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# Calculation of retention and selectivity in reversed-phase liquid chromatography

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ABSTRACT

A method has been developed to calculate retention in reversed-phase high-performance liquid chromatography based on the molecular structure of the analyte and characteristics of the sorbents and mobile phases. A simple approach based on solvophobic theory is used.

INTRODUCTION

One of the main problems in chromatography is to predict the retention of compounds by studying their structure and physicochemical properties. It is now impossible to predict retentions by precisely describing the chromatographic process and calculating intermolecular interactions in a chromatographic system. Methods using the correlation between different properties of analyte compounds and their retentions are now in widespread use. To calculate retention, use has been made of solubility parameters [1], retention indices [2–4], solvent interactions indices [5,6], the correlation between retention and hydrophobicity constants [7,8] distribution constants, molecular areas [7,9,10–19], Van der Waals volumes, dipole moments and the number of carbon atoms in the molecule [14,15], molecular connectivity [16–18], etc. Some of the approaches [19] use the relationship between the activity coefficients of a substance in a certain chromatographic system and retention. A calculation method has been proposed that involves two contributions to selectivity, a polar and a nonpolar one [20,21]. A series of alkylbenzenes are used to standardize the retention scale, which can then be employed to calculate the retention and selectivity of the compounds investigated for different mobile phase compositions. A method has recently been developed to predict the retention of compounds in reversed-phase high-performance liquid chromatography (RP-HPLC) based on the molecular structure of the analyte [22]. The retentions are calculated as retention indices on the alkyl aryl ketone scale. The increments for substitutions on aromatic and aliphatic carbons have been obtained [22,23], and a program for calculating retention indices has been developed [24]. A number of other studies have been reviewed [22].

Empirical correlation approaches are normally not associated with specific re-

tention theories, so that their applications are limited. To use these approaches one must have experimental results from studying the physico-chemical and chromatographic properties of compounds and also reference data (often unavailable) on new or rare compounds. At present there are several retention theories in RP-LC [25–38]. Without going into the details of each of these theories, it can be noted that they do not provide adequate means of calculating the retentions of compounds. The solvophobic theory [32–35] now seems to give the most suitable approach to calculating retention and selectivity; however, to determine the energy contributions to retention we must know such characteristics as the area of the hydrophobic contact with the sorbent surface, the acentric factor and dipole moments. Normally a full set of characteristics is not available and it is very difficult to derive them. The same is true of molecular statistical approaches [36–38] that require a preliminary determination or a complicated calculation of the activity coefficients for compounds in a chromatographic system.

The aim of this work was to study the possibility of developing of a simple method for calculating the retention and selectivity in RP-LC on octadecyl sorbents that would produce satisfactory results without preliminary wide-scale experiments.

THEORY

To develop a method for calculating retention and selectivity it is necessary to employ some model concepts of the retention mechanism, the surface layer structure and the character of interactions of retained substances with mobile and stationary phases (SP). Much theoretical and experimental evidence has recently been produced to show that a bonded hydrocarbon layer seems to have a structure intermediate between brush and liquid and the eluent molecules are able to penetrate this layer, producing a considerable effect on its properties [36,39,40]. The penetration increases with increasing solvent hydrophobicity [36,39]. It has also been shown that the chromatographic process simultaneously involves both the distribution and competitive adsorption in RP-LC. The distribution processes are dominant and the surface layer exhibits quasi-liquid properties [36,41–43]. To calculate approximately the retention and selectivity we propose to use a simple two-layer continuum model of a chromatographic system: (1) the surface of a modifier sorbent in RP-LC has a surface layer (SL) that involves ocatdecyl radicals and some of the components of a mobile phase (MP); (2) the SL is assumed to be a quasi-liquid that has its own characteristics, i.e., surface tension ($\gamma_s$) and dielectric constant ($\varepsilon_s$), and the SL characteristics vary with varing MP composition and sorbent properties; and (3) the molecules of a retained substances penetrate into the SL. The retention is determined by the difference in molecule solvation energies in the MP and SL.

We emphasize that the SL is regarded not as a layer of a liquid hydrocarbon but as a specific layer containing surface-fixed alkyl radicals and some amount of MP components. It is obvious that this layer should have characteristics different from those of a hydrocarbon.

By assuming a surface layer that has certain average characteristics and the possibility of a substance penetrating this layer, we can apply a simple procedure for calculating the retention in this case. The general expression for the retention is

$$\ln k' = \frac{-\Delta G}{RT} + \phi \tag{1}$$

where $\phi$ is the phase ratio. The retention is determined by the differences in the solvation energies in the distribution system [32]:

$$\Delta G = \Delta G_{\text{solv.s.}} - \Delta G_{\text{solv.m.}} \tag{2}$$

According to refs. 32, 35 and 44,

$$\Delta G_{\text{solv.}} \approx \Delta G_{\text{c}} \times \Delta G_{\text{int.}} \tag{3}$$

$$\Delta G = \Delta G_{\text{c.s.}} - \Delta G_{\text{c.m.}} + \Delta G_{\text{int.s.}} - \Delta G_{\text{int.m.}} \tag{4}$$

where $\Delta G_{\text{c.s.}}$ and $\Delta G_{\text{c.m.}}$ are the energies required to generate a cavity of molecular size in the SL and MP, respectively; $\Delta G_{\text{int.s.}}$ and $\Delta G_{\text{int.m.}}$ are the energies of the interaction of the molecules with the surrounding medium in the SI and MP, respectively.

The simplest version is [34]

$$\Delta G_{\text{c}} = NA\gamma + NA_1\gamma\,(k_1^{\text{e}} - 1) \tag{5}$$

where $N$ is Avogadro's numvber, $A$ is the cavity surface area in the liquid, $\gamma$ is the surface tension (for water $\gamma = 72.6 \cdot 10^{-3}\,\text{N m}^{-1}$), $A_1$ is the solvent molecule area and $k_1^{\text{e}}$ is the characteristic constant for every liquid (for water $k^{\text{e}} = 1.277$ [35,44]). To calculate the approximate value of $A$, the Van der Waals radius of a molecule is normally used with the molecule regarded as spherical [35,44]. In this instance an approximate value of the molecular area is derived whereas the value of the area of a cavity generated in the solvent appears to be more correct [35]. The simplest and the most exact way to determine the cavity area in a solvent is to use the experimental values of partial molar volumes of different compounds in this solvent. The modern methods of measurement make it possible to obtain values of partial molar volumes with an error of less than $0.1\,\text{cm}^3\,\text{mol}^{-1}$ [45]. The literature reports numerous data on partial molar volumes of different classes of compounds such as alcohols, hydrocarbons, ethers and amino acids. The values of partial molar volumes for several hundred substances have been collected [45]. Experimental data for many compounds have shown that the additivity of the action of separate molecular fragments is a good approximation for calculating molar volumes [45]. Thus, considering the cavity shape to be spherical, we can assume

$$A = N^{-2/3} \cdot 4.836 \left(\sum_i V_i\right)^{2/3} \tag{6}$$

where $V_i$ are the increments of partial molar of volumes of fragments. A large set of experimental values of partial molar volumes for different compounds [45] enables us to find the values of $\sum V_i$ for almost any structure. In addition simple equations have been proposed to calculate the values of $V_i$ with great accuracy [45–47]. Thus the values of $\Delta G_{\text{c}}$ can be calculated as follows:

$$\Delta G_{\text{c}} = N^{1/3}\,\gamma \cdot 4.836 \left[\left(\sum_i V_i\right)^{2/3} + v_{\text{m}}^{2/3}\,(k_{\text{m}}^{\text{e}} - 1)\right] \tag{7}$$

where $v_{\text{m}}$ is molar volume of MP.

Note that to simplify the calculations we use only the partial molar volumes obtained in water, assuming the cavity parameters in an SL and MP to be similar [45]. An important point is a correct choice of the form of the potential of the interaction of the solute with surrounding medium, $\Delta G_{int.}$. Solvophobic theory uses the sum of Van der Waals and electrostatic interactions [32–35,44]:

$$\Delta G_{int} \approx \Delta G_{vdW} + \Delta G_{e.s.}$$

Here Onsager's continuum model of a reactive field is used to calculate $\Delta G_{e.s.}$ [44,48] and a complicated expression derived by Haligoglu and Sinanoglu [32,44] is used to calculate the Van der Waals interaction energy. As mentioned above, to calculate this term, it is necessary to know the characteristics of a substance, which are unknown and difficult to obtain. It should be noted that almost all approaches for calculating the Van der Waals interaction energy are approximate and need either a great number of sophisticated characteristics of substances of a number of empirical parameters [49,50]. At present the continuum theories involving only electrostatic interactions are applied for an approximate calculation of the solvation energy [50–53]. We suggest that the molecule of a substance be considered as consisting of dipoles, each of which separately interfaces with the surrounding continuum. In this case,

$$\Delta G_{int.} \approx \Delta G_{e.s.} = -\frac{1}{2} \cdot \frac{2(\varepsilon - 1)}{(2\varepsilon + 1)} \cdot \sum_j \frac{\mu_j^2}{a_j^3} \qquad (8)$$

where $\mu_j$ are the bond dipole moments, $a_j$ the effective radius of an imaginary sphere in which the dipole is located and $\varepsilon$ the dielectric permitivity of the surrounding continuum.

Such an approach does not need quantum chemical methods to calculate the atom charges. The bond dipole moments are determined for almost all bonds and, in many instances, vary insignificantly for various compounds [54,55]. More strictly, each dipole is not surrounded by a totally closed sphere of solvent molecules; it is more correct to speak about ball segments. The approach proposed is based on the assumption that in different compounds the parameters of a ball segment in which the same dipole is located vary in a small range, so that to calculate the electrostatic energy this parameter can be approximated by the effective radius of the sphere ($a_j$). By substituting eqns. 7 and 8 in eqn. 4 we obtain

$$-\Delta G = N^{1/3} \cdot 4.836 \left[ (\gamma_m - \gamma_s)(\sum_i V_i)^{2/3} + \right.$$

$$\left. v_m^{2/3}(k_m^e - 1)\gamma_m - v_s^{2/3}(k_s^e - 1)\gamma_s \right] + [f(\varepsilon_s) - f(\varepsilon_m)] \sum_j \frac{\mu_j^2}{a_j^3} \qquad (9)$$

where $f(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$.

The expression obtained involves several unknown parameters of SL: $k_s^e$, $f(\varepsilon_s)$, $\gamma_s$ and $v_s$. To determine the parameters of the SL for a given sorbent and column, we

can use any standard substance, e.g., benzene, and calculate the values for SL relative to this standard. Then:

$$\ln k_x' = \frac{1}{RT}\left\{N^{1/3} \cdot 4.836 \, (\gamma_m - \gamma_s)[(\sum_i V_i)^{2/3} - (V_{st})^{2/3}] + \right.$$

$$\left. [f(\varepsilon_s) - f(\varepsilon_m)]\left(\sum_j \frac{\mu_j^2}{a_j^3} - \sum_j \frac{\mu_{j,st.}^2}{a_{j,st.}^3}\right)\right\} + \ln k_{st.}' \qquad (10)$$

Thus, when a standard substance is used it is not necessary to determine the values of $\sigma$, $v_s$ and $k_s^e$, which simplifies further calculations. Eqn. 10 can be reduced to a more useful form:

$$\ln k_x' = \ln k_{st.}' + 16.48 \, (\gamma_m - \gamma_s)[(\sum_i V_i)^{2/3} - (V_{st.})^{2/3}] +$$

where $\Delta G_{e.s.jH2O}$ and $\Delta G_{e.s.st.H2O}$ are the increments of the contribution $\Delta G_{e.s.}$ for dipole $j$ of molecule $x$ and the contribution of $(\Delta G)_{e.s.}$ for the standard substance in water, respectively. Here $\Delta G$ is expressed in kJ mol$^{-1}$, $\gamma$ in N m$^{-1}$ and $V$ in cm$^3$ mol$^{-1}$. The values of $\gamma_s$ and $f(\varepsilon_s)$ can easily be found by using, in addition to a standard, two or more reference substances. The simplest way is to solve eqn. 11 graphically for these reference substances, assuming ln $k_x'$ (calculated) $=$ ln $k_x'$ (experimental) (ln $k_{exp.}'$). Thus, eqn. 11 can be expressed in the form

$$0.8234 \, [f(\varepsilon_m) - f(\varepsilon_s)](\sum_j \Delta G_{e.s.jH_2O} - \Delta G_{e.s.st.H_2O}) \qquad (11)$$

$$f(\varepsilon_s) = -b\gamma_s + \beta \qquad (12)$$

where

$$\beta = \frac{\gamma_m b - f(\varepsilon_m)c + \ln k_{st.}' - \ln k_x'}{c}$$

$$b = 16.48 \, [(\sum_i V_i)^{2/3} - V_{st.}^{2/3}]$$

$$c = 0.8234 \, (\sum_j \Delta G_{e.s.jH_2O} - \Delta G_{e.s.st.H_2O})$$

Taking two arbitrary values of $\gamma_s$ and using eqn. 12, one can calculate two values of $f(\varepsilon)_s$ for each reference compound and construct plots of $\gamma_s$ vs. $f(\varepsilon)_s$ for these compounds. The coordinates of intersection point determine the values of SL parameters $[\gamma_s$ and $f(\varepsilon_s)]$. Naturally, to determine the values of $\gamma_s$ and $f(\varepsilon_s)$ more precisely, it is necessary to employ compounds that have a large difference in $\Delta G_c$ and $\Delta G_{e.s.}$, i.e., differing in size and polarity (e.g., ethylbenzene, benzophenone, o-cresol and phenol).

As the number of reference substances rises the error in determining $f(\varepsilon_s)$ and $\gamma_s$ decreases.

RESULTS AND DISCUSSION

To test the applicability of the above approach, we used the retention data for various aromatic compounds in refs. 56 and 57.

The basic equation for calculating the retention was eqn. 10 or 11. To determine the increments $V_i$ we used the values of partial molar volumes given for many compounds in ref. 45. The basic fragments of organic compounds are given in Table I.

TABLE I

INCREMENTS OF PARTIAL MOLAR VOLUMES FOR SOME FRAGMENTS

| Fragment[a] | $V_i$ (cm³ mol⁻¹) | Fragment[a] | $V_i$ (cm³ mol⁻¹) | Fragment | $V_i$ (cm³ mol⁻¹) |
|---|---|---|---|---|---|
| H(ar.) | 6.8 | –OH | 11.7 | –C–NH₂ ‖ O | 29.0 |
| –CH₂– | 16.0 | –CH₂OH | 28.2 | –CH–COOH │ NH₂ | 33.4 |
| –CH₃ | 26.4 | –COOH | 25.9 | | |
| –CH₃(ar.) | 22.5 | –COOH(ar.) | 23.5 | –N(CH₃)₂ | 49.2 |
| | | –C– ‖ O | 13.0 | –Cl | 20–22[b] |
| =CH– | 13.5 | O ‖ –C–O– | 20.0 | O ‖ –S– | 16.1 |
| –C₆H₅ | 74.5 | | | | |
| –C₆H₄– | 65.3 | O ‖ –C–H | 22.3 | –NH– | 7.0 |
| | | | | –C≡N | 20.5 |
| –C₆H₄N | 71.2 | –O–CH₃ | 31.5 | –NO₂ | 21.6 |
| –C₆H₃N | 64.9 | –O– | 5.2 | –NH₂ | 14.7 |

[a] ar. = Aryl.
[b] No data concerning the partial molar volumes of Cl-containing compounds have been elucidated in the literature. The $V_i$ value is derived from increments of the volume in molecular crystals [49].

Eqn. 8 involves an empirical parameter, the effective radius. This parameter may be derived either experimentally or using some physical considerations. We used the simple relationship $a_j = 1/2\,(r_1 + r_2)\,g$, where $r_1$ and $r_2$ are the Van der Waals radii of the atoms contained in the dipole and $g$ is a correlation parameter. The initial condition is $g = 1$, i.e., the radius of a sphere is half the sum of the Van der Waals atomic radii. Using this value and choosing benzene as a standard substance ($V_{st.} = 81.3$ cm³ mol⁻¹ [45] and $\Delta G_{e.s.st.H_2O} = -26.16$ kJ mol⁻¹ ($6C_{sp^2} - H$)) we resolved graphically eqn. 12 for phenol, ethylbenzene, o-cresol and benzophenone (Fig. 1). The $\sum_i V_i$ and $\sum_i \Delta G_{e.s.jH_2O}$ values for these compounds were calculated by using the increments from Tables I and II. Fig. 1 shows that the straight lines intersect in a very
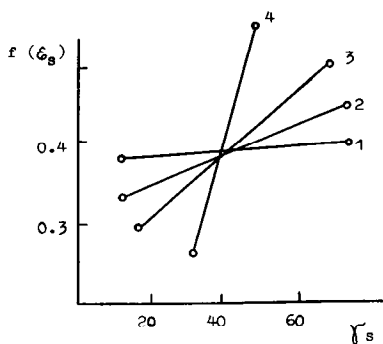
Fig. 1. Determination of SL parameters of Merck RP-18 sorbent [56]. For calculation of the two data points for each compound eqn. 12 was used. Compounds: 1 = phenol; 2 = o-cresol; 3 = benzophenone; 4 = ethylbenzene.

limited region, defining the limits $f(\varepsilon_s)$ = 0.38–0.40 ($\varepsilon_s$ = 5.5 + 7.0) and $\gamma_s$ = $36.10^{-3}$–$43 \cdot 10^{-3}$ N m$^{-1}$. These values seem to be reasonable for the parameter of a surface layer. It should be mentioned that the surface layer of a modified sorbent was characterized in ref. 33 by a quantity such as dielectric permittivity, and the value of $\varepsilon_s$ reported [33] was 35. A different value of $\varepsilon_s$ of 22 was derived in ref. 58 using another method of calculation and a different octadecyl sorbent. We used average values of the SL parameters $\gamma_s$ and $\varepsilon_s$ to caculate the capacity factors for all 35 compounds.

TABLE II

INCREMENTS OF $\Delta G_{e.s.jH_2O}$ FOR SOME DIPOLES

| Dipole[a] | $a_j \times 10^{10}$ (m)[b] | $g$ | $\mu_j$ (D) [54] | $-\Delta G_{e.s.jH_2O}$[c] (kJ mol$^{-1}$) |
|---|---|---|---|---|
| $C_{sp^2}$–H | 1.49 | 1.00 | 0.7 | 4.36 |
| $C_{sp^3}$–H | 1.49 | 1.00 | 0.4 | 1.42 |
| $C_{sp^2}$–$C_{sp^3}$ | 1.80 | 1.00 | 0.68 | 2.33 |
| $C_{sp^2}$–$C_{sp}$ | 1.80 | 1.00 | 1.15 | 6.68 |
| $C_{sp^3}$–$C_{sp}$ | 1.80 | 1.00 | 1.48 | 11.06 |
| C–O | 1.66 | 1.00 | 0.7 | 3.15 |
| C=O | 1.74 | 1.05 | 2.4 | 32.20 |
| C–N | 1.69 | 1.00 | 0.45 | 1.24 |
| C≡N | 2.37 | 1.40 | 3.1 | 21.25 |
| O–H(ar. acid) | 1.35 | 1.00 | 1.51 | 27.28 |
| O–H | 1.20 | 0.89 | 1.51 | 38.80 |
| N–H | 1.38 | 1.00 | 1.31 | 19.20 |
| N–O | 1.55 | 1.00 | 0.3 [55] | 0.71 |
| N=O | 2.20 | 1.42 | 2.0 [55] | 11.04 |
| C–Cl | 2.34 | 1.30 | 1.59 | 5.80 |
| C–S | 1.8 | 1.00 | 0.9 | 4.09 |

[a] ar. = aryl

[b] For calculation of $a_j = (r_1 + r_2)/2$, the Van der Waals radii ($r$) from ref. 49 were used: C = 0.18; H = 0.117; O = 0.152; N = 0.15; Cl = 0.18 nm.

[c] For calculation of $\Delta G_{e.s.jH_2O}$, eqn. 8 was used.

The calculated results show that the simplest approach to define the value of $a_j$ as half the sum of Van der Waals atomic radii generally results in good agreement between the calculated values of ln $k'$ and those of given in ref. 56.

By analysing deviations in calculating the retentions of benzyl alcohol, benzonitrile, nitrobenzene and chlorobenzene we found the values of $a_j$ for O–H, C = N, N = O and C–Cl dipoles that enabled us to obtain more exact results. Of course, the values of $a_j$ can be further refined by analysing systematic errors in calculating the retentions of series of compounds that belong to the same class.

The results of calculating $\Delta G_{e.s.}$ and the parameters for calculating these values are given in Table II, and show that the value of $g$ for the many dipoles is only slightly different from 1, except for the dipoles $C \equiv N$, N = O and C–Cl. Hence it is possible in many instances to apply the simplest approach to determine the value of $a_j$. The present method for calculating $\Delta G_{int}$ does not allow us to take into account the

TABLE III

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF LN $k'$

Sorbent: Merck RP-18 [56].

| Compound | Ln $k'_{calc}$ | Ln $k'_{exp}$ | Difference |
|---|---|---|---|
| Aniline | 2.63 | 2.94 | 0.31 |
| Dimethyl o-phthalate | 4.84 | 5.09 | − 0.25 |
| Phenol | 3.10 | 3.13 | 0.03 |
| 2,4-Dimethylphenol | 5.13 | 5.22 | 0.09 |
| Benzyl alcohol | 3.26 | 3.26 | − |
| Quinoline | 5.13 | 5.58 | − 0.45 |
| Benzaldehyde | 3.80 | 3.72 | − 0.08 |
| Anisole | 6.20 | 5.77 | 0.43 |
| o-Nitroaniline | 2.34 | 3.81 | − 1.47 |
| N,N-Dimethylaniline | 7.38 | 6.26 | 1.12 |
| m-Nitrophenol | 2.74 | 3.89 | − 1.15 |
| Toluene | 5.86 | 6.27 | − 0.41 |
| 2-Phenylethanol | 4.22 | 3.89 | 0.33 |
| Chlorobenzene | 6.08 | 6.44 | − 0.36 |
| m-Dinitrobenzene | 4.14 | 3.99 | 0.15 |
| Diethyl o-phthalate | 6.40 | 6.46 | − 0.06 |
| Benzonitrile | 4.00 | 4.00 | − |
| Benzophenone | 6.57 | 6.96 | − 0.39 |
| 1-Phenylethanol | 3.91 | 4.04 | − 0.13 |
| Ethylbenzene | 7.12 | 7.38 | − 0.26 |
| n-Nitroacetophenone | 4.01 | 4.18 | − 0.17 |
| Anethole | 8.60 | 8.13 | 0.47 |
| o-Cresol | 4.30 | 4.23 | 0.07 |
| Diphenyl ether | 8.18 | 8.58 | − 0.40 |
| Acetophenone | 4.47 | 4.34 | 0.13 |
| Biphenyl | 8.34 | 8.91 | − 0.57 |
| Nitrobenzene | 4.45 | 4.42 | − |
| Naphthalene | 7.17 | 11.81 | − 4.64 |
| 3-Phenylpropanol | 4.85 | 4.94 | − 0.09 |
| Anthracene | 9.22 | 12.84 | − 3.62 |
| N-Methylaniline | 5.08 | 5.01 | 0.07 |
| Benzene | 4.95 | 4.95 | − |

decrease in the interaction of a molecule of a substance with water produced by an intermolecular hydrogen bond (e.g., o-nitroaniline). We can introduce some correlations to calculate this effect. The value of 2–4 kJ mol$^{-1}$ (average hydrogen bond) seems to be a reasonable correction. To derive more adequate values of the corrections we must do additional research.

The results given in Table III show good agreement between the calculated values and those given in ref. 56. It is necessary to explain the difference between ln $k'_{calc}$ and ln $k'_{exp}$ for naphthalene and anthracene. The values of ln $k'$ in $H_2O$ for these compounds were derived by linearly extrapolating the values of ln $k'$ measured at high concentrations of methanol in MP [56]. It was shown later on that for naphthalene the dependence of ln $k'$ on methanol concentration passes through a maximum at low methanol concentration under RP-LC conditions [57]. Such an effect probably occurs with anthracene also. As a result, the values of ln $k'_{exp}$ derived by extrapolation would be overestimated in comparison with the real values. To test the method proposed once more, we analysed the retention data of various compounds on another column as used in ref. 57. In that case all the values of ln $k'$ were derived experimentally. It is known that when one changes from one sorbent to another (even of the same type), the retention of the same compounds varies, sometimes quite appreciably. Fig. 2 shows the plot of the correlation of the retention of the same substances obtained on two different columns with octadecyl sorbents. It is seen that there is virtually no correlation. Various surface structures of the stationary phases or the possible presence of unreacted silanol groups and consequently various contents of the mobile phase in SL can be reasons for such phenomena. From the proposed approach this implies that the surface tensions and dielectric permittivities of these sorbent SLs are very different. Therefore, to calculate the retention of compounds on a certain column we must first determine the characteristics of the SL. Taking, as in the former instance, benzene as a standard substance, we solved eqn. 12 graphically for three compounds. The intersection point determined the necessary parameters of
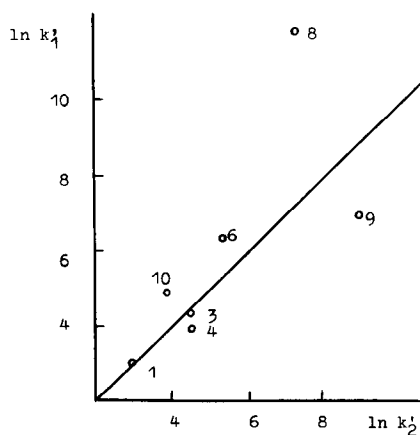


Fig. 2. Comparison of values of ln $k'$ in water on Merck RP-18 [56] and ODS-Hypersil [57]. Compounds: 1 = phenol; 3 = nitrobenzene; 4 = m-dinitrobenzene; 6 = chlorobenzene; 8 = naphthalene; 9 = benzophenone; 10 = benzene.
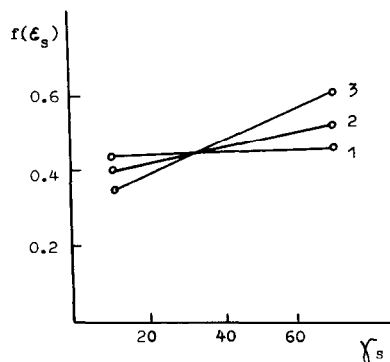
Fig. 3. Determination of SL parameters. Sorbent: ODS-Hypersil [57]. Compounds: 1 = phenol; 2 = nitrobenzene; 3 = benzophenone.
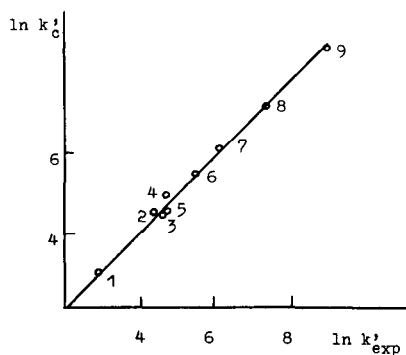
Fig. 4. Comparison of experimental [57] and calculated in ln $k'$ values. MP $H_2O$; $\gamma_s = 32 \cdot 10^{-3}$ N m$^{-1}$, $f(\varepsilon_s) = 0.435$ ($\varepsilon_s = 11.0$). Compounds: 2 = $p$-cresol; 5 = $p$-chlorophenol; 7 = 2,4-dichlorophenol; others as in Fig. 2.

the SL (Fig. 3). It is seen than the straight lines intersect in very limited range of values. Using these parameters of the SL, we calculated the retentions of all compounds. The results given in Fig. 4 and Table IV show good agreement between the theoretical and the experimental values, including those for naphthalene. It should be noted that for both columns the calculated $\phi$ values are very close to the typical value of 2.8 for RP columns [59].

It seems promising to extend the present approach to calculate the retentions of compounds belonging to different classes, and also to the case when eluents containing organic solvents are used. This research is in progress.

TABLE IV

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF LN $k'$

Sorbent: ODS Hypersil [57].

| Compound | Ln $k'_{exp}$ | Ln $k'_{calc}$ | Difference |
| --- | --- | --- | --- |
| Phenol | 3.12 | 3.05 | 0.07 |
| $p$-Cresol | 4.32 | 4.51 | −0.19 |
| Nitrobenzene | 4.49 | 4.37 | 0.12 |
| $m$-Dinitrobenzene | 4.58 | 4.96 | −0.38 |
| $p$-Chlorophenol | 4.62 | 4.49 | 0.13 |
| Chlorobenzene | 5.40 | 5.45 | −0.05 |
| 2,4-Dichlorophenol | 6.00 | 6.14 | −0.14 |
| Naphthalene | 7.22 | 7.23 | −0.01 |
| Benzophenone | 8.99 | 8.75 | 0.24 |

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