RELATIONS BETWEEN CHROMATOGRAPHIC PARAMETERS AND PHYSICAL PROPERTIES OF SOME ALKYL TERT-BUTYL ETHERS

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Retention parameters of alkyl tert-butyl ethers have been measured by gas chromatography using stationary phases of various polarity. The stationary phase polarity influences elution order of a pair alcohol/ether as well as their resolution degree. Dependence of log V_g *vs* boiling temperature of the ethers is linear within a given homologous series of compounds except for the first two members. The retention times of ethers and alcohols have been found to coincide when using di-n-heptyl phthalate as stationary phase.

Alkyl tert-butyl ethers are formed by reaction of isobutylene with alcohol at temperatures 80–100°C in the presence of an acid cation exchange resin[1] according to the following equation:

$$\mathrm{R{-}OH + CH_2{=}C(CH_3)_2 \xrightarrow{[H^+]} R{-}O{-}C(CH_3)_3} \qquad (A)$$

The technical product contains besides the ether formed also the unreacted alcohol, isobutylene, tert-butyl alcohol, and isobutylene dimers (2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene). Gas chromatography seems to be most suitable for both analysis of the technical ether and determination of purity of the final product.

Specific retention volumes and retention indexes of some alkyl tert-butyl ethers are given in a monograph by McReynolds[2]. Most of the alkyl tert-butyl ethers given in this paper have not yet been chromatographed, and some of them were prepared for the first time.

The aim of this work was to measure the retention parameters of the prepared alkyl tert-butyl ethers on stationary phases of various polarity and correlate the data obtained with physical properties of the ethers.

EXPERIMENTAL

The chromatographic measurements were carried out with a HP 5830 A chromatograph (Hewlett–Packard, U.S.A.) equipped with a FID detector. Temperatures of the columns are given in the respective tables. Temperature of the injection block and detector was 200°C. Nitrogen

was used as the carrier-gas, flow rates 24 cm^3 min^{-1}. The hydrogen pressure was 0·13 MPa. Columns and packings: 10% squalane (Merck, Darmstadt, DBR) or 10% Vupol 500 (ref.[3]), or 10% OV-17 (Applied Science Laboratories, U.S.A.), each on Chromaton N-AW-HMDS carrier, d_p = 0·16—0·20 mm (Lachema, Brno). Glass columns, L = 2·5 m, I.D. = 3 mm. 10% Igepal CO 880 (Erba, Italy) on Chromosorb W-NAW-HMDS, d_p = 0·149—0·177 mm (Supelco, U.S.A.), L = 4 m, I.D. = 3 mm. 10% Carbowax 1540 in a HIPAK Column 19005 A (Hewlett-Packard, U.S.A.), L = 1·8 m, I.D. = 2·2 mm.

The chromatographed ethers and their physical contants are given in Table I.

Dead times were calculated from elution times of n-alkanes by the method described by Šefčík[6,7].

RESULTS AND DISCUSSION

The reduced retention times t'_R, min, specific retention volumes (V_g, cm^3), and retention indexes (I) on the given stationary phases at several temperatures are given in Tables II—VI. The specific retention volumes on Carbowax 1 540 could not be calculated, because mass of the stationary phase in the column was not known.

TABLE I

Physical constants of alkyl tert-butyl ethers

Alkyl tert-butyl ether (Abbrev.)		B.p., °C		d_4^{20}, g cm^{-3}		n_D^{20}		Refs
		measured	lit.	measured	lit.	measured	lit.	
Methyl	(Me)	55·2	55·1—55·2	0·7290	0·7299	1·3690	1·3690	4
Ethyl	(Et)	73·0	73·0—73·1	0·7302	0·7300	1·3759	1·3760	4
				0·7417				5
Isopropyl	(iPr)	87·9	87·6	0·7425	0·742	1·3795	1·3798	4
			87—88				1·3799	5
Propyl	(Pr)	97·5	97·4	0·7480	0·7472[a]	1·3856	1·3830	4
Allyl	(Al)	99·5	99·2—100	0·7772	0·7770	1·4056	1·4011	5
Isobutyl	(iBu)	112·7	114	0·7533	0·7516	1·3928	1·3930	5
			111—112	0·7550	0·7550			5
Sec-butyl	(sBu)	114	101—102	0·7751	0·774	1·3958	1·3950[a]	5
Butyl	(Bu)	122	124	0·7618	0·7615	1·3925	1·3928	4
Amyl	(Am)	145·2	—	0·7776	—	1·4003	—	—
Hexyl	(Hx)	169·2	—	0·7937	—	1·4065	—	—
Cyclohexyl	(cH)	172·5	—	0·8680	—	1·4378	—	—
Heptyl	(Hp)	194·1	—	0·8090	—	1·4119	—	—
Octyl	(Oc)	218·0	—	0·8250	—	1·4186	—	—

[a] Data at 25°C.

TABLE II

Retention values of alkyl tert-butyl ethers on squalane

Alkyl tert-butyl ether	Column temperature, °C: 90		108		130		160		I 80—160°
	t'_R, min	V_g, cm^3	t'_R, min	V_g, cm^3	t'_R, min	V_g, cm^3	t'_R, min	V_g, cm^3	
Me[a]	1·45	38·7	0·98	25·7	0·60	15·2	—	—	565
Et	2·09	56·1	1·33	34·8	0·79	20·0	—	—	608
iPr	3·05	81·5	1·90	49·9	1·07	27·1	—	—	655
Pr	4·1	110	2·46	64·6	1·37	34·7	—	—	692
Al	4·5	120	3·65	69·6	1·42	35·9	—	—	700
iBu	6·3	168	3·53	92·7	1·86	47·1	—	—	741
sBu	7·1	190	4·0	105	2·07	52·4	—	—	758
Bu	9·2	247	5·0	133	2·56	64·9	—	—	791
Am	—	—	9·5	251	4·5	114	1·80	44·5	878
Hx	—	—	18·3	482	7·9	200	3·00	74·7	968
cH	—	—	25·3	664	11·6	295	4·6	115	1 028
Hp	—	—	36·2	952	14·8	375	5·9	125	1 063
Oc	—	—	71·2	1 868	27·8	705	8·5	212	1 156

[a] For abbreviations see Table I.

TABLE III

Retention values of alkyl tert-butyl ethers on Vupol 500

Alkyl tert-butyl ether	Column temperatures, °C: 80		100		120		140		I 80—140 °C
	t'_R, min	V_g, cm^3	t'_R, min	V_g, cm^3	t'_R, min	V_g, cm^3	t'_R, min	V_g, cm^3	
Me	0·98	26·1	0·58	15·4	0·37	9·7	—	—	552
Et	1·47	39·1	0·82	21·8	0·50	13·1	—	—	600
iPr	2·22	59·0	1·18	31·5	0·70	18·4	—	—	649
Pr	3·09	82·6	1·60	42·5	0·93	24·4	—	—	687
Al	3·34	88·8	1·71	45·4	0·99	26·0	—	—	696
iBu	4·8	127	2·35	62·4	1·32	34·7	—	—	737
sBu	5·4	143	2·56	68·0	1·45	38·1	—	—	751
Bu	7·1	190	3·32	88·2	1·81	47·6	—	—	783
Am	—	—	6·5	174	3·56	93·6	1·93	48·2	881
Hx	—	—	13·1	348	6·8	179	3·55	88·6	975
cH	—	—	17·2	456	8·0	210	4·0	99·8	1 002
Hp	—	—	26·2	696	13·4	351	6·6	164	1 071
Oc	—	—	52·7	1 400	25·9	681	12·2	304	1 167

TABLE IV

Retention values of alkyl tert-butyl ethers on Igepal CO 880

Alkyl tert-butyl ether	Column temperature, °C										I 40—120°C
	40		60		80		100		120		
	t'_R, min	V_g, cm^3	t'_R, min	V_g, cm^3	t'_R, min	V_g, cm^3	t'_R, min	V_g, cm^3	t'_R, min	V_g, cm^3	
Me	1·68	43·1	1·00	25·5	0·55	13·6	—	—	—	—	665
Et	1·94	49·8	1·18	30·1	0·60	14·1	—	—	—	—	683
iPr	2·53	64·9	1·44	36·7	0·84	20·8	—	—	—	—	709
Pr	3·53	90·6	1·94	49·4	1·08	26·7	—	—	—	—	745
Al	7·4	190	3·72	94·8	1·95	48·3	—	—	—	—	826
iBu	4·9	126	2·64	67·3	1·41	34·9	—	—	—	—	782
sBu	6·3	161	3·14	80·0	1·72	42·6	—	—	—	—	807
Bu	8·7	223	4·3	111	2·28	56·4	1·10	26·3	0·65	14·4	845
Am	—	—	—	—	4·2	104	2·07	49·4	1·16	25·5	945
Hx	—	—	—	—	8·0	198	3·81	91·0	2·08	45·7	1 042
cH	—	—	—	—	12·8	317	5·7	137	3·12	68·5	1 108
Hp	—	—	—	—	17·7	438	7·3	173	3·83	84·1	1 144
Oc	—	—	—	—	37·1	919	13·5	322	6·7	147	1 242

From the data in Tables II and III it can be seen that elution order on the non-polar phases agrees with the boiling temperatures of the ethers. *E.g.* allyl ether is eluated before isobutyl ether. However, on the mildly polar OV-17 the two compounds are eluated simultaneously, and on the polar Carbowax 1 540 the allyl ether is eluated after the butyl ether. This shift of the retention time to higher values is caused by interaction of mobile π electrons of double bond of allyl ether with polar centres of molecules of the stationary phase.

Polarity change of the stationary phase changes also the elution order of the pair alcohol/ether. Whereas on the non-polar phases (Squalane, Vupol 500) the alcohols are eluated before the corresponding tert-butyl ethers, on polar phases the elution order is reversed.

We also studied the problem of finding the stationary phase on which the two types of compounds will be eluated simultaneously, because such case could be encountered within practical analyses. We have measured the retention times of n-amyl alcohol and n-amyl tert-butyl ether on other stationary phases (di-n-decyl phthalate, dioctyl phthalate, dibutyl phthalate, tricresyl phosphate *etc.*). Differences of the retention indexes of the alcohol and the ether ($I_A - I_E$) were correlated with the

TABLE V
Retention values of alkyl tert-butyl ethers on OV-17

Alkyl tert-butyl ether	Column temperature, °C						I 80—110 °C
	80		100		110		
	t'_R, min	V_g, cm^3	t'_R, min	V_g, cm^3	t'_R, min	V_g, cm^3	
Me	0·96	26·7	0·45	11·8	0·32	8·3	617
Et	1·29	36·1	0·56	14·8	0·42	11·0	658
iPr	1·59	44·5	0·72	18·9	0·49	12·8	684
Pr	2·29	64·0	1·04	27·4	0·71	18·6	736
Al	2·81	78·6	1·22	32·2	0·85	22·2	762
iBu	2·81	78·6	1·22	32·2	0·85	22·2	762
sBu	3·35	93·7	1·46	38·5	0·99	25·9	785
Bu	4·7	130	2·00	52·7	1·37	36·0	830
Am	—	—	3·90	103	2·60	68·0	924
Hx	—	—	7·3	192	5·0	132	1 026
cH	35·5	993	11·7	308	9·1	238	1 092
Hp	—	—	14·9	393	9·7	253	1 124
Oc	—	—	29·4	773	18·2	476	1 228

sum of values of the McReynolds constants of 1-butanol and 1,4-dioxane[8] ($P = \Delta I_B + \Delta I_{1,4-D}$) for all the stationary phases used. From Fig. 1 the dependence is seen to be practically linear, crossing the y-axis at the point corresponding to such polarity of the stationary phase for which $I_A = I_E$. The stationary phase on which an alcohol will coincide with the corresponding tert–butyl ether should have the sum of the constant values of butanol and 1,4-dioxane about 150.

We have investigated other stationary phases and found that on di-n-heptyl phthalate, in fact, n-amyl alcohol and n-amyl tert-butyl ether are eluated simultaneously. As values of the McReynolds standards of this phase are not given in the cited literature, we give them in the present paper: $\Delta I_{benzene} = -11$, $\Delta I_{butanol} = 68$, $\Delta I_{2-pentanone} = 106$, $\Delta I_{1-nitropropane} = 260$, $\Delta I_{pyridine} = 150$, $\Delta I_{1,4-dioxane} = 75$. Sum of the ΔI values of butanol and 1,4-dioxane is 143, which agrees well with interpolation in Fig. 1.

Values of logarithms of specific retention volumes were correlated with boiling temperatures of the ethers. From Fig. 2 it can be seen that the dependences are linear for the homologous series except for its first two members. With non-polar phases (squalane, Vupol 500) the straight line involves also the points corresponding to isoalkyl ethers and allyl ether.

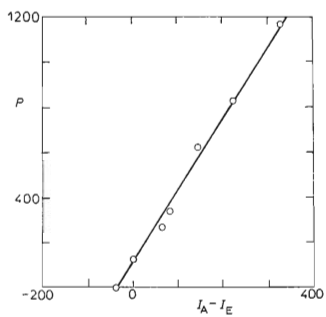

FIG. 1

Dependence of difference of retention indexes of amyl alcohol and amyl tert-butyl ether ($I_A - I_E$) on polarity of stationary phase ($P = \Delta I_B + \Delta I_{1,4-D}$)

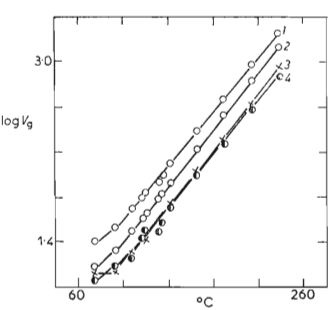

FIG. 2

Dependence of logarithm of specific retention volume V_g on boiling temperature of alkyl tert-butyl ethers. Stationary phases and column temperatures (t_c): *1* squalane, 108°C, *2* Vupol 500, 100°C, *3* OV-17, 100°C, *4* Igepal CO 880, 80°C.

Using the regression analysis we calculated coefficients of the linear equations and, hence, the boiling temperatures of the ethers, the second member of the homologous series being also involved in the analysis. From Table VII it is seen that there

TABLE VI

Retention values of alkyl tert-butyl ethers on Carbowax 1 540

Alkyl tert-butyl ether	Column temperature, °C									
	40		60		80		100		120	
	t'_R, min	I	t'_R, min	I	t'_R, min	I	t'_R, min	I	t'_R, min	I
Me	0·63	712	0·37	713	0·20	712	—	—	—	—
Et	0·63	712	0·37	713	0·20	712	—	—	—	—
iPr	0·81	739	0·46	739	0·23	737	—	—	—	—
Pr	1·18	764	0·57	766	0·28	763	—	—	—	—
Al	2·60	876	1·32	870	0·62	868	—	—	—	—
iBu	1·37	798	0·75	800	0·37	800	—	—	—	—
sBu	1·82	830	0·97	832	0·46	829	—	—	—	—
Bu	2·54	867	1·30	868	0·65	866	0·31	866	0·21	871
Am	—	—	—	—	1·16	965	0·56	965	0·34	966
Hx	—	—	—	—	2·30	1 065	1·01	1 067	0·57	1 067
cH	—	—	12·5	1 152	4·1	1 150	1·67	1 151	0·90	1 152
Hp	—	—	—	—	4·6	1 165	1·81	1 168	0·93	1 165
Oc	—	—	—	—	9·0	1 266	3·20	1 267	1·57	1 267

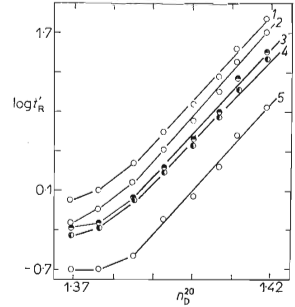

FIG. 3

Dependence of logarithm of reduced retention time on refractive index of alkyl tert-butyl ethers. Stationary phases and column temperatures (t_c): *1* squalane, 80°C, *2* Vupol 500, 100°C, *3* Igepal CO 880, 80°C, *4* OV-17, 100°C, *5* Carbowax 1 540, 80°C

is a very good agreement between the measured and the calculated values for the members of the homologous series. With non-polar phases a good agreement was found also for isoalkyl ethers, whereas great differences between the measured and calculated boiling temperatures were observed for cyclohexyl tert-butyl ether on all the stationary phases.

We also correlated logarithms of the reduced retention times with the refractive indices of the ethers. From Fig. 3 it is seen that the dependence is linear for the homologous series except for its first two members.

It can be stated that analysis of technical alkyl tert butyl ethers can be carried out with both non-polar and polar stationary phases. With squalane separation of the both isomeric trimethylpentenes is also possible. On polar stationary phases the retention times are shorter than on the non-polar ones. As alcohols are eluted after the corresponding tert-butyl ethers on these phases, these phases are more suitable for analyses of recuperated alcohols in which the ether component is present in low concentration only.

Di-n-heptyl phthalate is a remarkable stationary phase, because alcohols coincide with the corresponding tert-butyl ethers on this phase. The retention indexes of buta-

TABLE VII

Boiling points of alkyl tert-butyl ethers calculated from specific retention volumes

Alkyl tert-butyl ether	t_b, °C measured	t_b, calculated, °C			
		Stationary phase, t_c, °C			
		Squalane 108	Vupol 500 100	OV-17 100	Igepal CO 880 80
Et	73·0	73·9	73·4	74·4	71·4
iPr	87·9	86·8	86·3	82·3	85·8
Pr	97·5	96·2	96·6	96·9	95·1
Al	99·5	98·9	98·9	101·8	116·8
iBu	112·7	109·3	110·0	101·8	104·9
sBu	114·0	113·9	112·9	108·5	112·2
Bu	122·0	122·3	122·0	120·7	122·6
Am	145·5	145·5	145·6	145·1	144·9
Hx	169·2	169·2	169·6	167·9	168·7
cH	172·5	180·8	179·0	185·0	186·1
Hp	194·1	193·9	193·8	193·9	198·1
Oc	218·0	218·4	218·0	218·2	215·3

nol and 1,4-dioxane are very close, which indicates that the both compounds are eluated simultaneously in spite of their boiling temperatures being different (117·2 and 101·4°C, respectively). With all other dialkyl phthalates (dibutyl to diisodecyl) the retention index of butanol is higher than that of 1,4-dioxane.

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