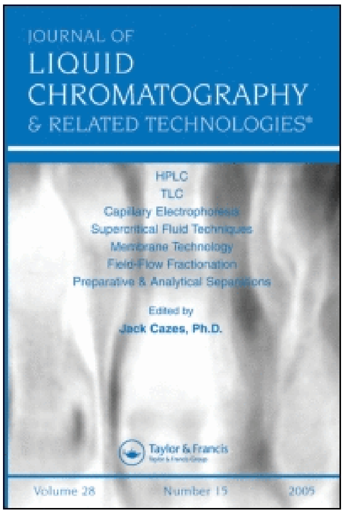

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DETERMINATION OF SOLUTE RETENTION FACTORS IN RPLC WITH PURE WATER AS EFFLUENT USING A NUMERICAL METHOD BASED ON THE OŚCIK'S EQUATION

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☐ *A numerical method based on the linear form of the Ościk equation was used for calculation of the logarithms of the retention factors of alkylbenzenes, PAHs, and several polar monosubstituted benzenes of a RPLC system with pure water as mobile phase. The author used a system consisting of a column packed with LiChrospher RP-18e and mobile phases containing methanol and acetonitrile as organic modifier of the mobile phase. Also, the influence of the kind of the organic modifier of the mobile phase as well as the range of its concentration on the calculated* $\log k_w$ *values was studied. Moreover, the correlations between the* $\log k_w$ *values determined by various methods and the partition coefficients in the n-octanol/water system (*$\log P$*) have been presented.*

The $\log k_w$ *values calculated by the numerical method do not practically depend on the concentration range of the organic modifier and show the best linear correlations with the experimental* $\log P$ *values, number of carbon atoms in alkylbenzenes (*n_C*), and the* $\log k_w$ *values determined by linear extrapolation from* $\log k$ *dependence on the volumetric fraction of methanol.*

Keywords aromatic solutes, column liquid chromatography, $\log p$, Ościk's equation, retention factor in pure water, reversed phase liquid chromatography

INTRODUCTION

The retention factor in pure water ($\log k_w$) is of great practical and theoretical importance in reversed phase liquid chromatography. Among other things, it is used in studies of quantitative structure retention relationship (QSRR).[1,2] It is also used in studies of the biological activity of substances as a measure of their hydrophobicity (or lipophilicity).[3–8] The most often used descriptor of hydrophobicity is the partition coefficient in a n-octanol/water system ($\log P$), but its experimental

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determination by the shaking flask method is troublesome and time consuming. Thus, the $\log P$ and $\log k_w$ linear relationship known as the equation of the Collander type is often used.[9] Moreover, the $\log k_w$ parameter serves as the characteristic of the properties of various sorbents used in adsorption and solid phase extraction techniques applied, for example, to concentrate diluted aqueous samples.[6,10,11]

Direct determination of the $\log k_w$ parameter, however, is for many strongly hydrophobic substances impossible, as the value of this parameter exceeds the order of magnitude of 10^2, that causes extension of the retention time and a strong broadening of the chromatographic peak. Therefore, in direct retention measurements in pure water possibly the shortest columns are used to reduce the analysis time.[12]

Instead of direct measurements for determination of $\log k_w$, appropriate calculations are most often used which are based on correlations of this parameter with some physicochemical constants, or most frequently with retention data in reversed phase systems, using mixed aqueous organic effluents. In this method, $\log k_w$ values are determined on the basis of a series of isocratic measurements at different concentrations of the organic modifier, most often methanol or acetonitrile, in a two component mobile phase and extrapolation of the relationship between $\log k$ and the volume (φ) or molar (x) fraction of the organic component to its zero content (to 100% of water). After Soczewiński et al. linear $\log k$ vs. φ relationship[13,14] (linear extrapolation), or rarely a square relationship resulting from the conception of Schoenmakers et al.[15] (parabolic extrapolation) is usually assumed.[12,16–18] However, none of these functions describes the substance retention when using an effluent rich in water, therefore, an additional term depending on $\varphi^{1/2}$ is sometimes introduced into the quadratic dependence.[17] The $\log k_w$ values determined by the extrapolation methods differ in regard to the kind of the function used for extrapolation. They also depend, to a high degree, on the range of the organic modifier concentrations at which measurements and then extrapolations are made. The lower is the content of the organic modifier in the range the more accurate are the obtained $\log k_w$ values. In the most frequently used concentration ranges (φ), the lowest concentration is 0,1–0,3 and the highest 0,8 depending on the substance properties and the shape of $\log k_w$ vs. φ curve.[12,16,19] It should be added, that although theoretically $\log k_w$ value is to depend only on the kind of the packing and not on the kind of the organic modifier, this influence is, however, in practice sometimes relatively considerable.[16]

Besides the extrapolation methods for determination of $\log k_w$ values, other methods can be also encountered. Werkhoven–Govie et al. proposed a method based on a single measurement of $\log k$ at a definite organic solvent concentration and using an appropriate correlation equation.[20] A retention model based on solvophobic theory was applied for this purpose by Wells et al., who used an equation correlating $\log k$ with the surface tension and dielectric constant of the effluent.[21,22] This method is, however, appropriate only for chromatographic systems in which acetonitrile is as the organic modifier. Correlation between the $\log k_w$ and logarithm of solubility in water ($\log S$) is the basis of the method of Thurman et al.[23] Jandera et al. used the sorption method to determine $\log k_w$.[12]

In the present paper the numerical method for $\log k_w$ determination based on the linear form of the Ościk's equation has been presented. It was already used for determination of the $\log k_w$ parameter and biological activity characteristic of a group of benzanilides,[24] benzamides,[25] pesticides,[26] and s-triazines[27] and others.[28–30] Here, this method was used to calculate the $\log k_w$ values for a group of aromatic substances including a homologous series of alkylbenzenes.

EXPERIMENTAL

HPLC Measurements

All chromatographic data were obtained using the Shimadzu Vp liquid chromatographic system equipped with a LC 10AT pump, SPD 10A UV-VIS detector, SCL 10A system controller, CTO-10 AS chromatographic oven, and Rheodyne injector valve with a 20 µL loop. The Class-Vp computer program controlling hardware, registering and storing data to determine the retention time was used.

A stainless steel column (12.5 cm × 4 mm, I.D.) packed with LiChrospher RP-18e particles 5 µm in diameter (Merck) was used in each experiment. Mixtures of methanol-water and acetonitrile-water were used as effluents. The methanol and acetonitrile molar fraction ranged from 0.1 to 0.9 at 0.1 steps. The mobile phase flow rate was $1\,\mathrm{mL\,min^{-1}}$. Only for eluents rich in water (molar fraction of organic modifier ranged from 0.1 to 0.3) was the flow rate $1.2\,\mathrm{mL\,min^{-1}}$. All measurements were made at 20°C. The test compounds were separately dissolved ($10^{-3}\,\mathrm{mg\,mL^{-1}}$) in the organic modifier and detected under UV light ($\lambda = 254\,\mathrm{nm}$). For calculation, average values of the retention factors from at least three experimental data were taken. The retention factor (k) was calculated according to:

$$k = \frac{(t_R - t_o)}{(t_o - t_{ec})} \qquad (1)$$

where t_R, t_o, and t_{ec} denote the gross retention time, the dead time, and the extra column time. The dead time was evaluated from the uracil peak, whereas the the extra column time was determined experimentally using azero-volume connection instead of the chromatographic column. The extra column volume was equal to 75 μL, and the extra column time was calculated from this value.

Materials

HPLC grade methanol and acetonitrile were purchased from Merck. Alkylbenzenes: benzene, toluene, ethylbenzene, propylbenzene, and butylbenzene, PAHs: naphthalene, antracene, phenantrene, chrysene, and fluorine, monosubstituted benzenes: phenol, aniline, nitrobenzene, chlorobenzene, and benzaldehyde, all of analytical grade, were obtained from various sources.

RESULTS AND DISCUSSION

The logarithm of the retention factor in pure water in the RPLC system, $\log k_w$, was determined using the numerical method based on the linear form of Ościk's equation.[31]

$$G(x) = \frac{x_o(1 - x_o)}{\log k - x_o \log k_o - (1 - x_o)\log k_w} = ax_o + b \qquad (2)$$

where x_o denotes the molar fraction of organic modifier in the mobile phase, k_o, k_w, and k are the solute retention factors in the pure organic modifier, pure water, and mixed eluent, respectively. The left term of this equation, designed as $G(x)$, is the linear function of the organic modifier molar fraction in the mobile phase. The presented numerical method is based on fitting $\log k_w$ parameter to Equation (2) to obtain the best linear relationship between $G(x)$ and x_o.

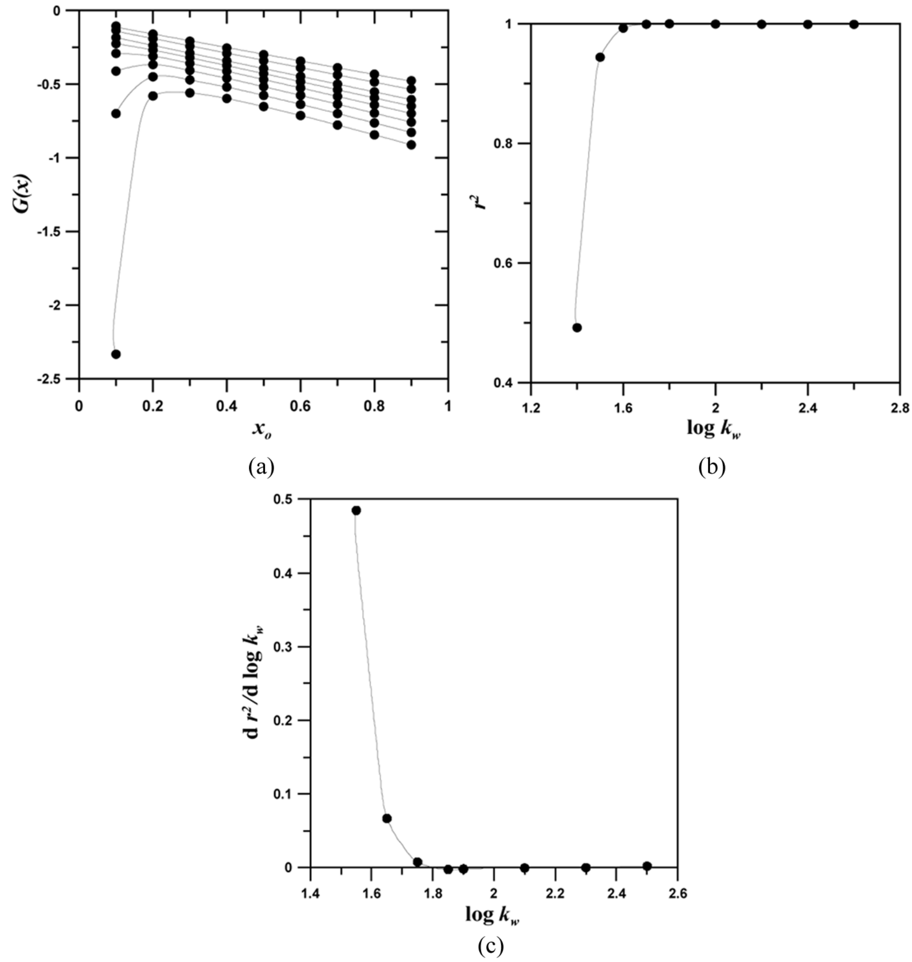
The logarithms of the retention factors in the organic modifier, $\log k_o$, were obtained by linear extrapolation of $\log k$ vs. x_o towards pure organic modifier. The retention factors (k) in the mixed effluent were measured experimentally at 0.1 increments of the molar fraction in the range from 0.1 to 0.9 molar fraction of methanol and acetonitrile for polar aromatic solutes and for benzene and toluene. For more hydrophobic substances, the x_o ranges were smaller due to a stronger retention: molar fraction of acetonitrile ranging from 0.2 to 0.9 except for chrysene with the range $x_o = 0.3$–0.9, and for methanole with molar fractions ranges 0.2–0.9, 0.3–0.9, 0.4–0.9, and even 0.5–0.9 depending on the hydrophobicity of solutes (Table 1).

The numerical method, as mentioned above, consists in inserting subsequent $\log k_w$ values at 0,1 steps to obtain straight line dependence

TABLE 1 Values of the Logarithms of the Retention Factor (log k) Determined at Various Concentrations of Organic the Modifier in the Mobile Phase on LiChrospherRP-18e

	Molar Fraction of Methanol(x_o)									Molar Fraction of Acetonitrile(x_o)								
Solute	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Benzene	1.57	1.28	0.95	0.63	0.39	0.15	−0.05	−0.24	−0.40	1.41	0.87	0.51	0.26	0.10	−0.05	−0.15	−0.24	−0.34
Toluene	2.07	1.71	1.30	0.92	0.63	0.36	0.13	−0.04	−0.26	1.81	1.12	0.70	0.46	0.25	0.08	−0.05	−0.15	−0.25
Ethylbenzene		2.09	1.61	1.17	0.83	0.51	0.26	0.07	−0.17									
Propylbenzene			1.97	1.46	1.07	0.71	0.42	0.19	−0.07		1.66	1.18	0.80	0.55	0.36	0.20	0.07	−0.06
Butylbenzene				1.75	1.31	0.91	0.59	0.33	0.04		1.97	1.33	0.98	0.72	0.51	0.35	0.18	0.06
Naphthalene		2.18	1.61	1.15	0.82	0.50	0.26	0.07	−0.16		1.35	0.86	0.57	0.35	0.18	0.04	−0.07	−0.15
Antracene			2.47	1.83	1.38	0.98	0.67	0.44	0.17		1.90	1.30	0.94	0.68	0.50	0.34	0.20	0.07
Phenantrene			2.33	1.72	1.30	0.91	0.61	0.38	0.12		1.84	1.22	0.87	0.61	0.44	0.28	0.15	0.02
Fluorene			2.18	1.62	1.23	0.86	0.57	0.35	0.10		1.71	1.13	0.79	0.55	0.36	0.22	0.08	−0.04
Chryzene					1.89	1.42	1.07	0.81	0.51			1.69	1.28	0.98	0.79	0.60	0.43	0.29
Phenol	0.90	0.54	0.22	−0.06	−0.24	−0.45	−0.64	−0.75	−0.90	0.64	0.20	0.02	−0.18	−0.35	−0.47	−0.55	−0.60	−0.64
Nitrobenzene	1.51	1.07	0.71	0.40	0.16	−0.08	−0.28	−0.37	−0.59	1.27	0.71	0.33	0.09	−0.10	−0.26	−0.40	−0.46	−0.53
Chlorobenzene	2.19	1.77	1.33	0.92	0.60	0.32	0.09	−0.08	−0.30	1.87	1.12	0.69	0.45	0.23	0.06	−0.07	−0.16	−0.26
Benzaldehyde	1.28	0.82	0.44	0.14	−0.06	−0.26	−0.42	−0.51	−0.62	1.40	0.86	0.50	0.26	0.07	−0.08	−0.20	−0.28	−0.36

(Equation (2)). Thus, the obtained relationships of $G(x)$ *vs.* the molar fraction of the organic modifier for different $\log k_w$ values for the model system, in which $\log k_o = -0.60$, $\log k_w = 1.80$ and $\log k$ values for the particular concentrations were calculated from the Ościk's equation,[31] is presented in Figure 1a. It can be seen, that if the inserted $\log k$ value is smaller than the real one (1.80) the diagram is not a straight line. After inserting the real value, the diagram becomes a straight line and remains so for values higher than the real $\log k_w$. The measure of fitting the straight line to the set of experimental points is the correlation coefficient or more often its square (r^2). As shown in Figure 1b, it reaches the value 1 for $\log k_w$



(a) (b)

(c)

FIGURE 1 Determination of $\log k_w$ using the numerical method for the model chromatographic system: $G(x)$ *vs.* x_o relationship for different $\log k_w$ values fitted to Equation (2). (a); relationship between the determination coefficient (r^2) and $\log \mathrm{k_w}$ (b); d r^2/dlog k_w vs. $\log k_w$ relationship.

equal or higher than the real value. The searched $\log k_w$ value is at the intersection of r^2 vs. $\log k_w$ relationship with line $y = 1$.

Unfortunately, in the case of real systems. the diagrams of these relationships have another, less sharp course, which is caused by measurement errors when determining $\log k$ values (Figures 2a and 2b). For r^2 vs. $\log k_w$ relationship, three regions of r^2 changes are visible: (I) a rapid increase of these values, (II) a small but still significant increase of the fitting coefficient, and (III) a negligible r^2 increase. The real $\log k_w$ value is contained in region II. Much more suitable for determination of $\log k_w$ is the differentiated relationship of r^2 vs. $\log k_w$ (Figures 1c and 2c). For

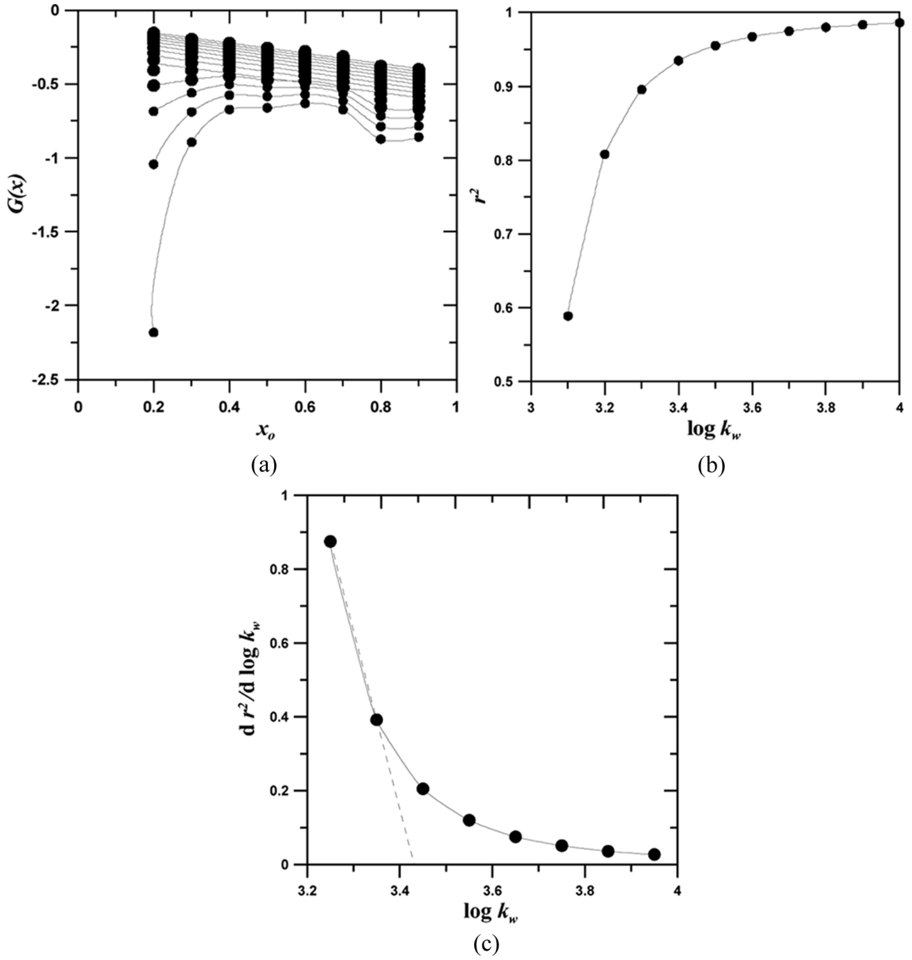


FIGURE 2 Determination of $\log k_w$ using the numerical method for ethylbenzene and methanol as organic modifier: $G(x)$ vs. x_o relationship for different $\log k_w$ values fitted to Equation (2). (a); relationship between the determination coefficient (r^2) and $\log \mathrm{k_w}$ (b); $\mathrm{d}r^2/\mathrm{dlog}\, k_w$ vs. $\log k_w$ relationship.

the model system, $dr^2/d\log k_w$ attains 0 for the real value of this parameter and does not change with its increase, but in the real system the derivative of the correlation coefficient does not usually attain 0 or a stable value at all, which, however, slightly decreases. The way of $\log k_w$ determination is shown in Figure 2c as the intersection of the straight line of the falling relationship part with X-axis.

Using the described method, the retention factor logarithms in pure water were determined for three groups of substances: alkylbenzenes, PAHs, and polar monosubstituted benzenes. The whole range of measured methanol and acetonitrile concentrations was used for calculations. The obtained results are presented in Table 2. Moreover, in the table $\log k_w$ values are listed, which were determined for both organic modifiers by means of parabolic and linear extrapolation using the relationship of the retention factor logarithm vs. the molar(x) and volume fraction(φ) of the organic modifier denoted as linear(x) and linear(φ), respectively. The whole concentration range for each substance was used to determine $\log k_w$ by the parabolic extrapolation method. The concentration range x of methanol and acetonitrile for which linear(x) extrapolation was made is given in Table 2. For those substances for which chromatographic measurement could be performed at 0.1 molar methanol fraction two concentrations ranges of the organic modifier were used to examine the effect of the applied x range on the $\log k_w$ values.

In the case of linear(φ) extrapolation for methanol, the concentration range(φ) from 0,35 to 0,8 was used, except those substances, for which, because of strong retention, measurements in this range could not be made, as: antracene, propylbenzene, phenantrene, and fluorene for which the concentration range 0.5–0.8, and for chrysene 0.7–0.9 was used. In the case of using acetonitrile as organic modifier, the following concentration ranges(φ) were used: from 0,25 to 0,8 for benzene, toluene, and polar monosubstituted benzenes, from 0.55 to 0.85 for chrysene, and from 0.4 to 0.8 for the remaining solutes.

Examples of the relationship of $\log k_w$ versus methanol and acetonitrile content for toluene (A) and phenol (B), as well as the way of $\log k_w$ determination by various extrapolation methods are given in Figure 3. For most substances studied the $\log k$ *vs.* φ relationships are practically linear in almost the whole concentration range of the organic modifier, although for some of them at a very high or very low content of the organic modifier a deviation from linearity can be seen. However, for the $\log k$ *vs.* x relationships only small linearity ranges are observed, thus, in this case, the concentration range used for extrapolation will have a big effect on the obtained $\log k_w$ values.

Regardless of the method used, the $\log k_w$ values estimated by using methanol as organic modifier are higher than those using acetonitrile.

TABLE 2 Retention Factors in Pure Water (log k_w) Estimated by Extrapolation of log k *vs.* x and log k *vs.* φ Relationships and Determined from the Linear Form of Ościk's Equation Using Methanol and Acetonitrile as Organic Modifier

			Linear Extrapolation							
			Using log k *vs.* x							
	Parabolic Extrapolation		Methanol		Acetonitrile		Using log k *vs.* φ		Numerical Method	
Solute	Methanol	Acetonitrile	$x_o = 0.1–0.6^a$	$x_o = 0.3–0.6^b$	$x_o = 0.1–0.6^c$	$x_o = 0.3–0.6$	Methanol	Acetonitrile	Methanol	Acetonitrile
Benzene	1.953	1.774	1.837	1.718	1.503	1.033	2.260	2.017	2.329	2.119
Toluene	2.542	2.219	2.382	2.202	1.887	1.304	2.893	2.499	2.943	2.540
Ethylbenzene	3.151	–	2.818	2.668	–	–	3.520	–	3.496	–
Propylbenzene	3.651	2.606	–	3.179	2.202	1.942	4.087	2.930	4.040	3.454
Butylbenzene	3.935	2.982	–	3.423	2.514	2.109	4.810	3.552	4.509	4.050
Naphthalene	3.319	2.199	2 .912	2.667	1.802	1.507	3.516	2.625	3.710	3.114
Antracene	4.553	2.896	–	3.879	2.432	2.052	4.806	3.458	4.607	4.127
Phenantrene	4.293	2.837	–	3.671	2.360	1.955	4.557	3.401	4.462	4.065
Chryzene	4.943	2.973	–	4.240	–	2.535	5.462	3.626	5.721	4.690
Fluorene	3.985	2.662	–	3.430	2.220	1.855	4.454	3.188	4.295	3.636
Phenol	1.250	0.918	1.089	0.853	0.717	0.493	1.393	1.068	1.754	1.354
Nitrobenzene	1.928	1.670	1.727	1.472	1.372	0.897	2.085	1.871	2.391	2.091
Chlorobenzene	2.712	2.292	2.515	2.300	1.933	1.307	3.044	2.580	3.092	2.891
Benzaldehyde	1.703	1.780	1.457	1.100	1.503	1.056	1.714	1.986	2.090	2.200

[a] For ethylbenzene and naphthalene $x_o = 0.2–0.6$.

[b] For butylbenzene $x_o = 0.4–0.6$ and for chryzene $x_o = 0.5–0.6$.

[c] For propylbenzene, butylbenzene and PAHs $x_o = 0.2–0.6$.

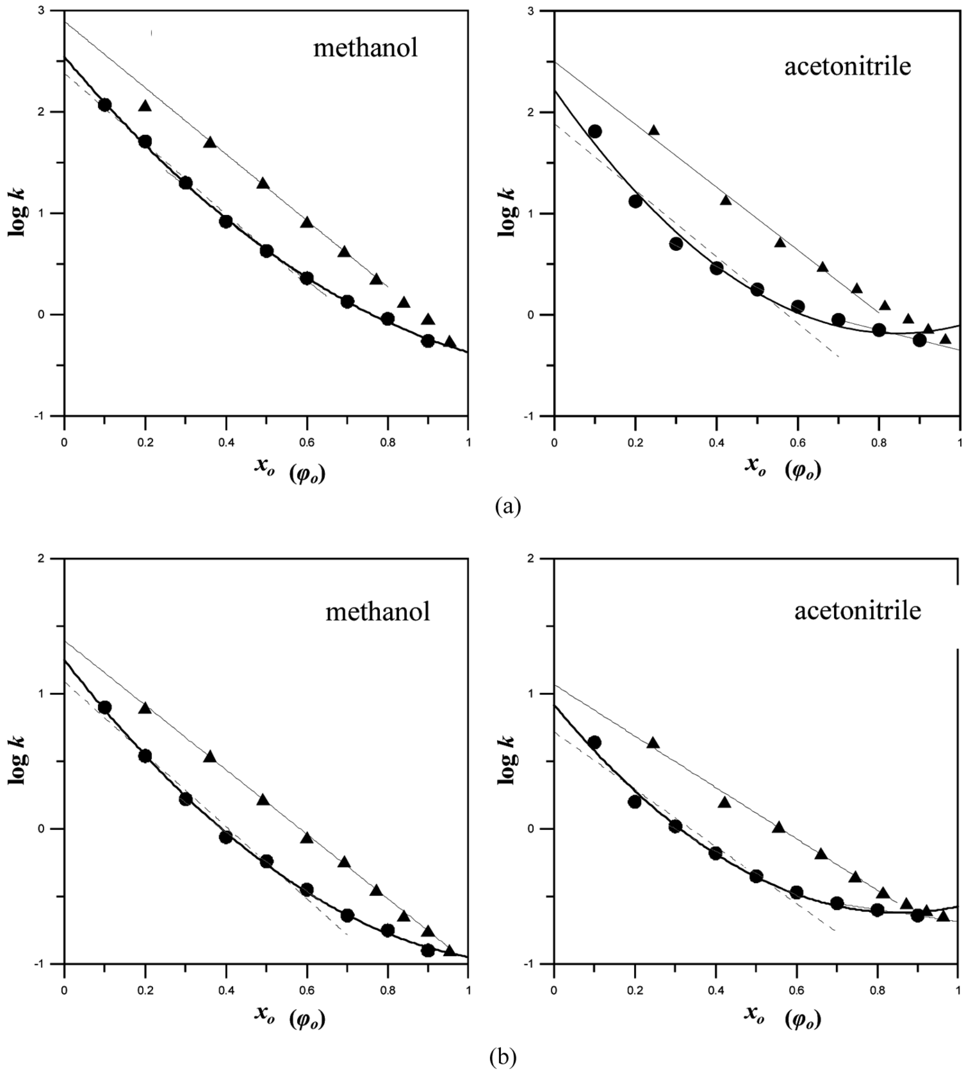


FIGURE 3 Determination of $\log k_w$ parameters by parabolic, linear(x) (●) and linear(φ) (▲) extrapolations for toluene (a) and phenol (b) using methanol and acetonitrile as organic modifier.

The parameters of linear correlation between the $\log k_w$ values estimated from methanol and acetonitrile are summarized in Table 3, and such exemplary relationships for the numerical method and linear(x) extrapolation in Figure 4. Analysis of the slopes and intercepts shows that in the case of the extrapolation methods, the differences of the $\log k_w$ values calculated by using various organic modifiers are considerable and depend on the values of this parameter. The greater the solute retention the bigger are the differences reaching even the value 2 for chrysene independently of

TABLE 3 Regression Data for log $k_{w(MeOH)}$ *vs.* $k_{w(ACN)}$ Correlations using Different Methods of log k_w Determination

Method	a	b	n	r^2	*SD*
Numerical	0.816	0.213	13	0.973	0.0293
Parabolic extrapolation	0.490	0.757	13	0.890	0.0466
Linear(x) extrapolation	0.513	0.194	13	0.994	0.0208
Linear(φ) extrapolation	0.563	0.730	13	0.944	0.0373

the extrapolation method. For substances of smaller hydrophobicity (benzene, toluene, polar monosubstituted benzenes) these differences are of the order 0.2–0.4. Particular attention deserves the fact that except for benzaldehyde the log k_w values determined by using acetonitrile are higher than those by using methanol, not only for the numerical method but also for parabolic and linear(φ) extrapolation. However, for the numerical method, the influence of the kind of organic modifier is considerably smaller. Only in this case does a good linear correlation also occur between the log k_w values calculated by using methanol and acetonitrile ($r^2 = 0{,}973$, $SD = 0{,}0293$), being disturbed only due to polar

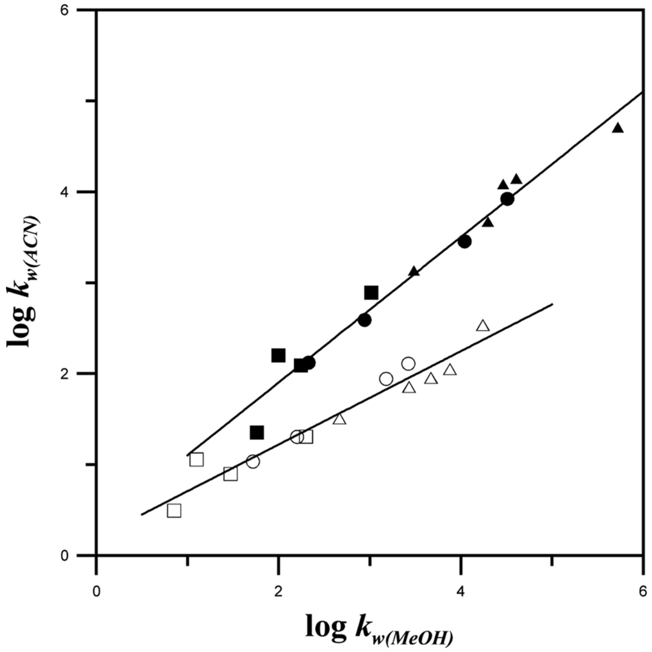


FIGURE 4 Correlation between the log k_w values obtained using methanol and acetonitrile as organic modifier; log k_w calculated by the numerical method (closed symbols) and by linear extrapolation(x) (open symbols) for alkylbenzenes (circles), PAHs (triangles) and polar benzene derivatives (squares).

monosubstituted benzenes for which this relationship is far from linear. In the case of the extrapolation methods, these relationships are far from linear ($r^2 = 0.890$, $SD = 0.0466$ for parabolic, $r^2 = 0.944$, $SD = 0.0208$ for linear(x), and $r^2 = 0.944$, $SD = 0.0373$ for linear(φ)).

In the extrapolation methods, the determined $\log k_w$ values are greatly influenced by the concentration range of the organic modifier used for calculations. Its greatest significance is in the case of linear (x) extrapolation, where the differences of $\log k_w$ values determined by using the concentration ranges 0.1–0.9 and 0.3–0.9 are from 0.119 for benzene to 0.357 for benzaldehyde when using methanol as organic modifier, and from 0.224 for phenol to 0.626 for chlorobenzene in the case of acetonitrile (Table 4). The lower are the concentrations of the organic modifier in the x range, the higher are the obtained $\log k_w$ values, being at the same time closer to real ones. On the other hand, such concentration ranges cannot be used for substances of a higher hydrophobicity due to a strong retention. To obtain comparable results, the same range of molar fractions of the organic modifier should be used for linear(x) extrapolation for all substances, which on the other hand, is connected with lowering the calculated $\log k_w$ values. This problem does not practically occur in the numerical method, where the differences between the $\log k_w$ values calculated by using various concentration ranges of methanol oscillate from 0.004 for nitrobenzene to 0.099 for benzaldehyde (Table 4), so they are on the average 10 times smaller than for the extrapolation method. Therefore, for calculations by the numerical method, the whole range of concentrations(x) at which the data were obtained was used for all solutes.

The $\log k_w$ values calculated by various methods differ considerably (Table 2). As regards the $\log k_w$ values determined by the extrapolation methods, the lowest are obtained by linear(x) extrapolation and the

TABLE 4 The Differences (Δ) Between log k_w Values Calculated by the Linear(x) Extrapolation using Concentration Ranges (x) of Methanol and of Acetonitrile from 0.1 to 0.6 and from 0.3 to 0.6 (Δ_{MeOH} and Δ_{ACN} Respectively) and by Numerical Method using Concentration Ranges (x) of Methanol from 0.1 to 0.9 and from 0.3 to 0.9 (Δ_{num})

Solute	Δ_{MeOH}	Δ_{ACN}	Δ_{num}
Benzene	0.119	0.470	−0.050
Toluene	0.180	0.583	0.017
Ethylbenzene	0.150	–	0.008
Napthalene	0.245	0.295	0.034
Phenol	0.236	0.224	−0.036
Nitrobenzene	0.255	0.475	−0.004
Chlorobenzene	0.215	0.626	−0.022
Benzaldehyde	0.357	0.447	−0.099

highest by linear(φ) extrapolation independently of the kind of the organic modifier used. The differences are bigger the stronger is the substance retained in the chromatographic column, and they exceed 1.2 for the strongest hydrophobic chrysene when using methanol as organic modifier. For substances of the smaller hydrophobicity (benzene, toluene, polar monosubstituted benzenes) the differences are of the order 0.3–0.5.

The $\log k_w$ values calculated by the numerical method are closer to those determined by linear(φ) extrapolation (differences between $\log k_w$ are in the range 0.024–0.376), and for some substances they are a little bigger than those of extrapolation (benzene, toluene, naphthalene, chrysene, phenol, nitrobenzene, chlorobenzene, benzaldehyde), but a little smaller for ethylbenzene, propylbenzene, butylbenzene, antracene, phencentrene, and fluorene (Table 4). Bigger $\log k_w$ values than those calculated by linear(φ) extrapolation have numerically determined values for substances of a smaller hydrophobicity, of which chryzene is an exception.

The correlations between the $\log k_w$ values calculated by the numerical method and those determined by the extrapolation methods are presented

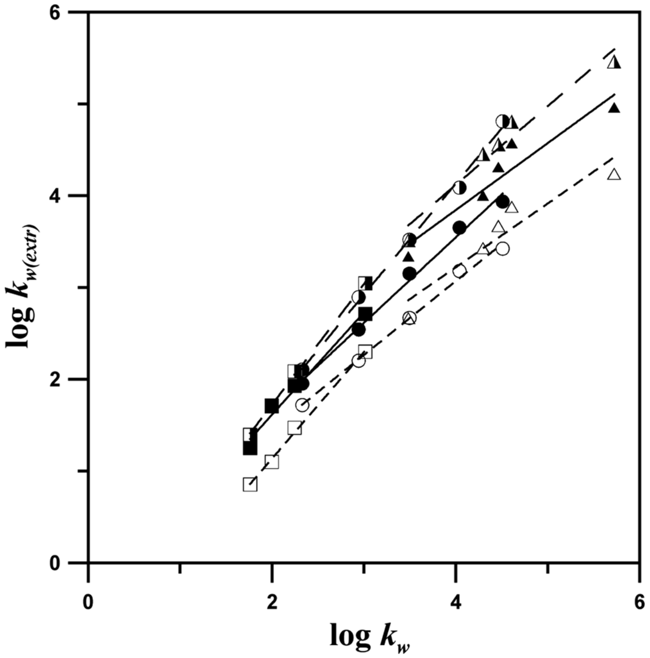


FIGURE 5 Correlation between the $\log k_w$ values calculated by the numerical method and obtained by different extrapolation methods: parabolic (closed symbols), linear(x) (open symbols) and linear(φ) (half-close symbols). Squares for polar benzene derivatives, circles for alkylbenzenes and triangles for PAHs.

TABLE 5 Regression Data for the Relationships of log k_w Calculated by the Numerical Method *versus* log k_w Determined by Different Extrapolation Methods Using Methanol as Organic Modifier

Solutes	Method	a	b	n	r^2	*SD*
Alkylbenzens	Parabolic extrapolation	0.933	−0.184	5	0.993	0.0064
	Linear (x) extrapolation	0.806	−0.152	5	0.995	0.0031
	Linear (φ) extrapolation	1.208	−0.702	5	0.997	0.0047
PAHs	Parabolic extrapolation	0.729	0.928	5	0.910	0.0451
	Linear (x) extrapolation	0.696	0.438	5	0.898	0.0472
	Linear (φ) extrapolation	0.857	0.689	5	0.960	0.0264
Polar benzene derivatives	Parabolic extrapolation	1.114	−0.614	4	0.981	0.0104
	Linear (x) extrapolation	1.162	−1,188	4	0.997	0.0020
	Linear (φ) extrapolation	1.314	−0.904	4	0.998	0.0011

in Figure 5 and Table 5, separately for each of the three studied groups. The best linear correlation for each group of substances is observed between the log k_w values calculated numerically and those determined by linear(φ) extrapolation ($r^2 = 0.997$, $SD = 0.0047$ for alkylbenzenes, $r^2 = 0.960$, $SD = 0.0264$ for PAHs and $r^2 = 0.998$, $SD = 0.0011$ for polar monosubstituted benzenes). Good linear correlations can be also observed between the log k_w values determined numerically and by parabolic extrapolation ($r^2 = 0.993$, $SD = 0.0064$ for alkylbenzenes and $r^2 = 0.981$, $SD =$ 0.0104 for polar monosubstituted benzenes), and those of linear (x) extrapolation ($r^2 = 0.995$, $SD = 0.0031$ for alkylbenzenes and $r^2 = 0.997$, $SD =$ 0.0020 for polar monosubstituted benzenes). They are, however, worse than the correlations of log k_w values determined numerically and by linear(φ) extrapolation. Moreover, analysis of the slopes and intercepts as well as that already presented in Table 2 show that only those values are close. The other extrapolation methods give log k_w values considerably lowered in relation to those calculated by the numerical method.

In reversed phase liquid chromatography a linear relationship between the logarithms of the retention factors and the number of carbon atoms (n_C) in the molecule is observed for the homologous series. This is caused by the fact that the methylene group regularly contributes to standard free enthalpy of solute molecules distribution between the mobile and stationary phase. In this paper, the influence of the number of carbon atoms in the side chain of alkylbenzenes was studied. The regression data presented in Table 6 and Figure 6 show that good linear correlations occur between the number of carbon atoms and log k_w values determined by all methods used. The best correlations, however, take place for the log k_w values calculated by the numerical method both for methanol and acetonitrile as organic modifiers ($r^2 = 0.998$, $SD = 0.0022$ and $r^2 = 0.999$, $SD = 0.0002$, respectively), as well as for log k_w determined by linear (φ) extrapolation using methanol ($r^2 = 0.997$, $SD = 0.0042$). Comparing the correlations

TABLE 6 Regression Data for the Relationships of $\log k_w$ Determined by Different Methods Versus C-Atoms Number in the Alkyl Group of Alkylbenzenes

Method	Organic Modifier	a	b	n	r^2	*SD*
Numerical	MeOH	0.546	2.372	5	0.998	0.0022
	ACN	0.447	2.128	4	0.999	0.0003
Parabolic extrapolation	MeOH	0.507	2.032	5	0.984	0.0142
	ACN	0.280	1.835	4	0.975	0.0100
Linear(x) extrapolation	MeOH	0.439	1.761	5	0.989	0.0072
	ACN	0.279	1.039	4	0.991	0.0024
Linear(φ) extrapolation	MeOH	0.660	2.163	5	0.997	0.0042
	ACN	0.350	2.049	5	0.961	0.0251

between the carbon number (n_C) and $\log k_w$ calculated from methanol by the numerical method and linear(φ) extrapolation, it can be found that despite a close r^2 values the *SD* value is almost two times higher for the latter. This indicates that in the case of $\log k_w$ values calculated by linear(φ) extrapolation some of them divert more from the linear relationship than those calculated by the extrapolation method. Thus, the best linear correlations occur in the case of the logarithms of the retention factors calculated by the numerical method, which is evidence that this method allows us to calculate most accurately the discussed parameters.

Both the logarithms of the retention factors in pure water ($\log k_w$) and those of the partition coefficients in the system n-octanol/water ($\log P$) are

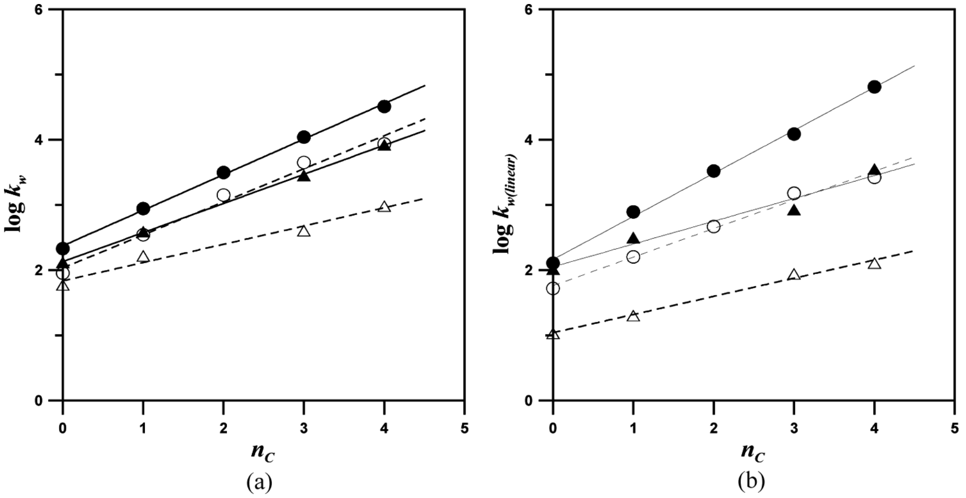
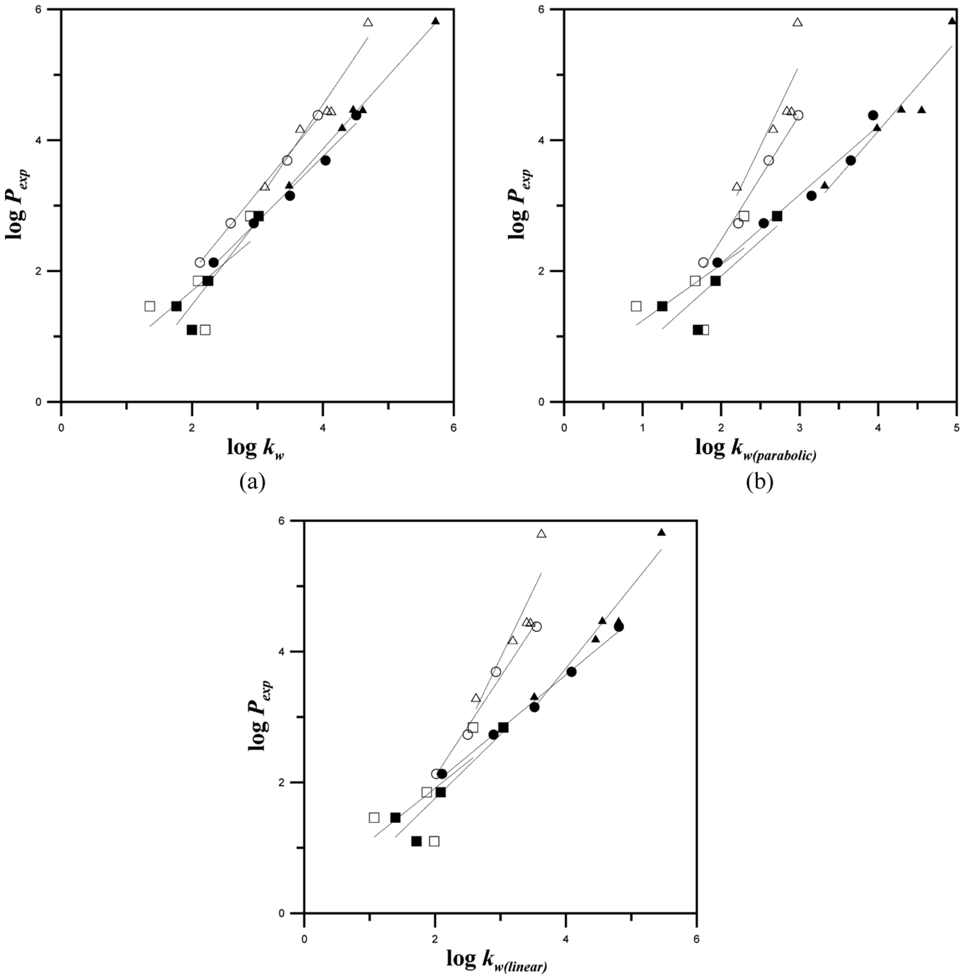


FIGURE 6 Relationships between the $\log k_w$ values and the number of C-atoms in the alkyl group of alkylbenzenes; $\log k_w$ calculated by the numerical method (closed symbols) and parabolic extrapolation (open symbols) (a); and by the linear(φ) (closed symbols) and linear(x) (open symbols) extrapolation (b). Methanol (circles) and acetonitrile (triangles) as organic modifier of effluent.

used as descriptors of hydrophobicity (or lipophilicity) of substances. Correlations between the log k_w values, calculated by the numerical method and determined by parabolic and linear (φ) extrapolation, and the experimental log P values[32] are presented in Figure 7, whereas the regression data are in Table 7. A relatively best linear correlation was obtained for alkylbenzenes ($r^2 = 0.987$, $r^2 = 0.961$ and $r^2 = 0.994$ for the numerical method, parabolic and linear (φ) extrapolation, respectively, using methanol as organic modifier and $r^2 = 0.997$, $r^2 = 0.987$ and



(a)

(b)

(c)

FIGURE 7 Correlations between log k_w and experimental log P values; log k_w obtained by the numerical method (a), parabolic extrapolation (b) and linear(φ) extrapolation (c) for alkylbenzenes (circles), PAHs (triangles) and polar benzene derivatives (squares). Methanol (closed symbols) and acetonitile (open symbols) as organic modifier of eluent.

TABLE 7 Regression Data for $\log k_w$ *vs.* $\log P$ Correlations using Different Methods of $\log k_w$ Determination

Solutes	Method	Organic Modifier	a	b	n	r^2	*SD*
Alkylbenzens	Numerical	MeOH	0.996	−0.234	5	0.987	0.0126
		ACN	1.223	−0.462	4	0.997	0.0039
	Parabolic extrapolation	MeOH	1.050	0.018	5	0.961	0.0386
		ACN	1.915	−1.355	4	0.987	0.0191
	Linear extrapolation	MeOH	0.826	0.339	5	0.994	0.0057
		ACN	1.518	−0.941	4	0.982	0.0269
PAHs	Numerical	MeOH	1.119	−0.610	5	0.995	0.0053
		ACN	1.486	−1.400	5	0.938	0.0665
	Parabolic extrapolation	MeOH	1.384	−1.397	5	0.888	0.1206
		ACN	2.504	−2.355	5	0.741	0.2804
	Linear(φ) extrapolation	MeOH	1.243	−1.228	5	0.941	0.0637
		ACN	2.076	−2.328	5	0.799	0.2170
Polar benzene derivatives	Numerical	MeOH	1.283	−1.080	4	0.864	0.1150
		ACN	0.845	0.008	4	0.503	0.4200
	Parabolic extrapolation	MeOH	1.074	−0.227	4	0.766	0.1972
		ACN	0.856	0.387	4	0.419	0.4910
	Linear extrapolation	MeOH	0.974	−0.193	4	0.861	0.1170
		ACN	0.801	0.310	4	0.441	0.4720

$r^2 = 0.982$ for the numerical method, parabolic, and linear(φ) extrapolation, respectively, using acetonitrile). In the case of polar substances, the correlations are very weak, because r^2 is within the limits from 0.864 (numerical method from methanol) to 0.419 (parabolic method from acetonitrile). This can result from the fact that the studied polar monosubstituded benzenes belong to different groups of substances differing considerably in their properties and showing different molecular interactions both in the mobile and stationary phase. In the case of polycyclic aromatic hydrocarbons (PAHs) only the $\log k_w$ values calculated by the numerical method and using methanol as organic modifier show a very good linear correlation with log P values ($r^2 = 0.995$, $SD = 0.0053$). It is considerably weaker when using acetonitrile as organic modifier of the mobile phase ($r^2 = 0.938$, $SD = 0.0665$). A relatively good linear correlation with log P values was also obtained for $\log k_w$ values determined by linear (φ) extrapolation using methanol ($r^2 = 0.941$, $SD = 0.0637$).

From the presented data it results that the best linear correlation with $\log P$ values is shown by the $\log k_w$ ones calculated by the numerical method. Better results, however, are obtained for this type of correlation performed separately for different groups of substances, because for correlations performed for all substances studied correlation parameters are only: $r^2 = 0.979$, $SD = 0.0409$ for the numerical method, $r^2 = 0.968$, $SD = 0.0625$ for linear(φ) extrapolation and $r^2 = 0.956$, $SD = 0.0853$ for parabolic extrapolation using methanol as organic modifier.

CONCLUSIONS

In this paper, a way of determining logarithms of retention factors in pure water ($\log k_w$) by the numerical method is presented and compared with different extrapolation methods.

A considerable influence of the kind of organic modifier used for measurements on the obtained $\log k_w$ values was found, particularly in the case of the extrapolation methods. This influence is not significant when the numerical method is used, where additionally a very good correlation occurs between the values of this parameter obtained by using various organic modifiers.

The range of the organic modifier concentrations at which measurements were made had the greatest influence on the obtained $\log k_w$ values by using linear(x) extrapolation, however, it is practically unimportant when using the numerical method. This is a significant advantage of this method because for substances of differentiated hydrophobicity chromatographic measurements are usually made in different concentration ranges of the organic modifier. Moreover, narrowing the concentration range used for extrapolation really improves the correlations between the obtained $\log k_w$ values, but on the other hand, it causes their values to be smaller than real ones.

The best correlations between the $\log k_w$ values determined by different methods occur when the numerical method and linear extrapolation using $\log k_w$ versus volume fraction of organic modifier relationship are used for $\log k_w$ determination. For these two methods, the best linear correlations were also obtained between $\log k_w$ values and the number of carbon atoms in the side chain of alkylbenzene (n_C) and $\log P$ values. In the latter case, more accurate results are obtained when correlating $\log k_w$ and $\log P$ values separately for the particular kinds of organic substances, best for the homologous series. So, the chromatographic $\log k_w$ indices, particularly those calculated by the numerical method, are good descriptors of hydrophobicity (or lipophilicity) of aromatic solutes.

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