthalate*			± *i*	*Apiezon L*			± *i*	*ΔI*
	110°	*130°*	*150°*		*110°*	*130°*	*150°*		
Me-S-Bu	—	869[a]	—		—	810[a]	—		59
Et-S-Bu	957	962	965	0.34	896	901	906	0.53	61
$\partial T/10°$	2.5	1.5			2.5	2.5			
Pr-S-Bu	1047	1052	1057	0.74	986	992	995	0.80	60
$\partial T/10°$	2.5	2.5			3	1.5			
Bu-S-Bu	1146	1148	1155	0.95	1082	1086	1092	0.71	62
$\partial T/10°$	1	3.5			2	2			

[a] Extrapolation.

TABLE VII

RETENTION INDICES OF HOMOLOGOUS ALKYL *sec.*-BUTYL SULPHIDES

Sulphide	*Isodecyl phthalate*			± *i*	*Apiezon L*			± *i*	*ΔI*
	110°	*130°*	*150°*		*110°*	*130°*	*150°*		
Me-S-*sec.*-Bu	843	849	853	0.49	784	790	796	0.30	59
∂T/10°	3	2			3	3			
Et-S-*sec.*-Bu	—	898[a]			—	841[a]	—		57
Pr-S-*sec.*-Bu	996	999	1005	0.58	940	946	951	0.32	53
∂T/10°	1.5	3			3	2.5			
iso-Pr-S-*sec.*-Bu	941	946	951	0.18	886	890	897	1.32	56
∂T/10°	2.5	2.5			2	3.5			
tert.-Bu-S-*sec.*-Bu	981	987	994	1.16	930	936	942	0.32	51
∂T/10°	2.5	3.5			3	3			

[a] Interpolation.

of nonbranched sulphides, it is notable that, at all the temperatures and on both columns, the retention index values of neighbouring members in a given homologous series differ from each other by about 100 units on a given stationary phase and at a given temperature. Anomalies occur only between lowest members of the homologous series, *i.e.* with those for which the number of carbon atoms does not exceed five.

A different situation occurs with branched sulphides (Tables VII and VIII). The retention indices for the homologous series of the branched nonsymmetrical secondary butyl sulphides are correlated with the number of CH_3 groups on the first carbon of the variable substituent in the molecule. In this case, the increment of the retention index due to the CH_3 group only amounts to about 50 units.

TABLE VIII

RETENTION INDICES OF DIFFERENT DIBUTYL SULPHIDES

Sulphide	*Isodecyl phthalate*			± *i*	*Apiezon L*			± *i*	*ΔI*
	110°	*130°*	*150°*		*110°*	*130°*	*150°*		
$(Bu)_2S$	1146	1148	1155	0.95	1082	1086	1092	0.71	62
∂T/10°	1	3.5			2	3			
$(iso\text{-}Bu)_2S$	1048	1052	1060	0.93	991	997	1003	1.32	55
∂T/10°	2	4			3	3			
$(sec.\text{-}Bu)_2S$	—	999[a]	—		—	952[a]	—		47
$(tert.\text{-}Bu)_2S$	968	975	982	0.60	913	920	927	0.47	55
∂T/10°	3.5	3.5			3.5	3.5			

[a] Calculated.

TABLE IX

RETENTION INDICES OF HOMOLOGOUS 2-ALKYL THIACYCLOPENTANES

Thiacyclopentane	*Isodecyl phthalate*			± *i*	*Apiezon L*			± *i*	*ΔI*
	120°	*130°*	*150°*		*120°*	*130°*	*150°*		
2-Me	—	936[a]	—		—	885[a]	—		51
2-Et	1026	1031	1039	1.28	977	981	994	1.08	50
$\partial T/10°$	5	4			4	6.5			
2-Pr	1120	1125	1139	1.04	1071	1077	1088	0.49	48
$\partial T/10°$	5	7			6	5.5			
2-Bu	1217	1221	1228	1.02	1168	1174	1182	1.33	47
$\partial T/10°$	4	3.5			6	4			

[a] Extrapolation.

In Table VIII, it is possible to follow the changes of the retention indices of the symmetrical dibutyl sulphides with the gradual shifting of the CH_2 group from the interior of the molecule to its periphery. In this series, (*sec.*-Bu)$_2$S has not been measured. It is possible to estimate from the retention indices of the isomers measured, that the retention index of (*sec.*-Bu)$_2$S will be within an interval confined by the retention index values of (*tert.*-Bu)$_2$S and (*iso*-Bu)$_2$S. The third KOVÁTS' rule[2] may be used to determine the above value. To do this, the retention indices of *tert.*-Bu-S-*sec.*-Bu ($I_{130}^{ApL} = 936$) and (*tert.*-Bu)$_2$S ($I_{130}^{ApL} = 920$) are used. Thus, employing numerical calculation, one obtains for (*sec.*-Bu)$_2$S at 130° on an Apiezon L column a retention index value of $I_{130}^{ApL} = 952$ and on the isodecyl phthalate column, at the same temperature, a value of $I_{130}^{IDP} = 999$.

If the retention index of (*sec.*-Bu)$_2$S is calculated by the second KOVÁTS' rule, *i.e.* from the difference between the boiling points of two isomeric sulphides, one obtains a value of $I_{130}^{ApL} = 966.5$ for the nonpolar column.

The accuracy of calculation is limited by the approximative character of the rules, and the values so obtained may be used for identification as a first approximation only.

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