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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF ALKYLBIPHENYLS ON SILICA

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SUMMARY

The influence of the molecular structure of 58 alkylbiphenyls and related compounds on their retention behaviour on silica has been studied. The moisture control system was incorporated into a closed circuit to maintain the long-term equilibration of the water content between the mobile and the stationary phase. The retention data have been expressed in the form of logarithms of capacity factor k'. The retention of the measured compounds is influenced by the number of alkyl groups, their length, shape and arrangement.

Retention increases if two or more substituents are in *ortho*-positions on one of aromatic rings. On the other hand, decreased retention is observed if there is substitution in the 2,6,2',6' positions, *i.e.* in *ortho*-positions with respect to the link between two aromatic rings. If these positions are more highly substituted the angle between two aromatic rings is increased and the approach of biphenyl molecule to the adsorption surface is impeded.

INTRODUCTION

The relation between the molecular structure of some mono- and diaromatic hydrocarbons and their adsorptivity on silica and alumina has been studied by Popl *et al.*[1-3]. High-performance liquid chromatography (HPLC) enables the more precise study of the relationship between the structure and the retention behaviour. In this relation, the retention data of alkylbenzenes[4] and alkylnaphthalenes[5] were measured, with silica as the stationary phase and *n*-pentane as the mobile phase. The next stage in this project is to measure retention data for 58 alkylbiphenyls under the same conditions.

EXPERIMENTAL

Apparatus

A Varian 8500 liquid chromatograph (Varian, Palo Alto, CA, U.S.A.) with a syringe pump was used. Sample injection was performed by the stop-flow technique

with a 10-μl syringe (Hamilton, Bonaduz, Switzerland) directly into the column, using a septumless injector. A UVM-4 multi-wavelength UV detector (Vývojové dílny ČSAV, Prague, Czechoslovakia) was operated at 254 nm. Chromatograms were recorded and retention times were measured with a 3390A reporting integrator (Hewlett-Packard, Avondale, PA, U.S.A.). A stainless-steel column (250 × 8 mm I.D.) with a tapered inlet (Varian), was filled using the slurry-packing technique with 7.5 μm irregularly shaped silica gel (Silasorb; Lachema, Brno, Czechoslovakia). The column and the lower part of injector were inserted in a water-jacket, kept at a constant temperature. The water content in the recycling mobile phase was maintained by a moisture control system (MCS) incorporated in closed circuit. The MCS was filled with 175 g of silica containing 0, 0.5 or 1% of water. The silica had been activated by heating for 4 h at 200°C. Deactivation was performed by addition of 0.5 or 1% of water, respectively.

Both the column and the MCS were kept at 25 ± 0.1°C. The MCS apparatus was described in detail previously[5]. Retention data were calculated on a HP-85 personal computer (Hewlett-Packard, Avondale, PA, U.S.A.) equipped with a 82905 B impact printer, a 82901 M dual disc drive and a 9872 A plotter. Visicalec software was used to prepare, compute, and print the table.

Chemicals

Of the series of 58 alkylbiphenyls used, some were synthesized[6-8] and the other 30 higher-molecular-range alkylbiphenyls were kindly given by Dr. E. A. Johnson of the National Institute for Biological Standards and Control (London, U.K.).

Mobile phase

n-Pentane (analytical reagent grade) was used as the mobile phase. Before use, it was distilled in glass and dried by percolating it over a silica gel column (Mikrosil, 100–150 μm; Lachema) that had been dried for 4 h at 200°C. The flow-rate of the mobile phase was 100 ml/h.

Procedure

Three or four injections were carried out for each sample. The samples were 10% solutions in isooctane. Before measurements, the column was stabilized by washing with fresh recycling mobile phase. The column activity was checked before the beginning of the measurement, then several times during the analysis and after the completion of the measurements, by injection of a test mixture of benzene, naphthalene and phenanthrene in isooctane. The dead volume of the column was determined by measuring the retention time of *n*-hexane.

RESULTS AND DISCUSSION

The values of retention times (t_x) and capacity factors (k') are given in Table I. Each value represents an average of three or four measurements of individual alkylbiphenyls. As in the case of alkylbenzenes[4], the range of retention data broadens with increasing number of carbon atoms. Polymethylbiphenyls with methyl groups in 4-, 3,4-, 3,4,3',4'- and 3,4,5,3',4',5'-positions, respectively, have the largest retention times in the range of corresponding compounds with the same number of carbon

TABLE I

RETENTION DATA FOR ALKYLBIPHENYLS

t_R = Retention time (min); k' = capacity factor; $t_X = t_R - t_0$ = adjusted retention time (min).

| Compound | Abbreviation | Deactivation of silica (concentration of water in moisture control system) | | | | | |
| | | 0% | | 0.5% | | 1% | |
		t_X	k'	t_X	k'	t_X	k'
Biphenyl	BIP	29.97	5.59	27.12	4.96	26.11	4.74
2-Methylbiphenyl	2-M-B	32.77	6.20	29.03	5.38	28.14	5.18
3-Methylbiphenyl	3-M-B	33.42	6.35	29.62	5.51	27.51	5.05
4-Methylbiphenyl	4-M-B	34.03	6.48	30.84	5.78	28.04	5.16
2,3-Dimethylbiphenyl	2,3-DM-B	40.31	7.86	35.75	6.86	32.07	6.05
2,4-Dimethylbiphenyl	2,4-DM-B	37.85	7.32	33.35	6.33	30.56	5.72
2,5-Dimethylbiphenyl	2,5-DM-B	36.60	7.04	32.11	6.06	29.27	5.43
3,4-Dimethylbiphenyl	3,4-DM-B	43.68	8.60	38.19	7.39	33.55	6.37
3,5-Dimethylbiphenyl	3,5-DM-B	38.29	7.42	34.22	6.52	31.71	5.97
3,4'-Dimethylbiphenyl	3,4'-DM-B	41.19	8.05	35.49	6.80	31.14	5.84
2,4'-Dimethylbiphenyl	2,4'-DM-B	39.95	7.78	34.00	6.47	31.02	5.82
3,3'-Dimethylbiphenyl	3,3'-DM-B	33.61	6.39	30.54	5.71	29.00	5.37
4,4'-Dimethylbiphenyl	4,4'-DM-B	39.00	7.57	35.29	6.76	32.19	6.07
2,2'-Dimethylbiphenyl	2,2'-DM-B	34.13	6.50	31.00	5.81	28.46	5.25
2,6-Dimethylbiphenyl	2,6-DM-B	35.02	6.70	30.93	5.80	27.94	5.14
2,3'-Dimethylbiphenyl	2,3'-DM-B	35.73	6.85	31.25	5.87	28.19	5.20
2,6,2'-Trimethylbiphenyl	2,6,2'-TM-B	32.84	6.22	29.37	5.45	27.01	4.94
3,5,4'-Trimethylbiphenyl	3,5,4'-TM-B	38.03	7.36	36.43	7.01	34.20	6.52
2,3,2',3'-Tetramethylbiphenyl	2,3,2',3'-TM-B	42.92	8.43	40.38	7.87	38.38	7.44
2,4,2',4'-Tetramethylbiphenyl	2,4,2',4'-TM-B	40.46	7.89	37.02	7.14	36.68	7.06
2,5,2',5'-Tetramethylbiphenyl	2,5,2',5'-TM-B	37.28	7.19	34.68	6.62	32.62	6.17
2,6,2',6'-Tetramethylbiphenyl	2,6,2',6'-TM-B	32.14	6.06	27.43	5.03	24.59	4.40
3,4,3',4'-Tetramethylbiphenyl	3,4,3',4'-TM-B	58.74	11.91	54.17	10.91	50.65	10.13
3,5,3',5'-Tetramethylbiphenyl	3,5,3',5'-TM-B	44.99	8.89	41.87	8.20	39.35	7.65
2,4,6,2',4',6'-Hexamethylbiphenyl	2,4,6,2',4',6'-HM-B	40.58	7.92	35.19	6.73	31.40	5.90
3,4,5,3',4',5'-Hexamethylbiphenyl	3,4,5,3',4',5'-HM-B	75.16	15.52	71.73	14.76	68.73	14.11
2-Ethylbiphenyl	2-E-B	32.00	6.03	28.72	5.31	25.97	4.71
3-Ethylbiphenyl	3-E-B	32.06	6.05	28.76	5.32	26.73	4.87
4-Ethylbiphenyl	4-E-B	32.84	6.22	29.51	5.49	27.21	4.98
Biduryl	BIDU	37.60	7.26	32.39	6.12	30.34	5.67
Biisoduryl	BI-i-DU	59.10	11.99	54.35	10.95	52.12	10.45
o-Terphenyl	O-TERPH	93.12	19.47	87.27	18.18	76.99	15.92
m-Terphenyl	M-TERPH	86.12	17.93	77.42	16.02	69.65	14.31
p-Terphenyl	P-TERPH	88.08	18.36	80.07	16.60	73.41	15.13
2-n-Propylbiphenyl	2-nP-B	29.44	5.47	26.57	4.84	24.67	4.42
4-n-Propylbiphenyl	4-nP-B	27.51	5.05	24.54	4.39	22.89	4.03
2-Isopropylbiphenyl	2-iP-B	30.00	5.59	27.31	5.00	25.92	4.70

TABLE I *(continued)*

Compound	Abbreviation	Deactivation of silica (concentration of water in moisture control system)					
		0%		0.5%		1%	
		t_X	k'	t_X	k'	t_X	k'
3-Isopropylbiphenyl	3-iP-B	30.82	5.77	27.88	5.13	25.33	4.57
4-Isopropylbiphenyl	4-iP-B	28.34	5.23	27.58	5.06	25.02	4.50
2-n-Butylbiphenyl	2-nB-B	27.21	4.98	24.36	4.35	22.69	3.99
4-n-Butylbiphenyl	4-nB-B	26.84	4.90	24.19	4.32	20.45	3.49
2-tert.-Butylbiphenyl	2-tB-B	27.95	5.14	24.58	4.40	22.56	3.96
3-tert.-Butylbiphenyl	3-tB-B	27.12	4.96	25.72	4.65	25.00	4.49
4-tert.-Butylbiphenyl	4-tB-B	27.53	5.05	25.54	4.61	24.82	4.45
3,4-Diisopropylbiphenyl	3,4-D-iP-B	29.66	5.52	25.67	4.64	23.00	4.05
3,4'-Diisopropylbiphenyl	3,4'-D-iP-B	29.19	5.42	25.33	4.57	23.44	4.15
3,5-Diisopropylbiphenyl	3,5-D-iP-B	27.01	4.94	22.57	3.96	19.17	3.21
3,3'-Diisopropylbiphenyl	3,3'-D-iP-B	27.50	5.04	25.01	4.50	23.30	4.12
2,2'-Di-tert.-butylbiphenyl	2,2'-D-tB-B	23.22	4.10	21.44	3.71	20.19	3.44
4,4'-Di-tert.-butylbiphenyl	4,4'-D-tB-B	24.13	4.30	22.62	3.97	21.47	3.72
Biphrehnithyl	BIPR	79.98	16.58	76.71	15.86	72.21	14.87
2-Isopropyl-5-methylbiphenyl	2-iP-5M-B	32.17	6.07	28.02	5.16	25.46	4.60
1,1-Diphenylethane	1,1-DPh-Et	30.22	5.64	27.73	5.09	25.78	4.67
1,2-Diphenylethane	1,2-DPh-Et	36.56	7.04	32.88	6.23	30.06	5.61
2-Methyldiphenylmethane	2-MDM	53.24	10.70	47.75	9.49	42.41	8.32
3-Methyldiphenylmethane	3-MDM	38.06	7.36	35.02	6.70	34.21	6.52
4-Methyldiphenylmethane	4-MDM	54.96	11.08	48.93	9.75	45.00	8.89
Cyclopropylmethane	CyP-Ph-M	16.18	2.56	14.27	2.14	12.98	1.85

atoms (see Fig. 1). The minimum retention times of the compounds with the same number of carbon atoms correspond to alkylbiphenyls where the *n*-alkyl chain is in position 2.
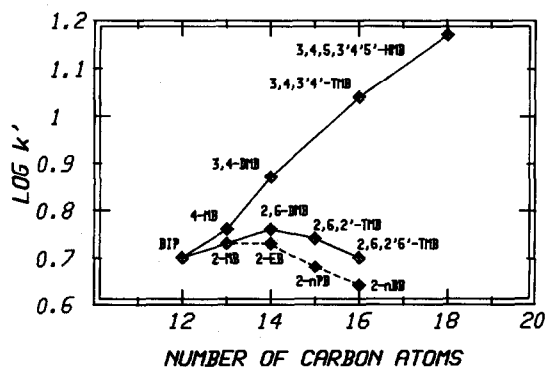

Fig. 1. Dependence of log k' of alkylbiphenyls on the number of carbon atoms. The dashed line represents data for alkylbiphenyls with an *n*-alkyl chain in 0.5% water in the MCS.
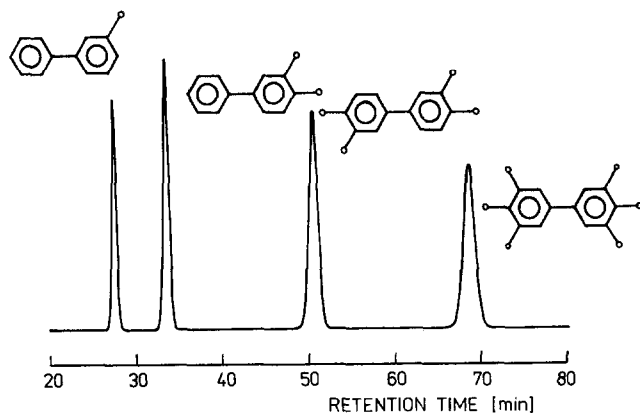
Fig. 2. Chromatogram of some methylbiphenyls with different numbers of methyl groups. Column, 250 × 8 mm I.D. packed with 7.5 μm silica gel; mobile phase, moisture-controlled *n*-pentane; 0.5% water in the MCS; flow-rate, 100 ml/h.

The main factors affecting the retention of alkylbiphenyls are: (i) the number of alkyl groups; (ii) the length of the alkyl groups; (iii) the arrangement of the alkyl groups (*ortho*-effect); (iv) the orientation of the aromatic rings; (v) the shape of the alkyl groups.

Number of alkyl groups

As the number of carbon atoms increases so the range of retention times broadens. With an increasing number of methyl groups in positions 3 and (especially) 4, the retention times increase (Fig. 2). On the other hand, introduction of further isopropyl groups to 3-isopropylbiphenyl results in lower retention times; thus 3,5-, 3,3'-, 3,4'-, and 3,4-diisopropylbiphenyl have lower retention times than both 3-iP-B and biphenyl itself. Also, introduction of an alkyl group to a sterically sensitive position (2), *i.e.*, the *ortho*-position with respect to the link between two aromatic rings, results in lowered retention times (Fig. 1).

Length of alkyl groups

As in the case of alkylbenzenes[4], the retention time decreases with increasing alkyl chain length. The largest effect of this type is observed for the 4-*n*-alkylbiphenyls measured, *viz.* 4-methyl-, 4-ethyl-, 4-*n*-propyl- and 4-*n*-butylbiphenyl. The dependence of log *k'* on the number of carbon atoms for 2-*n*-alkylbiphenyls is presented in Fig. 1. Fig. 3 shows a chromatogram of 2-methyl-, 2-ethyl-, 2-*n*-propyl-, and 2-*n*-butylbiphenyl. As for alkylbenzenes, it was expected that no substantial decrease in retention times would be observed for a further increase in the length of the *n*-alkyl chain.

Alkyl arrangement

For methylbiphenyls and ethylbiphenyls, there is a general increase in retention time in the order of 2-methyl, 3-methyl, 4-methyl, and similarly 2-ethyl, 3-ethyl, 4-ethyl. In case of larger alkyl groups, the situation is complicated by the length, shape, and position of the alkyl groups and subsequent effects on the orientation of the two
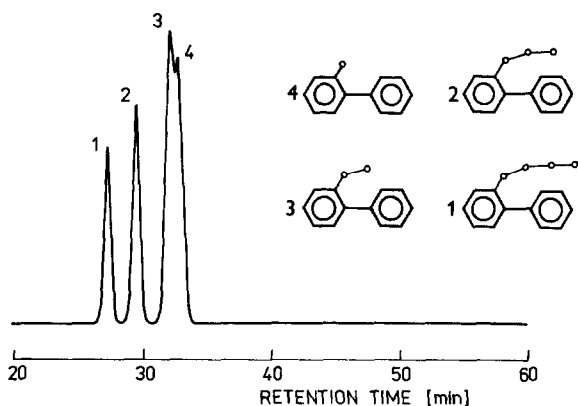
Fig. 3. Chromatogram of some *n*-alkylbiphenyls. Column, 250 × 8 mm I.D. packed with 7.5 μm silica gel; mobile phase, moisture-controlled *n*-pentane; 0.5% water in the MCS; flow-rate, 100 ml/h.

aromatic rings. In the case of methylbenzenes, *ortho*-substituted compounds are characterized by a markedly higher retention time than *meta*- and *para*-derivatives (the elution times of the latter two groups are almost identical). In the case of alkylbiphenyls, substitution in positions 2,6,2',6' results in an increase in the angle between the ring planes, which complicates the adsorption mechanism.

For methylbiphenyls, the retention time increases as the methyl groups are positioned nearer to each other. The highest retention is achieved when the methyl groups are mutually *ortho*. This trend is observed also in case of more substituted methylbiphenyls (see *e.g.* an apparent increase in retention for 3,5,4' trimethylbiphenyl with respect to 2,6,2'-trimethylbiphenyl, or even more substantial retention increase for 3,4,5,3',4',5'-hexamethylbiphenyl with respect to 2,4,6,2',4',6'-hexamethylbiphenyl.

Fig. 4 describes the dependence of log k' on the number of substituents for methylbiphenyls substituted in positions 3 and 4. An approximately linear depen-
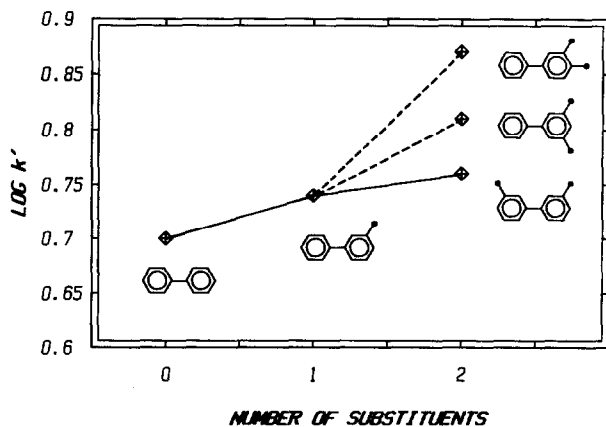

Fig. 4. Dependence of log k' on the number of carbon atoms for biphenyl, 3-methylbiphenyl and some dimethylbiphenyls substituted in positions 3 and 4; 0.5% water in the MCS.
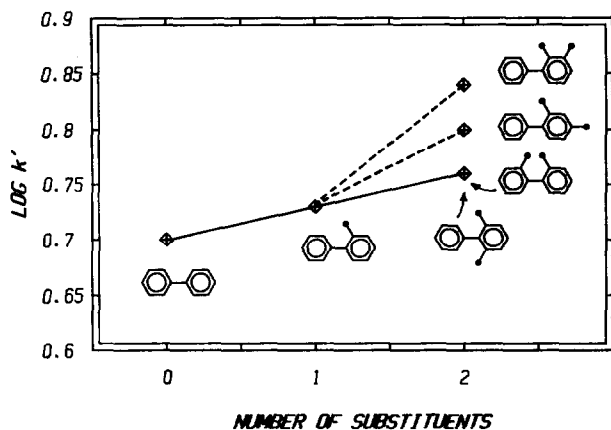
Fig. 5. Dependence of log k' on the number of carbon atoms for biphenyl, 2-methylbiphenyl and some dimethylbiphenyls substituted in position 2; 0.5% water in the MCS.

dence is observed in the series of biphenyl, 3-methylbiphenyl, 3,3'-dimethylbiphenyl. A longer retention time is observed for 3,5-dimethylbiphenyl, where two substituents are located on a single ring. The longest retention time observed was that of 3,4-dimethylbiphenyl, which has mutually *ortho* methyl groups.

Similarly, the retention also increases for biphenyls with one or more substituents in positions 2 or 6. Fig. 5 shows the dependence of log k' on the number of substituents for the mentioned compounds. A linear dependence is again observed between log k' and the number of methyls in the order biphenyl, 2-methylbiphenyl 2,2'-dimethylbiphenyl. 2,6-Dimethylbiphenyl has the same retention time as 2,2'-dimethylbiphenyl. Retention times of the other dimethylbiphenyls increase in the following order: 2,6- < 2,5- < 2,4- < 2,3-dimethylbiphenyl. The highest value was observed for 2,3-dimethylbiphenyl, *i.e.* two methyl groups in mutually *ortho* positions.
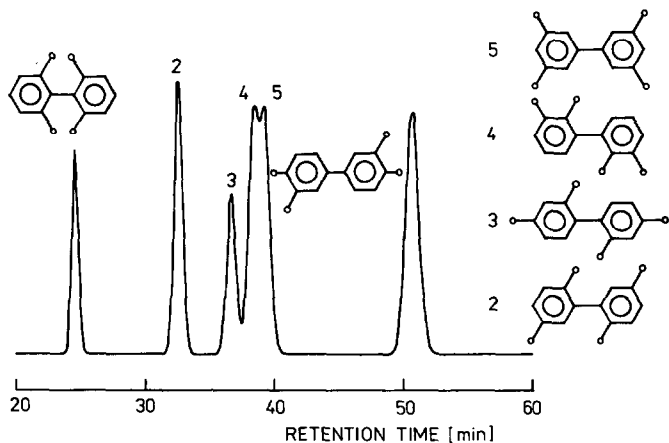

Fig. 6. Chromatogram of some tetramethylbiphenyls. Column, 250 × 8 mm I.D. packed with 7.5 μm silica gel; mobile phase, moisture-controlled *n*-pentane; 0.5% water in the MCS; flow-rate, 100 ml/h.

Orientation of the rings

Most of the biphenyl derivatives do not have planar molecules when in solution. The interplanar angle of biphenyl itself has been estimated at 23–26° (ref. 10). The introduction of substituents into the sterically sensitive 2,6,2' and 6' positions causes the angle between the ring planes to increase. This angle is 70° for 2,6-dimethyl-, 73° for 2,2'-dimethyl-, and 80° for 2,6,2',6'-tetramethylbiphenyl, respectively (ref. 10). On the other hand, substitution in the position 4 results in a decrease of the interplanar angle: 4-methylbiphenyl and 4,4'-dimethylbiphenyl have planar molecules[11,12].

Changes in the retention behaviour of biphenyl derivatives due to rotation of benzene ring planes are of substantial importance for their adsorption on alumina[13,14]. The chromatographic behaviour of biphenyl compounds on silica gel is also affected, although this change has less marked effects because of the different adsorption mechanism on silica gel. Fig. 6 shows a chromatogram for tetramethylbiphenyls: the 2,6,2',6' derivative is eluted first, with a retention time similar-to-those of the methylbiphenyls; next, tetramethylbiphenyls substituted in positions 2 and 2' are eluted, *viz.* the 2,5,2',5', 2,4,2',4' and 2,3,2',3' derivatives, the retention is gradually increasing with the decreasing distance between methyl groups on a single ring; the final two tetramethylbiphenyls are not substituted in positions 2 and 2', and the longest retention time is that of 3,4,3',4'-tetramethylbiphenyl, in which the *ortho* effect is at its strongest.

The three octamethylbiphenyls may serve as another example. The shortest retention time is observed for biduryl (2,3,5,6,2',3',5',6'-octamethylbiphenyl), which is substituted in all sterically sensitive positions (*viz.* 2,6,2' and 6'). Its retention time is in the range of those of the dimethylbiphenyls. It is followed by biisoduryl (2,3,4,6,2',3',4',6'-octamethylbiphenyl), whose longer retention time may be ascribed to *ortho*-substitution in positions 3,4,3' and 4'. The longest elution time is that of biprehnithyl (2,3,4,5,2',3',4',5'-octamethylbiphenyl), which has a smaller interplanar angle than either of the other two octamethyl compounds; moreover, a substantial increase in retention is due to substitution in positions 3,4,5,3',4' and 5'.
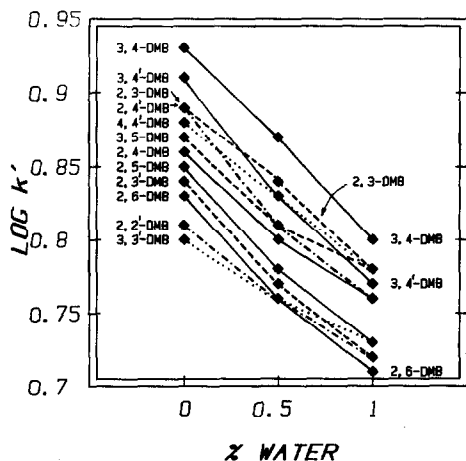

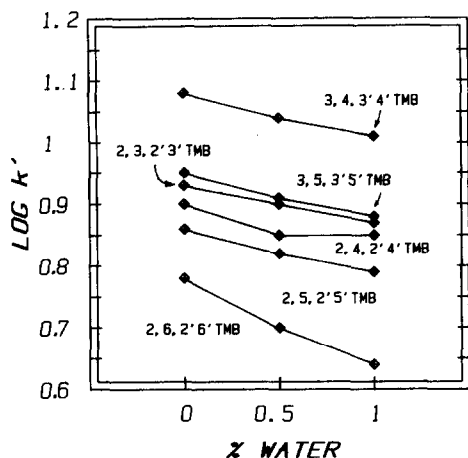Fig. 7. Variation of log k' for a series of dimethylbiphenyls with the content of water in the MCS.

Fig. 8. Variation of log k' for a series of tetramethylbiphenyls with the content of water in the MCS.

Shape of the alkyl group

Alkylbiphenyls with short alkyl groups (especially methyl) have longer retention times than those with long substituents in the same positions. As in the case of alkylbenzenes, compounds with the alkyl chain branched at the α-carbon atom have longer retention times than the corresponding compounds with one alkyl group and the same number of carbon atoms: *e.g.*, the retention times of 2- and 4-isopropylbiphenyls are longer than those of 2- and 4-*n*-propylbiphenyls, and 2- and 4-*tert.*-butylbiphenyls have also higher retention times than the corresponding 2- and 4-*n*-butylbiphenyls.

Influence of water content in the mobile phase

The elution times of the alkylbiphenyls investigated decrease with increasing water content in the mobile phase. Fig. 7 shows the dependence of log k' on the water content as determined by the MCS for a series of dimethylbiphenyls, and Fig. 8 shows the same dependence for tetramethylbiphenyls. It is evident from Fig. 7 that selectivity is strongly influenced by changes in the water content. The separation of dimethylbiphenyls is best when the mobile phase contains the minimum of water, namely dry *n*-pentane. On the other hand, the application of the MCS leads to a good reproducibility of the retention data. The reproducibility at water content concentrations of 0.5 and 1.0% is better when the MCS is applied, therefore the recommended minimum water content is 0.2%[15].

ACKNOWLEDGEMENT

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