Note

High-performance liquid chromatography of alkylnaphthalenes and phenylnaphthalenes on alumina

JANA PUNČOCHÁŘOVÁ, JINDŘICH VAŘEKA, LUDĚK VODIČKA and JOSEF KŘÍŽ*
Laboratory of Synthetic Fuels, Institute of Chemical Technology, Suchbátarova 5, CS-16628 Prague 6 (Czechoslovakia)
(First received June 21st, 1989; revised manuscript received September 20th, 1989)

The relationship between the molecular structure of mono- and diaromatic hydrocarbons and their adsorptivity on silica and alumina has been studied by Snyder[1,2], Klemm *et al.*[3] and, more precisely, by Popl and co-workers[4–6]. The influence of molecular structure on the intermolecular interactions with the adsorbent (hydroxylated and silanized silica gels) and eluent has been studied by Ageev *et al.*[7,8], using polymethyl- and monoalkylbenzenes and also five alkylnaphthalenes among other polynuclear aromatic hydrocarbons as test compounds.

Adsorption systems with long-term equilibration of the water content between the mobile and the stationary phases have been used for the high-performance liquid chromatographic (HPLC) study of the retention behaviour of some alkylbenzenes[9], alkylnaphthalenes[10] and alkylbiphenyls[11] on silica and alkylbenzenes on alumina[12].

The aim of this study was to obtain HPLC data for alkylnaphthalenes in order to study the relationship between their molecular structure and retention behaviour on alumina.

EXPERIMENTAL

Apparatus

A Model 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 5-μl syringe (Hamilton, Bonaduz, Switzerland). 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 Model 3390A reporting integrator (Hewlett-Packard, Avondale, PA, U.S.A.).

A stainless-steel column (150 mm × 4 mm I.D.) was packed using the slurry-packing technique with 7.5-μm alumina (Alusorb 160 Neutral; Lachema, Brno, Czechoslovakia). The water content in the recycling mobile phase was maintained by a moisture control system (MCS) incorporated in a closed circuit. The MCS was filled with 150 g of silica containing 0.5, 1 and 2% of water. The MCS apparatus was described in detail previously[10]. Both the column and the MCS were maintained at 25 $\pm$ 0.1°C. Retention data were calculated on a Hewlett-Packard HP-85 computer equipped with a 82905B impact printer, 82901M dual-disk drive and 7475A plotter. Visicalc software was used to prepare, compute and print the data.

Chemicals

A series of alkylnaphthalene isomers were used. Some of them were commercial products from various manufacturers and the others were kindly donated by Dr. Fryčka of Urxovy závody (Valašské Meziříčí, Czechoslovakia).

Mobile phase

Pure *n*-pentane (VEB Jenapharm, Laboratorchemie Apolda, G.D.R.) was used as the mobile phase. Before use, it was distilled on a glass perforated-plate column with exclusion of moisture and stored over Nalsit A4 molecular sieves (Chemické Závody Juraja Dimitrova, Bratislava, Czechoslovakia). The flow-rate of the mobile phase was 60 ml/h.

Procedure

Three or four measurements were used for each sample. The samples were 10% solutions in isooctane. The column was stabilized before the measurement by washing with fresh mobile phase. The time for equilibration of the column depends on the amount of water contained in the MCS. The column activity was checked before the beginning of the measurement, several times during the analysis and after completion of the measurement, by injecting a test mixture of benzene, naphthalene and biphenyl in isooctane. The dead time of the column was determined as the time interval from the moment of injection to the time when the trace for the solvent disturbance crossed the baseline. The solvent disturbance peak was generated by *n*-hexane.

RESULTS AND DISCUSSION

The retention times, t_R, and capacity factors, k', for 0.5, 1 and 2% water in the MCS are given in Table I. Each value represents an average of three or four measurements for individual alkylnaphthalenes; the reproducibility is within the range 1–2%.

Three main factors that affect the adsorption of alkylbenzenes on silica and alumina[9,12] and alkylnaphthalenes on silica[10] have been discussed previously: (i) the number and shape of the alkyl groups, (ii) the length of the alkyl groups and (iii) the arrangement of the alkyl groups (*ortho* effect).

Number of alkyl groups

Fig. 1 shows the dependence of log k' on the number of carbon atoms for some of the measured compounds. With increasing number of carbon atoms, the range of the retention data broadens.

In relation to the adsorption of alkylnaphthalenes on alumina, the retention is significantly influenced by the number of alkyl groups. The retention increases with increasing number of methyl groups in every position. Similar behaviour has been observed for alkylbenzenes adsorbed on alumina[12].

Length of alkyl groups

Not enough compounds were available for the effect of increasing the chain length of the alkyl groups on retention to be studied in more detail. However, both ethylnaphthalenes studied have shorter retentions than the corresponding methyl

TABLE I

RETENTION DATA FOR ALKYLNAPHTHALENES ON ALUMINA

t_R = Retention time (min); k' = capacity factor = $(t_R - t_0)/t_0$, where t_0 = retention time of unretained compound (hexane) = 1.95 min; MCS = moisture control system.

| Compound	Abbreviation	Concentration of water in MCS (%)					
		0.5		1		2	
		t_R	k'	t_R	k'	t_R	k'
Naphthalene	N	6.76	2.47	6.23	2.19	4.20	1.15
1-Methylnaphthalene	1-MN	8.68	3.45	7.97	3.09	4.92	1.52
2-Methylnaphthalene	2-MN	8.70	3.46	8.05	3.13	4.94	1.53
1-Ethylnaphthalene	1-EN	7.94	3.07	7.31	2.75	4.59	1.35
2-Ethylnaphthalene	2-EN	7.82	3.01	7.09	2.64	4.50	1.31
1,2-Dimethylnaphthalene	1,2-DMN	12.02	5.16	10.79	4.53	6.00	2.08
1,3-Dimethylnaphthalene	1,3-DMN	11.70	5.00	10.48	4.37	5.91	2.03
1,4-Dimethylnaphthalene	1,4-DMN	12.26	5.29	11.03	4.66	6.10	2.13
1,6-Dimethylnaphthalene	1,6-DMN	12.10	5.21	10.83	4.55	6.03	2.09
1,7-Dimethylnaphthalene	1,7-DMN	12.20	5.26	10.85	4.56	6.01	2.08
1,8-Dimethylnaphthalene	1,8-DMN	14.56	6.47	12.72	5.52	6.82	2.50
2,3-Dimethylnaphthalene	2,3-DMN	14.78	6.58	12.89	5.61	6.87	2.52
2,6-Dimethylnaphthalene	2,6-DMN	12.04	5.17	10.73	4.50	6.01	2.08
2,7-Dimethylnaphthalene	2,7-DMN	12.36	5.34	11.00	4.64	5.98	2.07
1-Allylnaphthalene	1-AN	11.23	4.76	9.67	3.96	5.56	1.85
1,3,7-Trimethylnaphthalene	1,3,7-TMN	18.41	8.44	16.52	7.47	7.78	2.99
2,3,5-Trimethylnaphthalene	2,3,5-TMN	23.91	11.26	20.69	9.61	9.47	3.86
2,3,6-Trimethylnaphthalene	2,3,6-TMN	22.94	10.76	20.17	9.34	9.15	3.69
1-Phenylnaphthalene	1-PhN	15.92	7.16	13.45	5.90	7.52	2.86
2-Phenylnaphthalene	2-PhN	51.00	25.15	38.00	18.49	17.75	8.10
Acenaphthene	Acen	14.30	6.33	12.59	5.46	6.61	2.39
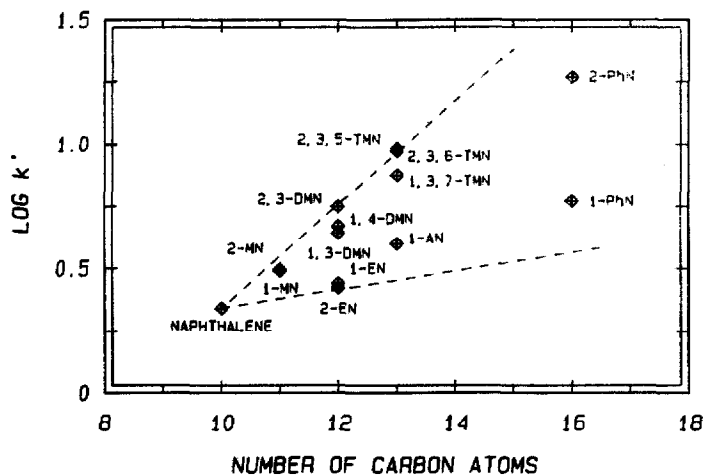
Fig. 1. Dependence of log k' on the number of carbon atoms in alkylnaphthalenes. The range of the retention of all the alkylnaphthalenes is limited by dashed lines. Column, 150 × 4 mm I.D. packed with 7.5-μm alumina. Eluent, n-pentane, 1% water in the MCS. Abbreviations are given in Table I.
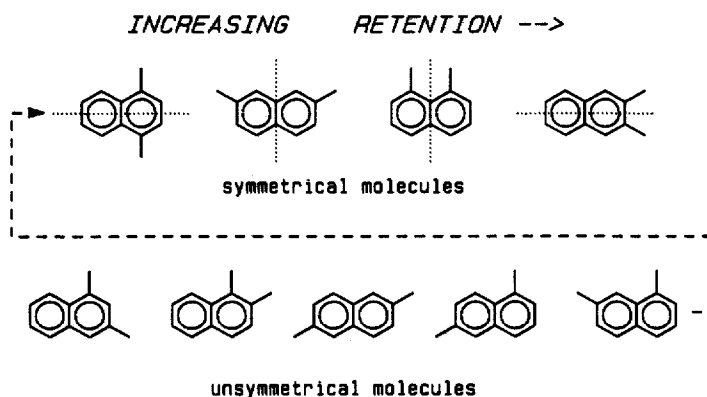
Fig. 2. Scheme illustrating the retention order of symmetrical and non-symmetrical dimethylnaphthalenes.

derivatives (see Fig. 1). On comparing the behaviour of alkylbenzenes on alumina with our results it can be expected that a further increase in chain length will not influence the retention to a great extent.

Arrangement of the alkyl groups

Dimethylnaphthalene homologues can serve as an example for studying the influence of the arrangement of methyl groups on retention. While the distance between the two methyl groups is the main factor that affects the retention of dimethylnaphthalenes on silica[10], there is a new influencing factor on alumina, namely the symmetry of the molecule. The longest retention times are shown by derivatives with axes of symmetry. For the symmetrical compounds, the retention increases with decrease in the distance between the two methyl groups owing to the change of the electron density distribution in the molecule and therefore stronger non-specific interaction with the stationary phase[7,8]. The retention order of all measured
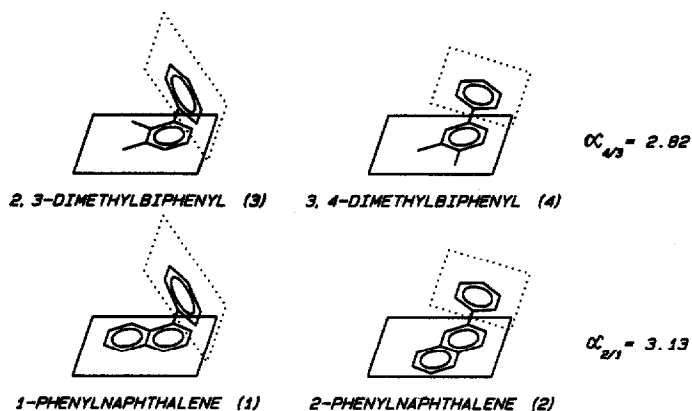

Fig. 3. Influence of the geometrical arrangement of molecules on retention. The selectivities are compared for the pairs 2,3- and 3,4-dimethylbiphenyl and 1- and 2-phenylnaphthalene.

symmetrical and non-symmetrical dimethylnaphthalenes is based on the scheme shown in Fig. 2. The retention of acenaphthene is close to that of 1,8-dimethylnaphthalene, a compound with a similar structure.

The influence of α- and β-substitution on retention has been mentioned by several workers. Snyder[2] and Kucharczyk et al.[13] found that 2-methylnaphthalene eluted before 1-methylnaphthalene, whereas Klemm et al.[3] found the same retention for both compounds. Popl et al. [5,6] reported that 2-methyl- and 2-ethylnaphthalene have lower retentions than the 1-substituted derivatives and that the retention of 2-phenylnaphthalene is substantially higher than that of 1-phenylnaphthalene.

In the present experimental arrangement, for all concentrations of water in MCS the differences between the retentions of the compounds substituted by small alkyl groups are not significant; 2-methyl- has a higher retention than 1-methylnaphthalene whereas 2-ethyl has a shorter retention than 1-ethylnaphthalene.

In agreement with Popl et al.'s work[5], a significant difference was found for the pair of phenylnaphthalenes; the substantionally higher retention of 2-phenylnaphthalene can be explained by the rotation of the benzene ring around the naphthalene–phenyl bond. Owing to a higher interaction of a phenyl group located in the α-position with the naphthalene skeleton (steric hindrance), the interplanar angle of 1-phenylnaphthalene is larger than that of 2-phenylnaphthalene and therefore the ability of the former to be adsorbed on the surface of alumina is smaller. Such behaviour is similar to the adsorption of biphenyl molecules on alumina[14], where the retention of the molecules is strongly influenced by the rotation of both phenyl rings owing to substitution in the sterically sensitive 2- and 6-positions (see Fig. 3).

Influence of water content in the mobile phase

The elution times of alkylnaphthalenes decrease with increasing water content in the mobile phase. Fig. 4 shows the dependence of log k' on the water content as determined by MCS. The retention decreases monotonously and the selectivity is not influenced to a great extent.
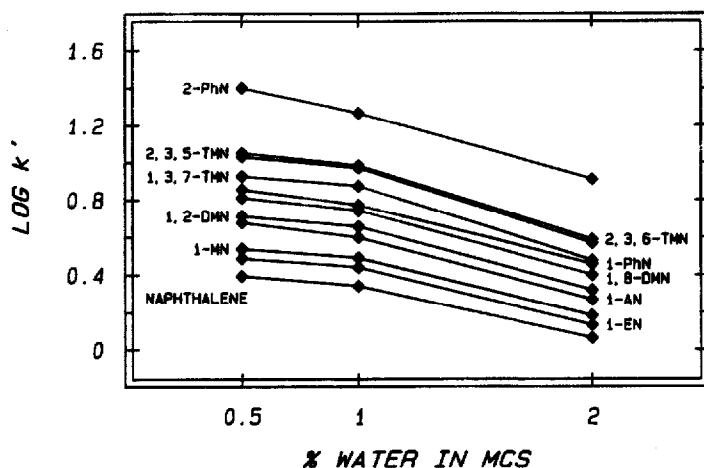

Fig. 4. Variation of log k' for several alkylnaphthalenes with concentration of water in the moisture control system (MCS).
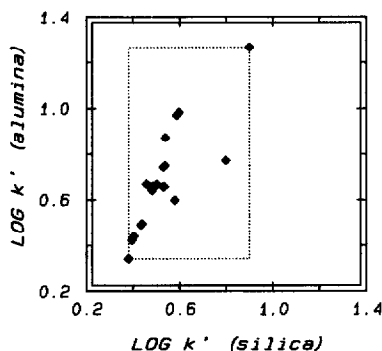
Fig. 5. Comparison of log k' values for all measured alkylnaphthalenes on alumina and silica. Silica[10] column (250 × 8 mm I.D.) packed with 7.5-μm silica gel (Silasorb; Lachema).

Comparison of alumina and silica

The retention behaviour of all the measured compounds using both alumina and silica[10] adsorbents is show in Fig. 5. It is evident that for the alkylnaphthalenes investigated alumina provides a better separation than silica.

REFERENCES

1 L. R. Snyder, *The Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968.
2 L. R. Snyder, *J. Chromatogr.*, 6 (1961) 22.
3 L. H. Klemm, D. S. W. Chia, C. E. Klopfenstein and K. B. Desay, *J. Chromatogr.*, 30 (1967) 476.
4 M. Popl, V. Dolanský and J. Mostecký, *J. Chromatogr.*, 117 (1976) 117.
5 M. Popl, V. Dolanský and J. Mostecký, *J. Chromatogr.*, 91 (1974) 649.
6 M. Popl, V. Dolanský and J. Mostecký, *Collect. Czech. Chem. Commun.*, 39 (1974) 1836.
7 A. N. Ageev, A. V. Kiselev and Ya. I. Yashin, *Chromatographia*, 13 (1980) 669.
8 A. N. Ageev, A. V. Kiselev and Ya. I. Yashin, *Chromatographia*, 14 (1981) 638.
9 J. Kříž, L. Vodička, J. Punčochářová and M. Kuraš, *J. Chromatogr.*, 219 (1981) 53.
10 J. Punčochářová, L. Vodička and J. Kříž, *J. Chromatogr.*, 267 (1983) 222.
11 J. Kříž, J. Punčochářová and L. Vodička, *J. Chromatogr.*, 354 (1986) 145.
12 J. Kříž, J. Punčochářová, L. Vodička and J. Vařeka, *J. Chromatogr.*, 437 (1988) 177.
13 N. Kucharczyk, J. Fohl and J. Vymětal, *J. Chromatogr.*, 11 (1963) 55.
14 J. Kříž, L. Vodička and E. A. Johnson, in preparation.