

Intermolecular interactions and selectivity of polyaromatic hydrocarbons separation in liquid chromatography

S.N.Lanin and Yu.S.Nikitin

M.V.Lomonosov State University of Moscow, Department of Chemistry,
119899 Moscow, USSR

Abstract - A mathematical modelling method and principle of additivity for investigations of intermolecular interactions and selectivity of polyaromatic hydrocarbons separation in high performance liquid chromatography is described. The proposed correlation equations show good correlation for all chromatographic systems under investigation and can be used to predict retentions of different substances.

INTRODUCTION

Mathematical modelling of the chromatographic process for determining the correlation dependence between molecular parameters and physical properties of sorbates and their retention with the subsequent computerized experiment appears to be one of the most promising approaches. It enables one to predict the properties of a chromatographic system and to optimize its composition and the conditions for the separation (the direct task) as well as to study the intermolecular interactions, molecular structure of the sorbates, their retention mechanisms and physico-chemical properties, to identify the chromatographic zones corresponding to the components of complex mixtures of unknown composition (the reverse task) [1-15]. The development of universal automated systems of chemical analysis and expert systems is also a perspective and widely applicable area of using the modelling of chromatographic processes. The retention and separation selectivity of substances in high performance liquid chromatography (HPLC) depend on the sorbates nature, the structure and surface chemistry of the sorbent, the composition of the eluent, that is, the parameters determining the intermolecular interaction of the chromatographic system components.

Some of the most toxic and widely spread pollutants of the environment are the polycyclic aromatic hydrocarbons (PAHs). Many of them are cancer-producing. PAHs have been established as priority pollutants by the Environmental Protection Agency. This is determined the particular attention to the investigation of this class of substances.

CALCULATION PROCEDURE

The principle of additivity is often applied in studying the dependence between the structure and the chromatographic retention of the molecules. According to this principle, the free energy of the molecule sorption (ΔG) can be expressed as a linear combination of energies (ΔG_i) referring to different fragments of the molecule

$$\Delta G = \sum \Delta G_i \quad (1)$$

In the present study we have restricted ourselves by investigating the chromatographic retention of unsubstituted polyaromatic hydrocarbons and, therefore, have used the equations [7,8] which we proposed earlier, for the description of their behaviour in the chromatographic system

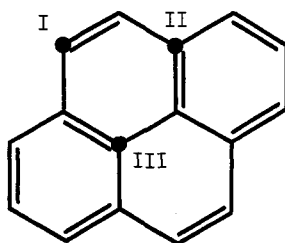
$$\log k' = B_1 n_I + B_2 n_{II} + B_3 n_{III} + B_4 (n_\pi/L) + B_0 \quad (2)$$

$$\log k' = D_1 n_I + D_2 (n_{II} + n_{III}) + D_3 (n_\pi/L) + D_0 \quad (3)$$

$$\log k' = E_1 n_I + E_2 (n_{II} + n_{III}) + E_3 (n_\pi/L) + E_4 C + E_0, \quad (4)$$

where k' is the capacity factor, n_I is the number of carbon atoms of type I, n_{II} is the number of carbon atoms of type II, n_{III} is the number of carbon atoms of type III, n_π is the number of π -electrons in the molecule, L is the PAH molecule length along

the main axis, \bar{A} [16], C is the content of the organic component (in the case of the reversed-phase HPLC) or the polar additive (in the case of the normal-phase HPLC) in the binary eluent, vol.%, B_i , D_i , E_i are the equation coefficients. The types of the carbon atoms differing in their environment and, therefore, characterized by different distribution of electron density [5,6,17] in unsubstituted PAHs, for example, in the pyrene molecule, are given below.



The coefficients in eq. (2), (3), (4) can be considered as the increments referring to various fragments of the molecule according to eq. (1). In this case the coefficients B_0 , D_0 and E_0 seem to be interpreted as a contribution to the retention equivalent to nonspecific interactions of the averaged molecule of the hypothetical hydrocarbon which does not contain aromatic carbon atoms and therefore the coefficients are highly sensitive to the composition changes of the mobile phase [8].

RESULTS AND DISCUSSION

First of all it should be noted that different types of intermolecular interactions dominate (Table 1) the retention of substances in normal-phase (NP) and reversed-phase (RP) versions of HPLC. Thus if the retention of PAHs in NP HPLC in the first approximation is mainly determined by SI of sorbate-eluent, that in RP HPLC it is determined by NI of sorbate-sorbent, eluent-sorbent and SI of sorbate-eluent [3]. Consequently, in order to establish an adequate universal mathematical retention model for PAH (for NP and RP HPLC), the correlation equations should include the number of members required for taking all types of interactions occurring in the chromatographic system into account, i.e., that the mathematical model can be readily transformed into a physical one (physico-chemical one).

The first three members in the most general eq. (2) should reflect the difference in the specific interaction of the carbon atoms (types I, II, III of the PAH molecules) with the polar sorbent or eluent (Table 1). The fourth member (n_{π}/L) takes the mean linear density of the π -electron cloud in the PAH molecule into account and enables the identification of the differences of SI of isomeric molecules. The values of all these coefficients B_i are proportional to the increments of the distribution coefficients (between the mobile and stationary phases of the chromatographic system) belonging to different fragments of the PAH molecule.

TABLE 1. Types of the interactions (specific and nonspecific - SI and NI respectively) in normal-phase (NP) and reversed-phase (RP) HPLC

| Component of chromatographic system | N P H P L C | | R P H P L C | |
|---|-------------|-----------------|-------------------------------------|--------------------|
| | Sorbate | Sorbent (polar) | Component of chromatographic system | Sorbate (nonpolar) |
| Sorbent (polar) | SI (NI)* | | Sorbent (nonpolar) | NI (SI)** |
| Eluent (nonpolar) | NI | NI | Eluent (polar) | SI (NI) |
| Eluent (weakly polar, modified by a polar additive) | NI, SI | NI, SI | | |

* in parentheses are given the interactions which are realized but do not determine the retention of the sorbate (secondary)

** on residual silanol groups, especially in the absence of the "end-capping" operation

Previously we have shown [8] that in the case of RP HPLC, the eq. (3) coefficients are the linear functions of the content (vol.%) of water (or an organic component) in the eluent

$$D_1 = G_1C - G_{o,1} \quad (5)$$

$$D_2 = G_2C - G_{o,2} \quad (6)$$

$$D_3 = G_3C - G_{o,3} \quad (7)$$

$$D_o = G_oC - G_{o,o} \quad , \quad (8)$$

where C is the content of the organic component in the polar eluent (RP HPLC) , G_i and $G_{o,i}$ are the equation coefficients.

Introducing eqs. (5-8) in eq. (3), we get

$$\begin{aligned} \log k' = & C[G_1n_I + G_2(n_{II} + n_{III}) + G_3(n_{\pi/L}) + G_o] + \\ & [G_{o,1}n_I + G_{o,2}(n_{II} + n_{III}) + G_{o,3}(n_{\pi/L})] + G_{o,o} \end{aligned} \quad (9)$$

Comparing eq. (4) and (9), we get

$$E_o = G_{o,o} \quad (10)$$

$$E_1 = G_{o,1} \quad (11)$$

$$E_2 = G_{o,2} \quad (12)$$

$$E_3 = G_{o,3} \quad (13)$$

$$E_4 = [G_1n_I + G_2(n_{II} + n_{III}) + G_3(n_{\pi/L}) + G_o] \quad (14)$$

Of interest is to compare eq. (3) and (4) with the equation in Ref. 18

$$\log k'_w = \log k - S \Phi \quad , \quad (15)$$

where Φ is the volume fraction of organic component in the mobile phase, S is the coefficient, k'_w is the value of k' (found by extrapolation) for the water mobile phase (when $\Phi = 0$). The values of S are approximately constant, as Φ is varied, though each substance will have a characteristic value S; the values of S can also differ when the organic component of the mobile phase or chromatographic column is changed.

Having eqs. (4) and (15), we see that

$$= C/100 \quad (16)$$

$$S = E_4 \quad (17)$$

$$\log k_w = E_1n_I + E_2(n_{II} + n_{III}) + E_3n_{\pi/L} + E_o \quad (18)$$

Thus it follows that the coefficient S in eq. (15) in the general case is not constant for the given chromatographic system and can depend on the structure of the adsorbate molecule and is a sufficiently complex value.

The mean values of coefficients E_1 , E_2 , E_3 and E_o were calculated on the basis of the system of similar eqs. (4), then, substituting them and the values of $\log k'$ in eq. (4), we found the values of $E_{4,i}$ for individual PAHs. Having solved the system of eqs. (15), we found the following values of coefficients G_i : $G_1 = 9.92 \cdot 10^{-5}$, $G_2 = -2.95 \cdot 10^{-5}$, $G_3 = -9.35 \cdot 10^{-5}$, $G_o = -3.11 \cdot 10^{-2}$, which show that G_o is three magnitudes of order greater than other G_i in terms of its absolute value and, consequently, is the determining value in calculating E_4 . Thus, in our case G_o does not appear to be the function of the adsorbate structure and nature, that is, it is equal for all unsubstituted PAHs, but coefficient $S \approx 4$ is approximately constant and depends only on the nature of the organic component of the water-organic mobile phases (for the given sorbent and at the given temperature).

Tables 2 and 3 give the results of treatment of the experimental data on the PAHs retention [5,19] in RP HPLC systems by using eq. (3) and the data on the retention of normal hydrocarbons [19] by using eq. (19)

$$\log k' = H_1n_c + H_2C + H_o \quad , \quad (19)$$

where n_c is the number of the carbon atoms in the n-alkane molecule, C is the concentration, vol.%, H_1 , H_2 and H_o are equation coefficients.

TABLE 2. Retention of PAHs in RP HPLC. Coefficients E_1 , E_2 , E_3 , E_4 , E_0 , correlation coefficients*, multiple correlation coefficient (R) and Fisher criteria (F) for equation (4)

| Sorbent | Organic component of the eluent | E_1 | E_2 | E_3 | E_4 | E_0 | R | F |
|----------|---------------------------------|--------|--------|---------|---------|--------|--------|------|
| MCH-10** | Ethanol | 0.0442 | 0.1016 | -0.1221 | -0.0309 | 1.8392 | 0.9959 | 1918 |
| MikroPak | | (.552) | (.590) | (.514) | (-.761) | | | |
| YMC** | Acetonitrile | 0.0447 | 0.0561 | -0.1272 | -0.0304 | 1.8242 | 0.9924 | 441 |
| | | (.496) | (.494) | (.413) | (-.856) | | | |
| Phenyl | Tetrahydrofuran | 0.0368 | 0.0041 | -0.0432 | -0.0223 | 1.2930 | 0.9839 | 83 |
| | | (.557) | (.519) | (.406) | (-.811) | | | |
| YMC*** | Acetonitrile | 0.0186 | 0.1295 | -0.3816 | -0.0306 | 2.7299 | 0.9966 | 403 |
| | | (.653) | (.667) | (.562) | (-.734) | | | |
| ODS | Tetrahydrofuran | 0.0096 | 0.0161 | -0.1665 | -0.0259 | 2.0860 | 0.9941 | 230 |
| | | (.232) | (.203) | (.126) | (-.963) | | | |

* correlation coefficients E_i with $\log k'$ are given in parentheses

** for calculations, the retention values for benzene, naphthalene, phenanthrene, anthracene, pyrene, triphenylene, chrysene, tetraphene, perylene, benz(a)pyrene, 1,2,7,8-dibenzanthracene, 1,2,5,6-dibenzanthracene, 1,12-benzperylene, coronene were used, the ethanol content in water from 60 to 100 vol.%, column temperature 39°C

*** for calculations, the retention values for benzene, naphthalene, phenanthrene, anthracene, pyrene, chrysene, tetracene, benz(a)pyrene on the YMC phenyl with the content of acetonitrile and tetrahydrofuran in water from 50 to 80 and 50 to 60 vol.%, and on the YMC ODS - from 70 to 90 and 60 to 70 vol.% respectively.

Table 2 shows that the acetonitrile mobile phase is more selective towards the separation of isomeric PAHs than the tetrahydrofuran one in the case of both stationary phases of YMC (phenyl and octadecyl), the selectivity on C18 being higher than on the phenyl phase. At the same time, the phenyl phase is characterized by greater values of E_1 as compared with C18 (that is, it is characterized by greater affinity to the carbon atom of type I). It is also characterized by a higher selectivity towards the carbon atoms of various types (compare the values of coefficients E_1 and E_2) when the tetrahydrofuran mobile phase is used. It should be noted that E_2 is less than E_1 only in this particular case (the YMC-phenyl-tetrahydrofuran system). Close values of the coefficient E_4 (at THF and ACN) for all the systems concerned are indicative of a relatively weak effect of the nature of the mobile phase organic component on the retention both in the case of PAHs and n-alkanes (Table 3). The ethanol mobile phase is characterized by relatively high values of the coefficients E_1 , E_2 , E_3 , but its selectivity is less than the acetonitrile phase.

Tables 2 and 3 show that the carbon atoms of type I of the PAH molecule weakly interact with the stationary phase as compared with the carbon atoms of n-alkanes (in the case of the acetonitrile mobile phase it is more noticeable, though the E_1 coefficients for ACN phase are greater than for THF phase). This difference in the behaviour of PAH and n-alkanes can be due to the fact that the distribution constant of saturated hydrocarbons between the hydrophobic sorbent and the polar stationary phase (as well as the relative increments accounted for one carbon atom) is greater than that of PAHs whose electrons are able to specifically interact with the mobile phase.

The results given in Table 4 show that the proposed model also successfully can be used for application in NP HPLC. As would be expected, inversion (in comparison with RP HPLC) the phase polarity of the chromatographic system resulted in a change of the sign of the coefficients E_3 and E_0 . It accounts for the fact that the coefficient E_3 characterizing SI of π -electrons with the polar groups of the components of the mobile phases and sorbents will reflect an increase in the PAH retention (in the case of NP HPLC) and a decrease in their retention (in the case of RP HPLC). A change in the sign of E_0 reflecting the contribution of NI to the PAH retention corresponds to the character of the n-alkanes distribution between the polar and nonpolar (weakly polar) components of the chromatographic system.

TABLE 3. Retention of n-alkanes in RP HPLC. Coefficients H_1 , H_2 , H_0 , correlation coefficients*, multiple correlation coefficient (R) and Fisher criteria (F) for eq. (19)

| Sorbent | Organic component of the eluent | H_1 | H_2 | H_0 | R | F |
|---------|---------------------------------|----------|-----------|--------|--------|-----|
| YMC** | Acetonitrile | 0.0854 | -0.0336 | 1.9682 | 0.9912 | 564 |
| Phenyl | | (0.3843) | (-0.8664) | | | |
| | Tetrahydrofuran | 0.0540 | -0.0288 | 1.7596 | 0.9863 | 161 |
| | | (0.6562) | (-0.7364) | | | |

* correlation coefficients H_1 with $\log k'$ are given in parentheses

** for calculations, the retention values for pentane, hexane, heptane, octane, decane, dodecane on the YMC phenyl stationary phase were used (the content of acetonitrile and tetrahydrofuran in water from 50 to 80 and from 50 to 60 vol.% respectively).

TABLE 4. Retention of PAHs in NP HPLC. Coefficients E_1 , E_2 , E_3 , E_4 , E_0 , correlation coefficients*, multiple correlation coefficient (R) and Fisher criteria (F) for eq. (4)

| Sorbent | Polar component of the eluent | E_1 | E_2 | E_3 | E_4 | E_0 | R | F |
|-----------------------|-------------------------------|------------------|------------------|------------------|--------------------|---------|--------|-----|
| SiO ₂ ** | chloroform (0-15 vol.%) | 0.0702 (.362) | 0.0109 (.347) | 0.1360 (.293) | -0.0620 (-.848) | -1.0737 | 0.9330 | |
| MicroPak | chloroform (3-15 vol.%) | 0.0620 (.548) | 0.0106 (.540) | 0.1418 (.463) | -0.0408 (-.787) | -1.2181 | 0.9873 | 454 |
| NH ₂ -10** | chloroform (0-25 vol.%) | 0.0706 (.516) | 0.0456 (.588) | 0.2051 (.518) | -0.0360 (-.755) | -1.1886 | 0.9705 | 295 |
| MicroPak | chloroform (5-25 vol.%) | 0.0625 (.625) | 0.0420 (.724) | 0.2125 (.645) | -0.0282 (-.644) | -1.2287 | 0.9873 | 579 |
| | isopropanol (0-20 vol.%) | 0.0721 (.474) | 0.0406 (.536) | 0.2250 (.475) | -0.0360 (-.576) | -1.5443 | 0.8015 | 33 |
| | isopropanol (3-20 vol.%) | 0.0643 (.793) | 0.0359 (.912) | 0.2363 (.817) | -0.0108 (-.285) | -1.8056 | 0.9885 | 643 |
| CN-10** | chloroform (0-20 vol.%) | 0.0730 (.505) | 0.0113 (.476) | 0.1244 (.398) | -0.0331 (-.823) | -1.1618 | 0.9830 | 615 |
| MicroPak | chloroform (1-20 vol.%) | 0.0699 (.522) | 0.0106 (.493) | 0.1230 (.413) | -0.0314 (-.811) | -1.1450 | 0.9841 | 558 |

* correlation coefficients E_1 with $\log k'$ are given in parentheses

** for calculations, the retention values for naphthalene, anthracene, phenanthrene, pyrene, tetracene, tetraphene, chrysene, triphenylene, benz(a)pyrene, perylene, 1,12-benzperylene, coronen, 1,2,7,8-dibenzanthracene were used at the column temperature 29°C.

The sign of the coefficients E_1 and E_2 does not depend on the type of the chromatographic system (RP or NP). However, in NP HPLC $E_1 > E_2$, while in the case of RP HPLC $E_1 < E_2$ since the atoms of type I having greater electron density as compared with the atoms of type II and III much stronger interact with a more polar mobile phase. An increased concentration (C, eq. 4) due to the modifying additive to the mobile phase results in less retention of PAHs in all the cases ($E_4 < 0$). It follows from Table 4 that the character of PAH retention at small concentrations of the additive, which is indicated by smaller values of the multiple correlation coefficients and Fisher criteria when the chromatographic systems containing the modified and nonmodified mobile phases are simultaneously described by eq. (4). That may be due to the property of the surface - its energetic and geometric heterogeneity which is practically imperceptible when 3-5 vol.% of the modifying component is introduced [20,21]. Nevertheless, the proposed model operates satisfactorily within a wide range of the mobile phases compositions.

CONCLUSION

The proposed mathematical model and the correlation equations universal for the given class of compounds enable the prediction of the retention of unsubstituted polyaromatic hydrocarbons depending on their structure. The application of the coefficients of the proposed equations enables the evaluation of the separation selectivity of substances and the effect of the nature and composition of the mobile phases. The equation adequately describes the retention of polyaromatic hydrocarbons both in the normal-phase and reversed-phase HPLC with various sorbents differing in the surface chemistry.

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