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Note

High-performance liquid chromatography of alkylnaphthalenes on silica

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The influence of the molecular structure of some alkylnaphthalenes and other aromatic hydrocarbons on their adsorptivity on silica and alumina has been studied previously[1–3]. The problem of reproducible measurements of high-performance liquid chromatographic (HPLC) retention data on silica or alumina using pentane or another hydrocarbon as the mobile phase is connected with long-term equilibration of the water content between the mobile and stationary phases. This equilibration can take several weeks, especially when the column is dried by passing a "very dry" mobile phase and the retention data of compounds having long retention times are measured. This problem can be overcome by mobile phase recycling and incorporating a moisture control system into a closed circuit[4].

The aim of this study was to obtain more precise and reproducible HPLC data on alkylnaphthalenes for studying the relationship between their molecular structure and retention behaviour. The work is related to that on the HPLC of alkylbenzenes on silica[5].

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. In order to maintain the level of the mobile phase in the MCS more accurately and easily, the original MCS apparatus designed by Engelhard was modified as shown in Fig. 1.
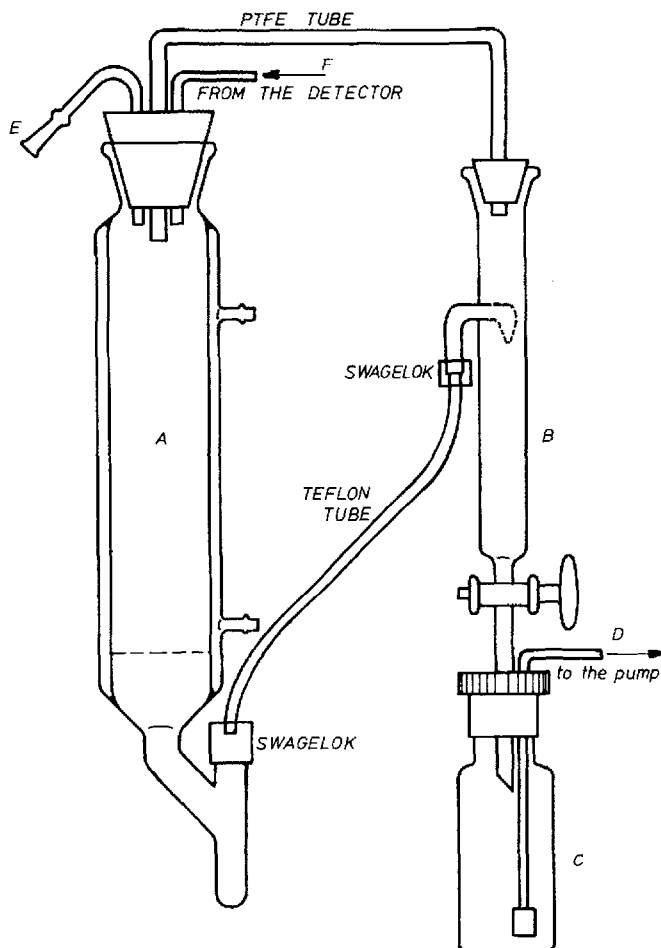

Fig. 1. Moisture control system (MCS). A = Thermostated funnel for silica coated with a defined amount of water; B = funnel keeping a constant level of the mobile phase; C = eluent reservoir (original Varian); D = suction line to the pump; E = drying tube filed with blue silica gel; F = output line from the detector.

Chemicals

Some of the 21 naphthalene standards were commercial products from various manufacturers; other were kindly given by Dr. Fryčka of Urxovy závody, Valašské Meziříči.

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 the measurements, the column was stabilized by washing with fresh recycling 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, then several times during the analysis and after the completion of the measurements again, by injection of a test mixture of benzene, naphthalene and phenanthrene in isooctane.

RESULTS AND DISCUSSION

The values of the retention times (t_x) and the capacity factors (k') are given in Table I. Each value represents an average obtained from three or four retention time measurements of individual alkylnaphthalenes. Fig. 2 shows the dependence of log k' on the water content in the MCS and Fig. 3 shows the same for a series of dimethylnaphthalenes.

TABLE I

RETENTION DATA FOR ALKYLNAPHTHALENES

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

| Compound	Deactivation of silica (concentration of water in moisture control system)					
	0%		0.5%		1%	
	t_x	k'	t_x	k'	t_x	k'
Naphthalene	12.91	2.80	11.59	2.52	11.05	2.40
1-Methylnaphthalene	14.28	3.10	12.50	2.72	12.46	2.71
2-Methylnaphthalene	14.80	3.22	12.86	2.79	12.63	2.75
1-Ethylnaphthalene	13.15	2.86	11.87	2.58	11.64	2.53
2-Ethylnaphthalene	12.98	2.82	11.64	2.53	11.42	2.48
1,2-Dimethylnaphthalene	17.43	3.79	16.16	3.51	15.59	3.39
1,3-Dimethylnaphthalene	17.78	3.87	14.00	3.04	13.96	3.03
1,4-Dimethylnaphthalene	15.85	3.45	13.20	2.87	13.15	2.86
1,5-Dimethylnaphthalene	16.03	3.48	14.00	3.04	13.89	3.02
1,6-Dimethylnaphthalene	16.90	3.67	14.25	3.09	14.19	3.08
1,7-Dimethylnaphthalene	15.93	3.46	15.16	3.29	14.04	3.05
1,8-Dimethylnaphthalene	18.83	4.09	15.73	3.42	15.54	3.38
2,3-Dimethylnaphthalene	18.45	4.01	15.84	3.44	15.84	3.44
2,6-Dimethylnaphthalene	16.65	3.62	13.89	3.02	13.82	3.00
2,7-Dimethylnaphthalene	17.10	3.72	14.68	3.19	14.65	3.18
1-Allylnaphthalene			17.99	3.91	17.46	3.79
2,3,5-Trimethylnaphthalene	21.05	4.58	19.74	4.29	18.19	3.95
2,3,6-Trimethylnaphthalene	20.74	4.51	19.29	4.19	17.74	3.86
1,3,7-Trimethylnaphthalene	19.70	4.28			15.89	3.45
1-Phenylnaphthalene	35.60	7.74	30.73	6.68	28.90	6.28
2-Phenylnaphthalene	43.98	9.56	39.12	8.50	36.54	7.94
Acenaphthene					14.95	3.25
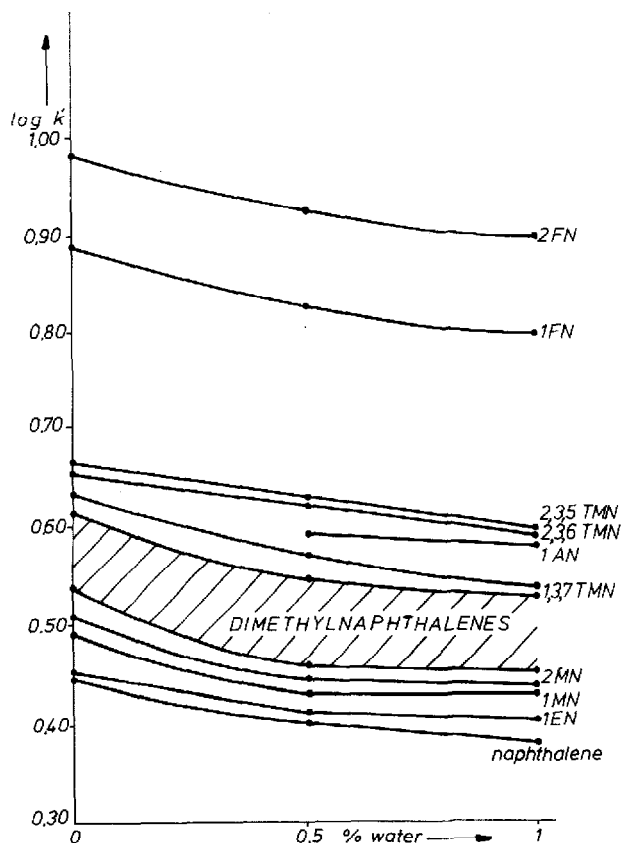
Fig. 2. Variation of log k' for alkylnaphthalenes with the concentration of water in the moisture control system. MN = Methylnaphthalene; EN = ethylnaphthalene; DMN = dimethylnaphthalene; TMN = trimethylnaphthalene; FN = phenylnaphthalene; AN = allylnaphthalene.

It is evident that not only the absolute but also the relative retentions are sensitive functions of the water content in the eluent. The sensitivity is higher for compounds having longer retention times. With naphthalenes, an MCS containing at least 0.5% of water should be used. Above this level, the values are more reproducible and the relationships between molecular structure and retention data can be easily interpreted.

Three main factors affecting the adsorption of alkylbenzenes were discussed previously[5]: (i) the length of the alkyl group; (ii) the arrangement of the alkyl groups (*ortho* effect); and (iii) the number and shape of the alkyl groups. With dimethylnaphthalenes there is another factor influencing the retention, namely the α- or β-position of the substituents in the molecule.

A decrease in retention time owing to an increase in alkyl chain length can be demonstrated only with the shorter t_x value of 2-ethylnaphthalenes in relation to the t_x values of methylnaphthalenes. As in the alkylbenzene series, the retention increases when more methyl groups are present.

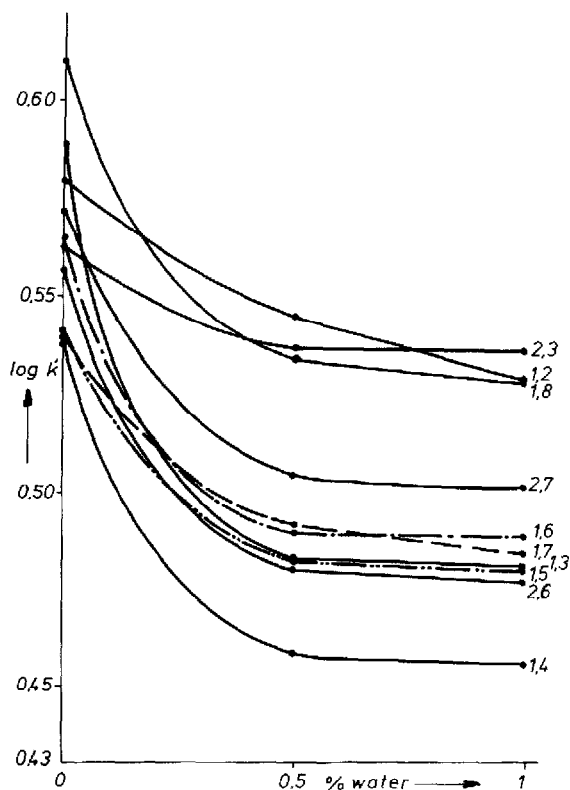Both the arrangement of the alkyl groups and their location in the α- or β-

Fig. 3. Variation of log k' for dimethylnaphthalenes with the concentration of water in the moisture control system.

position affect the retentions of dimethylnaphthalenes (DMN). All ten isomers can be approximately separated into two main groups (Fig. 3). The first consists of isomers with methyl groups in the *ortho*-position (2,3-DMN and 1,2-DMN) or methyl groups that are very close to each other (1,8-DMN).

In the second group, isomers having mostly one methyl group in the α- and one in the β-position are eluted. This group includes 2,6-DMN compounds, which have both methyl groups in β-positions, on opposite sides of the molecule.

2,7-DMN, which has methyl groups situated in β-positions on both rings of the molecule, has a retention time shorter than the compounds of the first group and longer than the compounds of the second group.

1,4-DMN, which has both methyl groups in α-positions on opposite sides of one ring of the molecule, has the shortest retention time of all alkylnaphthalenes measured.

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