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Peculiarities of aromatic hydrocarbon retention in normal-phase high-performance liquid chromatography with eluents containing halide derivatives

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ABSTRACT

The possibility of regulating the retention and selectivity of monoalkyl- and polymethyl-substituted aromatic hydrocarbons in normal-phase high-performance liquid chromatography was investigated by modifying the non-polar (hexane) mobile phase with halide derivatives of hydrocarbons. Dichloromethane, chloroform, carbon tetrachloride and ethyl bromide were employed as modifiers. The decrease in relative retention for small mole fractions of modifier in the eluent increased with decrease in the polarity. The retention mechanism of the aromatic hydrocarbons is discussed. Chromatograms for the group separation of diesel fuel aromatic hydrocarbons are presented.

INTRODUCTION

The group separation and determination of aromatic hydrocarbons (AHs) is of great importance for the analysis of petroleum products. Normal-phase high-performance liquid chromatography (HPLC) has been successfully employed for determining mono- and bicyclic aromatic hydrocarbons (MAH and BAH) in light fuels (gasolines) [1–3]. The separation of AHs into groups is much worse for fuels having higher boiling points (jet and diesel fuels). For instance, the overlapping of MAH and BAH peaks is due to the fact that polymethylbenzenes are eluted simultaneously with alkyl naphthalenes. It is possible to increase the selectivity of the chromatographic system to the group separation of AHs by changing either the nature of the adsorbent or the nature and composition of the eluent [4–6].

This paper deals with an investigation of the possibility of regulating the retention and separation selectivity of monoalkyl- and polymethyl-substituted AHs in normal-phase HPLC with hydroxylated silica gel as a polar sorbent by modifying the non-polar eluent (hexane) with chloro derivatives of methane and ethyl bromide. These modifiers are π -electron donors and form molecular π -complexes with AHs [7].

EXPERIMENTAL

The investigation was carried out using a Milichrome microcolumn liquid chromatograph equipped with an electromechanical syringe pump (capacity 2500 μ l,

eluent consumption 2–600 $\mu\text{l}/\text{min}$) and a spectrophotometric detector (spectral range 190–360 nm). Stainless-steel columns (62×2 mm I.D.) were packed with silica gel Silasorb 600 of specific surface area 600 m^2/g and mean particle diameter 5 μm , with an efficiency of 3000 theoretical plates (with respect to phenanthrene). The columns were packed using the suspension technique.

Two-component mixtures (from 99.5:0.5 to 90:10, v/v) of hexane with dichloromethane, chloroform, carbon tetrachloride and ethyl bromide were employed as eluents. Polymethyl- and monoalkylbenzenes and polyaromatic hydrocarbons were used as adsorbates.

RESULTS AND DISCUSSION

The effect of the eluent on the retention of a substance was determined according to Snyder [8,9] using four types of intermolecular interactions with sorbates: dispersion, induction, donor–acceptor (including hydrogen bonding) and dielectric (ion solvation). The total effect of all types of interactions characterizes the eluent polarity, whereas the mostly manifested effect of one of these types indicates the eluent selectivity [8]. The haloalkanes used as modifiers of the mobile phase in this work are distinguished by the number and the nature of the halogen atoms and belong, according to Snyder [8,9], to different selectivity groups: dichloromethane (group 5: solvents preferably interacting with substances having a high dipole moment), chloroform (group 8: proton donors), carbon tetrachloride (group O: non-polar molecules) and ethyl bromide (group 6a). In addition to selectivity, these solvents also differ in their polarity, which is expressed by the parameter P' which indicates the relative activity of the solvent [8,10]. The characteristics of the eluent modifiers used here are given in Table I.

In normal-phase HPLC the capacity factor of a substance ($k' = V'_R/V_0$, where V'_R and V_0 are the adjusted and dead retention volumes, respectively) is inversely proportional to the eluent polarity. In our experiments, the introduction of all modifying additives into the eluent resulted in a decreased retention (Figs. 1 and 2). In this instance, the dependence $1/V'_R = f(N_b)$ for the most polar additives (chloroform and dichloromethane) is linear over the entire range (from 0 to $0.2N_b$) of the additive amount (Fig. 1a,b) and that for less polar additives (carbon tetrachloride and ethyl bromide) in the range $N_b = 0.01$ – 0.02 exhibits a break for the derivatives of benzene and naphthalene. It can be seen from Figs. 1c and 2 that in the range of small N_b

TABLE I
CHARACTERISTICS OF HALIDE-CONTAINING MODIFIERS OF THE MOBILE PHASE

Substance	Elution strength on		Polarity, P'	Dielectric constant (20°C)	Group selectivity after Snyder [8,9]
	SiO_2	Al_2O_3			
Dichloromethane	0.32	0.42	3.1	8.9	5
Chloroform	0.26	0.40	4.1	4.8	8
Carbon tetrachloride	0.11	0.18	1.6	2.24	0
Ethyl bromide	—	0.37	2.0	9.34	6a

(0.01–0.02) the increase in $1/V'_R$ with increase in N_b depends on the nature of the modifier; it is least for CHCl_3 and increases in the order $\text{CH}_2\text{Cl}_2 < \text{CCl}_4 < \text{C}_2\text{H}_5\text{Br}$.

If we use the data from Figs. 1 and 2 and plot the dependence of value $\tan \beta = \partial(1/V'_R)/\partial N_b$, which characterizes the effect of the addition of modifier to the eluent on the retention, on the polarity of the eluent, P' (Fig. 3), we observe an unexpected regularity: the relative decrease in retention in the range of small N_b is increased owing to a decrease in the polarity of the modifying additive rather than to an increase. This effect may result from the formation of molecular associates (π -complexes) in solution of the sorbate–modifier type. This effect is seen most clearly when

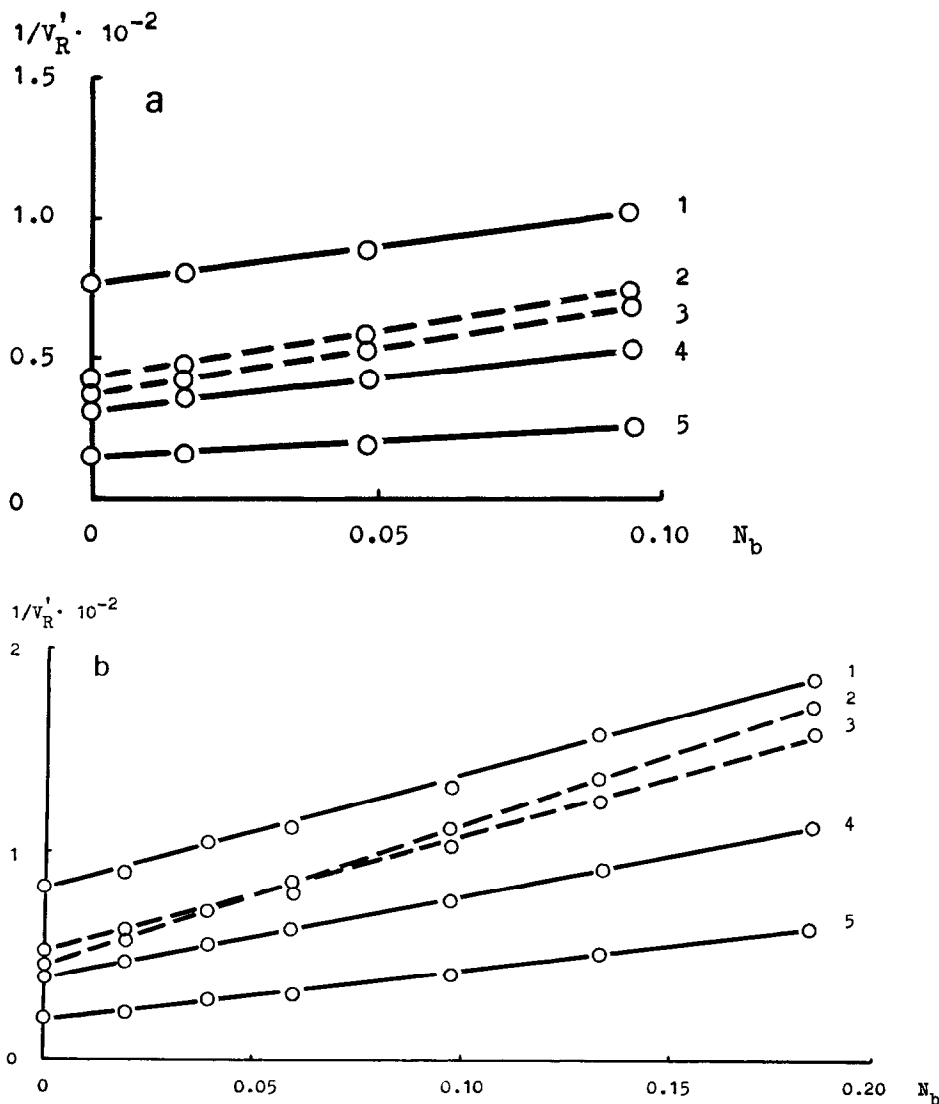


Fig. 1.

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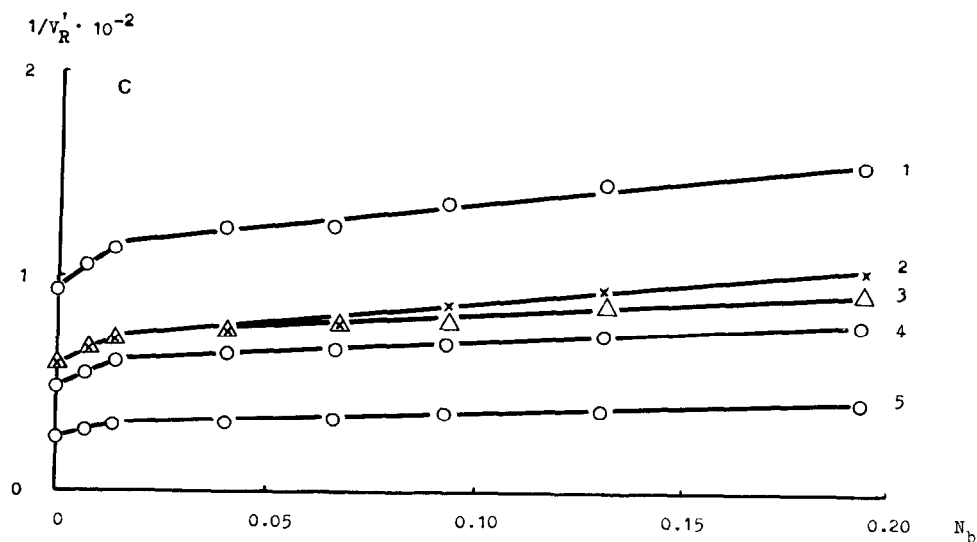


Fig. 1. Dependence of the inverse of the retention of aromatic hydrocarbons ($1/V_R'$) on the mole fraction of the modifier (N_b) in hexane: (a) dichloromethane; (b) chloroform; (c) carbon tetrachloride. 1 = Benzene; 2 = 1,2,4,5-tetramethylbenzene; 3 = 2-*n*-hexylnaphthalene; 4 = naphthalene; 5 = phenanthrene.

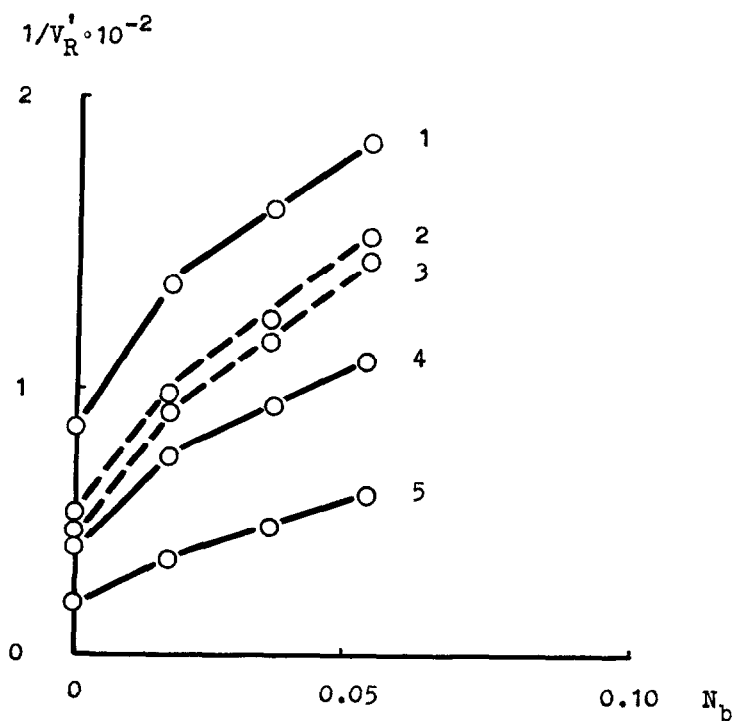


Fig. 2. Dependence of the inverse of the retention of aromatic hydrocarbons ($1/V_R'$) on the mole fraction of ethyl bromide (N_b) in hexane. 1 = Benzene; 2 = 1,2,4,5-tetramethylbenzene; 3 = 2-*n*-hexylnaphthalene; 4 = naphthalene; 5 = phenanthrene.

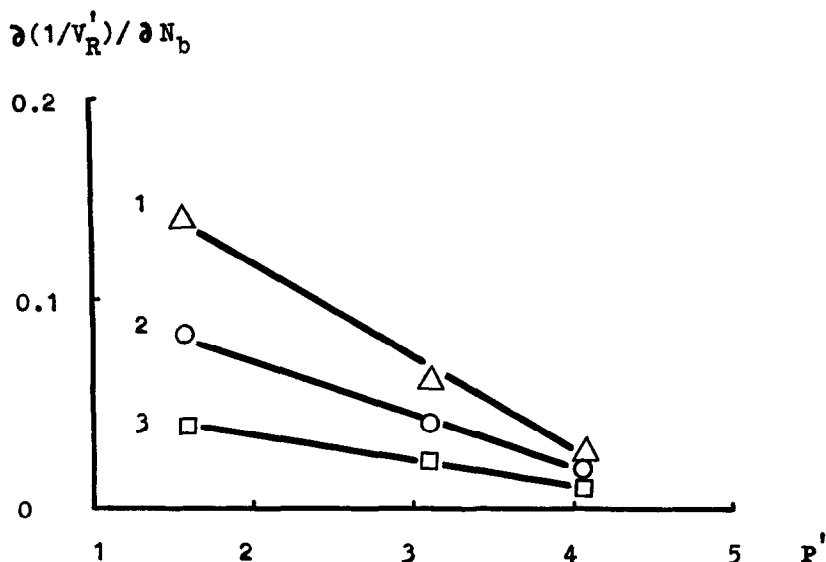


Fig. 3. Dependence of $\partial(1/V_R^i)/\partial N_b$ on the modifier polarity (P'). 1 = Benzene; 2 = naphthalene; 3 = phenanthrene.

non-polar carbon tetrachloride weakly adsorbed from solution in hexane on silica is used as the modifier.

Another important characteristic of the chromatographic system determining the availability of this system for the analysis of the given sorbates was found to be the selectivity of the retention of substances having various natures and structures, $\alpha = V_{R,2}'/V_{R,1}'$, where $V_{R,1}'$ and $V_{R,2}'$ are the adjusted retention volumes of substances 1 and 2, respectively. Table II gives the relative retentions of monoalkylnaphthalene

TABLE II

SELECTIVITY OF THE RETENTION OF 2-*n*-HEXYLNAPHTHALENE TOWARDS 1,2,4,5-TETRAMETHYLBENZENE ($\alpha_{\text{HN/TMB}}$) DEPENDING ON THE NATURE AND COMPOSITION OF THE ELUENT

Concentration of modifier (% v/v)	Dichloromethane	Chloroform	Carbon tetrachloride	Ethyl bromide
0	1.01	1.04	1.01	1.01
0.5	—	—	1.01	—
1.0	0.97	1.05	1.01	1.03
2.0	0.99	—	—	1.05
3.0	1.02	1.08	1.00	1.06
5.0	1.05	—	0.99	—
6.0	—	1.01	—	—
7.0	1.10	—	0.98	—
10.0	1.09	—	0.96	—
15.0	—	—	0.93	—
20.0	—	—	0.92	—

(*n*-hexylnaphthalene) with respect to polymethylbenzene (1,2,4,5-tetramethylbenzene) depending on the nature and composition of the eluent ($\alpha_{\text{HN/TMB}} = V'_{\text{R,HN}}/V'_{\text{R,TMB}}$). The value of $\alpha_{\text{HN/TMB}}$ can characterize the selectivity of the group separation of mono- and bicyclic hydrocarbons. As it is seen from Table II, for low dichloromethane contents in the eluent (1.0%, v/v) the value of $\alpha_{\text{HN/TMB}}$ is the lowest (0.97) and increases monotonically to $\alpha = 1.1$ at 7.0–10.0% (v/v). When chloroform and ethyl bromide are used as additives, the selectivity is lower ($\alpha = 1.06$ – 1.08) at 3.0% (v/v); further increases in the amount of the modifier are not feasible because of an abrupt decrease in the retention of the AHs with $\text{C}_2\text{H}_5\text{Br}$ (Fig. 2) and a decrease in the

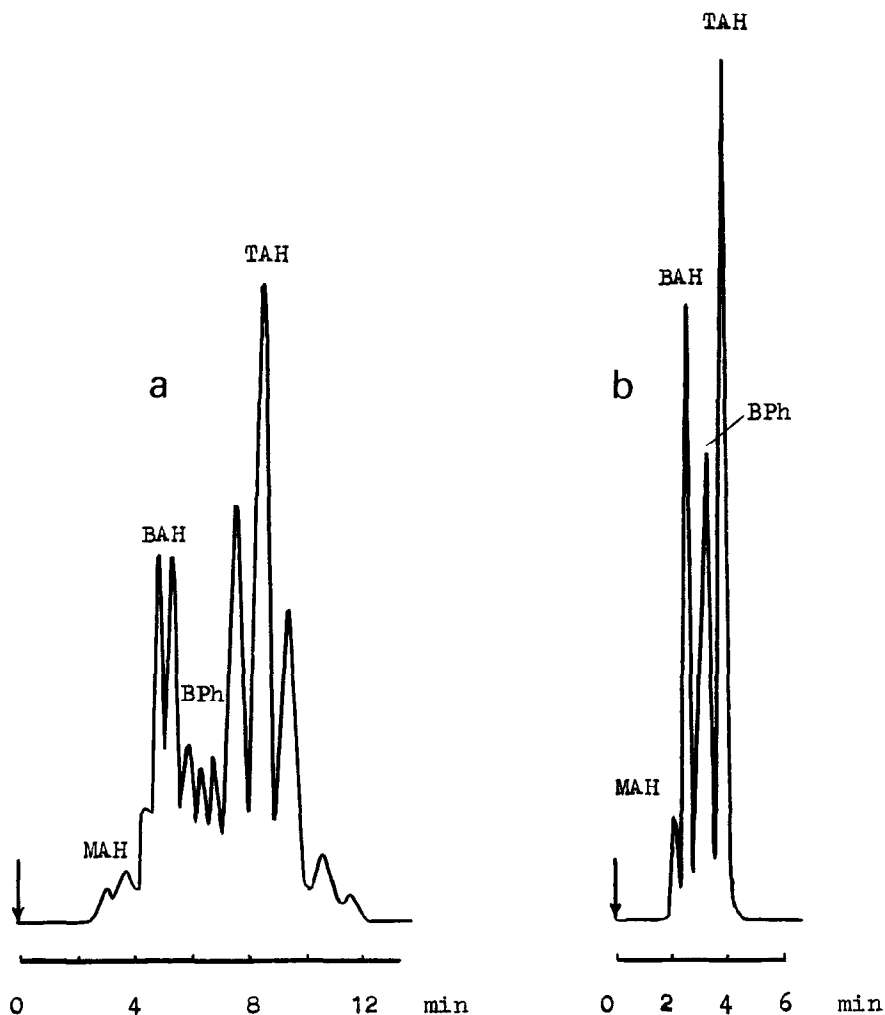


Fig. 4. Chromatograms of diesel fuel. MAHs, BAHs, TAHs are mono-, bi- and tricyclic aromatic hydrocarbons, respectively, and BPh are aromatic hydrocarbons of the biphenyl series. Mobile phase: (a) *n*-hexane; (b) *n*-hexane-dichloromethane (93:7, v/v). Column (62×2 mm I.D.) packed with Silasorb 600 (5 μm). Flow-rate of the mobile phase, 100 $\mu\text{l}/\text{min}$. A spectrophotometer (254 nm) was used as the detector.

selectivity with CHCl_3 (Table II). The value of α is about 1.06 for separation (resolution, $R_s = 1$) of two substances with low retention (k_1 and $k_2 \approx 1$) on a conventional column (30 cm \times 4.6 mm I.D.) with an efficiency of 15 000–20 000 theoretical plates [11].

Chromatography of a real sample of petroleum products showed that the group separation of aromatic hydrocarbons in diesel fuel is optimum with *n*-hexane-dichloromethane (93:7) as eluent (Fig. 4b). In contrast to pure *n*-hexane (Fig. 4a), the former eluent permits a better group separation of mono- and bicyclic AHs and eliminates the undesirable separation of alkyl- and methyl-substituted AHs (Fig. 4b) belonging to the same group (MAH, BAH, etc.).

We shall now consider the reasons for the changes in the selectivity of hydroxylated silica gel with respect to AHs using *n*-hexane with haloalkane additives as the eluent. Figs. 5 and 6 exemplify the dependences of $\log k'$ on the number of carbon atoms, n_c , for aromatic hydrocarbons of various structures with CHCl_3 and CH_2Cl_2 being used as the additives to *n*-hexane. Analogous dependences can also be plotted

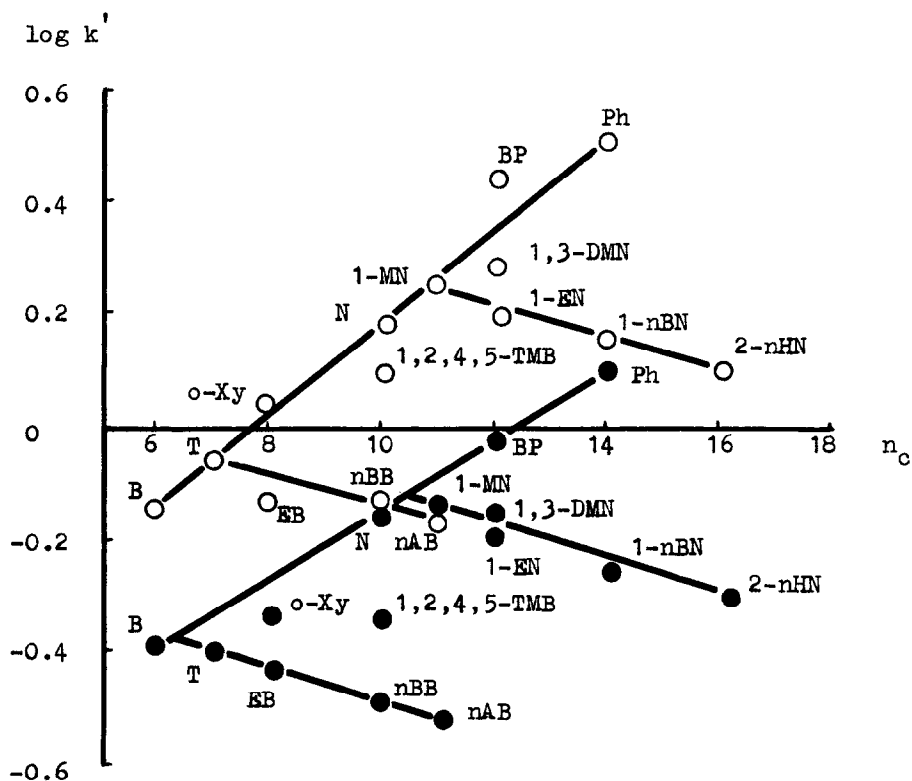


Fig. 5. Dependence of $\log k'$ on the number of carbon atoms (n_c) for individual aromatic hydrocarbons. Eluent: \circ = dried *n*-hexane; \bullet = dried *n*-hexane-dichloromethane (93:7, v/v). B = benzene; T = toluene; o-Xy = *o*-xylene; 1,2,4,5-TMB = tetramethylbenzene; EB = ethylbenzene; nBB = *n*-butylbenzene; nAB = *n*-amylnaphthalene; N = naphthalene; 1-MN = 1-methylnaphthalene; 1,3-DMN = 1,3-dimethylnaphthalene; 1-EN = 1-ethylnaphthalene; 1-nBN = 1-*n*-butyl-naphthalene; 2-nHN = 2-*n*-hexyl-naphthalene; BN = biphenyl; Ph = phenanthrene.

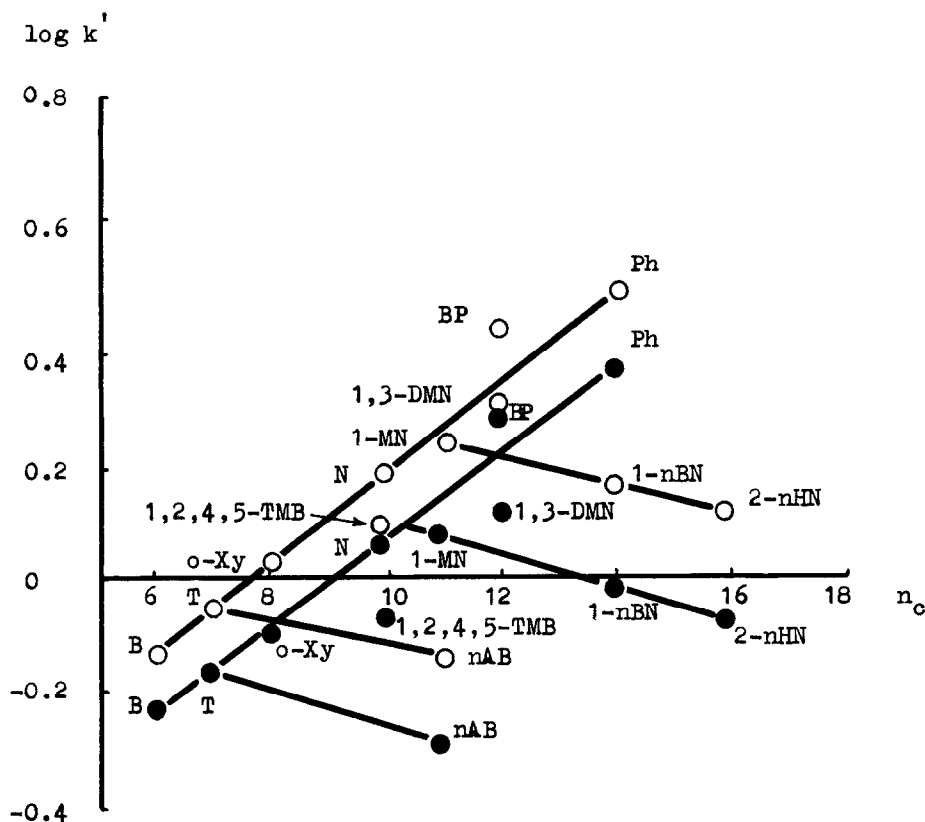


Fig. 6. Dependence of $\log k'$ on the number of carbon atoms (n_c) for individual aromatic hydrocarbons. Eluent: \circ = dried *n*-hexane; \bullet = dried *n*-hexane-chloroform (94:6, v/v). Compounds as in Fig. 5.

for eluents of various composition containing CCl_4 and $\text{C}_2\text{H}_5\text{Br}$. It can be seen from Figs. 5 and 6 that a good linear dependence of $\log k'$ on n_c is observed in the benzene-naphthalene-phenanthrene series for all the eluents. It has also been found experimentally that an increasing content of haloalkane in the eluent results in a decreasing retention of aromatic hydrocarbons, this retention differing from one modifier to another. The slope of the linear dependences of $\log k'$ on n_c in the benzene-naphthalene-phenanthrene series does not change with increase in the concentration of chloroform in the eluent, whereas with CH_2Cl_2 it slightly decreases (Figs. 5 and 6). For *n*-alkylbenzenes and *n*-alkylnaphthalenes, $\log k'$ decreases almost linearly with elongation of the alkyl chain. In comparison with monoalkyl-substituted AHs and unsubstituted AHs (benzene, naphthalene and phenanthrene) the modifier has a greater effect on the retention of methyl-substituted AHs, particularly when CH_2Cl_2 is used (Fig. 5).

When elution is carried out with *n*-hexane, the points characterizing the retention of methylbenzenes (toluene and *o*-xylene) and methylnaphthalenes (1-methylnaphthalene and 1,3-dimethylnaphthalene) lie near the straight line of the $\log k'$

dependence on n_c for benzene–naphthalene–phenanthrene; 1,2,4,5-tetramethylbenzene is eluted simultaneously with 2-*n*-hexylnaphthalene. However, with the eluent of optimum composition [*n*-hexane–CH₂Cl₂ (93:7, v/v)] the points for methyl-substituted AHs lie below the corresponding straight line of $\log k' = f(n_c)$ for benzene–naphthalene–phenanthrene; here 1,2,4,5-tetramethylbenzene is eluted earlier than 2-*n*-hexylnaphthalene. Hence it follows that the increasing selectivity of the separation of MAHs and BAHs in diesel fuel with the use of dichloromethane as the modifier results from the fact that the latter interacts much more strongly with methyl-substituted AHs than with other alkyl derivatives.

CONCLUSIONS

Studies of the effect of modifying the eluent with haloalkanes on the retention of substituted hydrocarbons in normal-phase HPLC have shown an inversely proportional dependence of the decrease in relative retention on the polarity of the mobile phase. The selectivity of the separation of mono- and bicyclic aromatic hydrocarbons depends on the nature of the modifying additive and its concentration in the eluent. The eluent *n*-hexane–dichloromethane (93:7, v/v) has been found to be optimum for the group separation of aromatic hydrocarbons in diesel fuels by normal-phase HPLC.

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