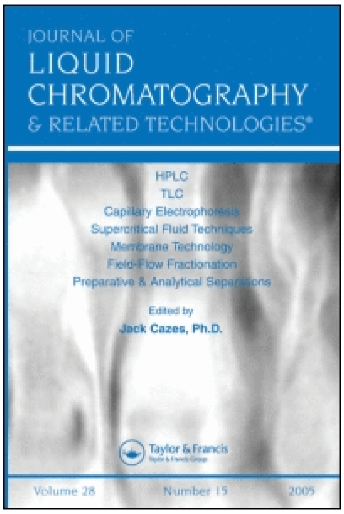

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Application of Ościk's Equation for Description of Solute Retention in RP HPLC and Calculation of Retention Factor in Water

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Abstract: Ościk's Equation, assuming the partition displacement model for a chromatographic process is proposed, for the description of solute retention in reversed phase liquid chromatography. Moreover, a numerical method of calculation of solutes retention factors in water, derived from the linear form of this Equation is presented. Theoretical investigations are applied to the literature of the RP HPLC results obtained for a group of model solutes, i.e., alkyl benzene homologues and test substances of different polarities chromatographed using three chemically bonded stationary phases: RP-8 (octylsilyl-silica), ODS (octadecylsilyl-silica) and PLRP-S (polystyrene-divinylbenzene polymer, PS-DVB) and water-methanol and/or water-acetonitrile mixtures as effluents. Calculated chromatographic parameters were analyzed as hydrophobicity indices and related to experimental and calculated log P values.

Keywords: Alkyl benzenes, Lipophilicity, Retention factor in water, Reversed phase chromatography

INTRODUCTION

Currently, chromatography is one of the most popular analytical techniques widely applied in the pharmaceutical industry, environmental protection, medicine, or agriculture. Theoretical studies on retention

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mechanisms are important not only from a practical point of view-they simplify the optimization of chromatographic separation, but also for better understanding the mechanism of the process and factors affecting it. Chromatography is not only a separation technique-all chromatographic system elements have an influence on retention that is the source of turning information, and can be employed for characterizing mobile or stationary phase or solute properties. The most spectacular is using reversed phase chromatography results in QSARs or QSRRs studies.[1] At present, RP LC is most often used to evaluate the hydrophobicity of new synthesized compounds, and the retention factor in water is regarded as a standard hydrophobicity index.[1–5]

The most complete model of a chromatographic process, based on statistical thermodynamics and including majority of molecular interactions appearing in chromatographic system, was proposed by Martire and Boehm,[6] but resulting Equations are to such extant complicated that they do not have great practical weight.

Jaroniec and Martire[7–9] undertook complex studies on the chromatographic process mechanism and assuming partition or adsorption for both processes, stationary phase formation, and solute distribution between mobile and stationary phases, classified as the majority of known models of solute retention. An interesting result obtained by Jaroniec[9] is that the general expression derived in the studies leads to simple and well known relationships used for description of solute retention in liquid chromatography. Namely, assuming adsorption responsible for solute distribution, at higher concentrations of the most active solvent in the effluent, Snyder-Soczewiński's Equation is obtained.[10–11] On the other hand, assuming the partition mechanism of solute distribution one can derive Ościk's Equation.[12] According to Jaroniec, the mixed mechanism of chromatographic process, i.e., adsorption for stationary phase formation and partition for solute distribution, is the most probable in reversed phase liquid chromatography, and the last Equation should correctly describe solute retention in this system. So far, Ościk's Equation was used in both, adsorption[12] and reversed phase chromatography,[13–15] and the linear form of this Equation was proposed to evaluate hydrophobicity of different bioactive compounds.[16–23]

According to Ościk's Equation there is a following relationship between solute retention and two component mobile phase composition:

$$\log k_{s(12)} = x_1^l \log k_{s(1)} + x_2^l \log k_{s(2)} + (x_1^\sigma - x_1^l)\left(\log\frac{k_{s(1)}}{k_{s(2)}} + A_{s(12)}\right) \quad (1)$$

where, $k_{s(1)}$, $k_{s(2)}$ and $k_{s(12)}$ are solute retention factors in organic modifier (1) water (2) and mixture $(1+2)$, respectively; x_1^l and x_2^l are molar fractions of organic modifier and water in the bulk phase, and x_1^σ is a molar fraction of organic modifier in the surface phase. $A_{s(12)}$ parameter is defined as follows:

$$A_{s(12)} = \frac{\mu^l_{s(1)} - \mu^l_{s(2)}}{2.30RT} = \log \kappa_{s(12)} \tag{2}$$

where $\mu^l_{s(1)}$ and $\mu^l_{s(2)}$ are solute standard chemical potentials in organic modifier and water, respectively, and $\kappa_{s(12)}$ is the hypothetical, rational coefficient for solute partitioning between organic modifier and water. According to this definition, $A_{s(12)}$ describes molecular interactions existing in the bulk phase, i.e., between solute and mobile phase components.

In the four parameter Equation (1), three of them, i.e., $k_{s(1)}$, $k_{s(2)}$ and $A_{s(12)}$ are constant for given a chromatographic system (solute, mobile, and stationary phases) while the last one, i.e., x_1^σ depends on x_1^l. In earlier studies[24,13–15] for calculation of x_1^σ value, Everett's Equation[25] was proposed:

$$x_1^\sigma = \frac{K_{12}x_1^l}{1 + x_1^l(K_{12} - 1)} \tag{3}$$

In this Equation K_{12} is the adsorption equilibrium constant in the system binary solvent solid. Introducing Equation (3) to the general Equation (1) we obtain the linear form of Ościk's Equation:[24,13–17]

$$G(x_1^l) = \frac{x_1^l x_2^l}{\log k_{s(12)} - x_1^l \log k_{s(1)} - x_2^l \log k_{s(2)}} = ax_1^l + b \tag{4}$$

The left term of Equation (4) is denoted as $G(x_1^l)$ and a and b are regression parameters of linear relationship $G(x_1^l)$ vs. x_1^l described by the following Equations:

$$a = \frac{1}{\log \frac{k_{s(1)}}{k_{s(2)}} + A_{s(12)}} \tag{5}$$

and

$$b = \frac{a}{K_{12} - 1} \tag{6}$$

So, $A_{s(12)}$ and K_{12} values characterizing the chromatographic system and solute are calculated from the following formulas resulting from Equations (5) and (6):

$$K_{12} = \frac{a}{b} + 1 \tag{7}$$

Table 1. $\log k_{s(1)}$ and $\log k_{s(2)}$ values calculated for chromatographed solutes

	RP-8/water-methanol		RP-8/water-acetonitrile		ODS/water-acetonitrile		PLRP-S/water-acetonitrile	
Solute	$\log k_{s(1)}$	$\log k_{s(2)}$	$\log k_{s(1)}$	$\log k_{s(2)}$	$\log k_{s(1)}$	$\log k_{s(2)}$	$\log k_{s(1)}$	$\log k_{s(2)}$
Standards								
Toluene	–0.989	2.828	–0.707	2.211	–0.643	2.943	–0.442	3.060
Ethyl benzene	–1.003	3.411	–0.661	2.530	–0.587	3.287	–0.387	3.475
Propyl benzene	–1.047	3.836	–0.690	2.892	–0.501	3.702	–0.318	4.014
Butyl benzene	–1.091	4.437	–0.618	3.465	–0.447	4.099	–0.306	4.168
Hexyl benzene	–	–	–0.675	4.242	–	–		–
Test compounds								
Benzamide	–0.903	1.344	–0.432	0.658	–1.255	1.350	–0.922	1.152
p-cresol	–1.107	2.136	–0.579	1.648	–1.038	1.928	–0.912	2.546
Benzaldehyde	–1.015	2.167	–0.664	1.484	–1.387	2.112	–0.553	2.561
Acetophenone	–0.948	2.233	–0.633	1.477	–0.831	2.048	–0.564	2.533
Nitrobenzene	–0.996	2.216	–0.693	1.841	–1.070	2.396	–0.554	3.012
Methylbenzoate	–1.069	2.714	–0.670	1.788	–0.731	2.455	–0.487	2.936
Benzophenone	–1.090	3.695	–0.736	2.552	–0.824	3.590	–0.318	3.296
Biphenyl	–1.437	4.323	–0.742	3.214	–0.559	3.568	–0.073	4.789

Table 2. Correlation matrix obtained for numerical $\log k_{s(2)}$ parameters calculated from different chromatographic systems

	RP-8 water-methanol	RP-8 water-acetonitrile	ODS water-acetonitrile	PLRP-S water-acetonitrile
RP-8		$R = 0.9818$	$R = 0.9558$	$R = 0.9387$
Water-methanol	–	$sd = 0.195$	$sd = 0.303$	$sd = 0.355$
RP-8			$R = 0.9541$	$R = 0.9601$
Water-acetonitrile	–	–	$sd = 0.256$	$sd = 0.239$
ODS				$R = 0.8805$
Water-acetonitrile	–	–	–	$sd = 0.449$

and

$$A_{s(12)} = \frac{1}{a} - \log\frac{k_{s(1)}}{k_{s(2)}} \tag{8}$$

RESULTS AND DISCUSSION

In the studies, literature experimental data obtained by Sanagi et al.[26] by the RP HPLC technique for a group of model solutes, i.e., alkyl benzene homologues and test substances of different polarities using three chemically bonded stationary phases: RP-8 (octylsilyl-silica), ODS

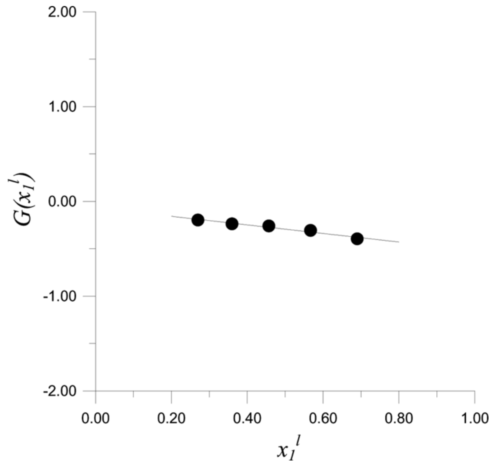


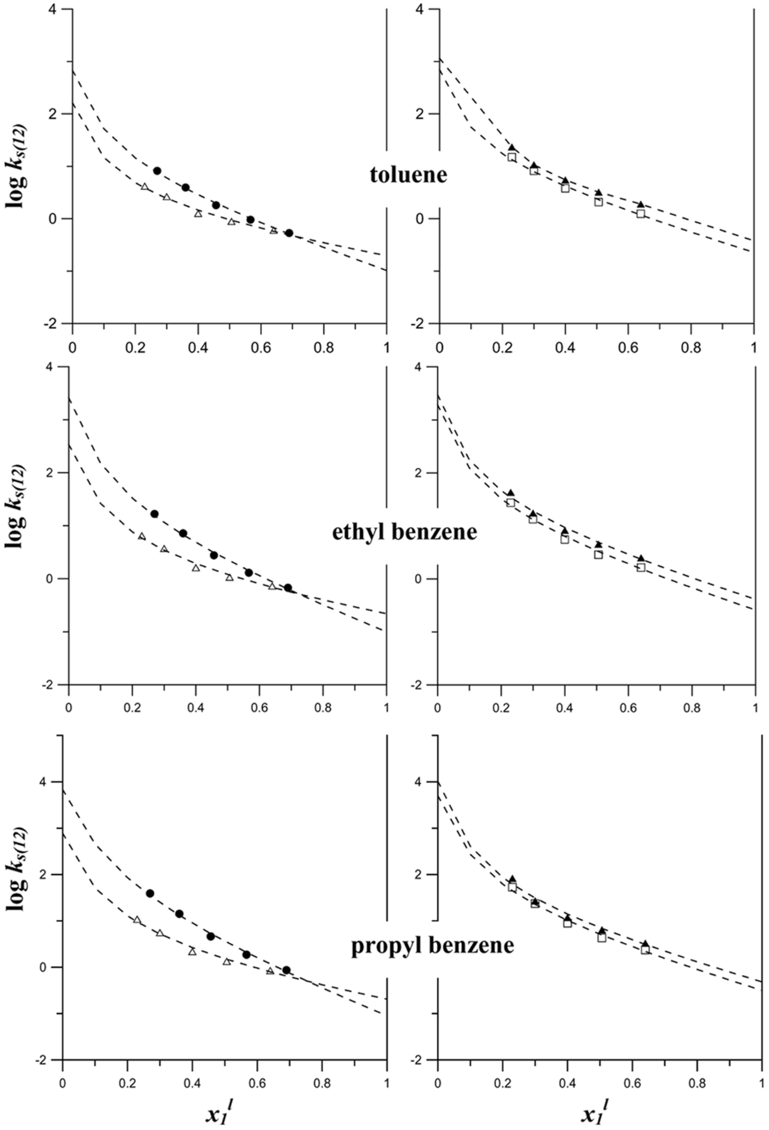
Figure 1. $G(x_1^l)$ vs. x_1^l relationship obtained for ethyl benzene in the RP-8/water-methanol system: $G(x_1^l) = -0.452x_1^l - 0.068; n = 4; R = 0.9814; sd = 0.017$.

(octadecylsilyl-silica), and PLRP-S (polystyrene-divinylbenzene polymer, PS-DVB), and water-methanol and/or water-acetonitrile mixtures as effluents were tested. Sanagi and coworkers investigated the use of alkyl benzenes as a retention index scale in reversed phase HPLC; moreover, chosen test compounds having different functional groups were used to examine the diversity of the scale. In our studies, only a part of experimental data obtained by the authors were helpful; we need at least four experimental $\log k_{s(12)}$ values in a given chromatographic system to make use of Equation (1) for description of solute retention, or Equation (4) to calculate $\log k_{s(2)}$, i.e., retention parameter in water, for each solute.

According to Equation (1) to calculate $\log k_{s(12)}$ parameter, the following values: $\log k_{s(1)}$, $\log k_{s(2)}$, $A_{s(12)}$ and x_1^{σ} characterizing the chromatographic system have to be determined. In our investigations $\log k_{s(1)}$ was evaluated by linear extrapolation of experimental data towards zero concentration of water in the mobile phase, i.e., pure organic modifier as effluent, while $\log k_{s(2)}$ was calculated using the numerical method based on the linear form of Ościk's Equation (Equation (4)). In this method, described in detail in our earlier works,[16,17] $\log k_{s(2)}$ is calculated by numerical fitting to Equation (4) in order to obtain the linearity between the term $G(x_1^l)$ and x_1^l. The results are presented in Table 1. Calculated retention factors in water, $\log k_{s(2)}$,

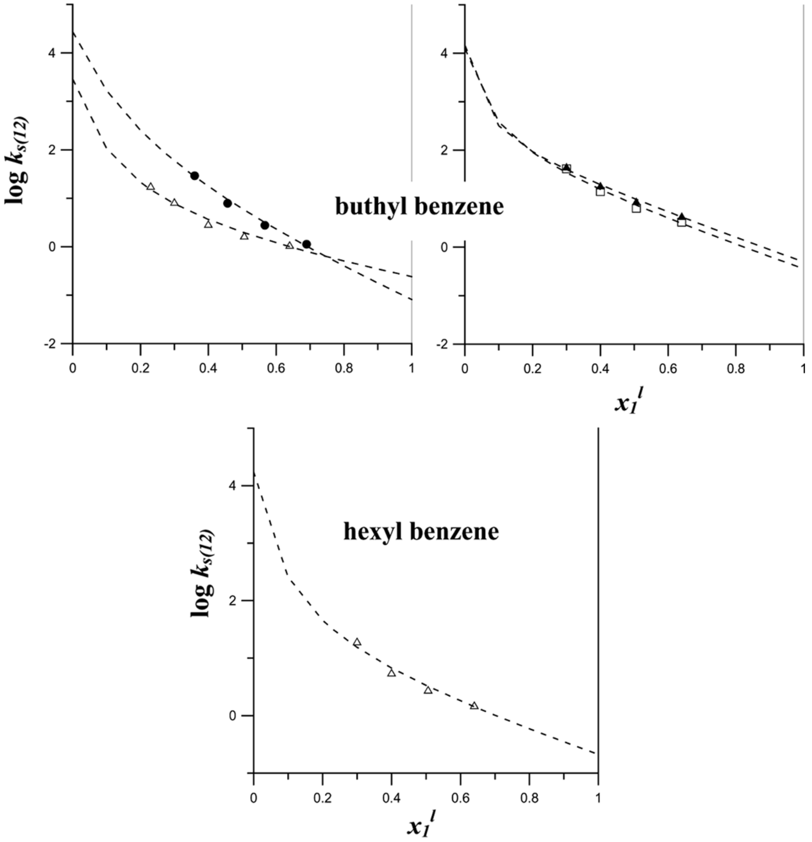
Table 3. K_{12} and $A_{s(12)}$ parameters calculated acc. to Equations (7) and (8)

	RP-8/water-methanol		RP-8/water-acetonitrile		ODS/water-acetonitrile		PLRP-S/water-acetonitrile	
Solute	K_{12}	$A_{s(12)}$	K_{12}	$A_{s(12)}$	K_{12}	$A_{s(12)}$	K_{12}	$A_{s(12)}$
Standards								
Toluene	8.65	1.95	8.49	0.96	9.89	1.72	10.10	1.61
Ethyl benzene	7.63	2.20	7.45	0.95	8.71	1.80	9.17	1.77
Propyl benzene	5.82	2.52	6.98	1.13	7.99	1.92	8.52	1.81
Butyl benzene	4.61	2.76	7.34	1.13	12.51	2.33	20.41	2.43
Hexyl benzene	–	–	10.60	1.87	–	–	–	–
Test compounds								
Benzamide	9.53	0.30	9.97	−0.27	22.47	1.37	6.81	0.27
p-cresol	8.83	1.31	9.41	0.21	14.44	1.51	13.58	1.17
Benzaldehyde	8.96	1.09	11.29	0.57	471.72	2.47	8.28	0.98
Acetophenone	8.11	1.09	9.92	0.54	14.66	1.35	20.67	1.36
Nitrobenzene	8.49	1.43	8.98	0.69	17.59	2.05	6.98	1.22
Methylbenzoate	6.92	1.55	8.37	0.67	11.17	1.38	10.09	1.28
Benzophenone	5.73	1.84	8.37	0.97	9.05	1.77	7.62	1.77
Biphenyl	6.74	2.60	8.54	1.19	14.62	2.08	35.59	2.29



(a)

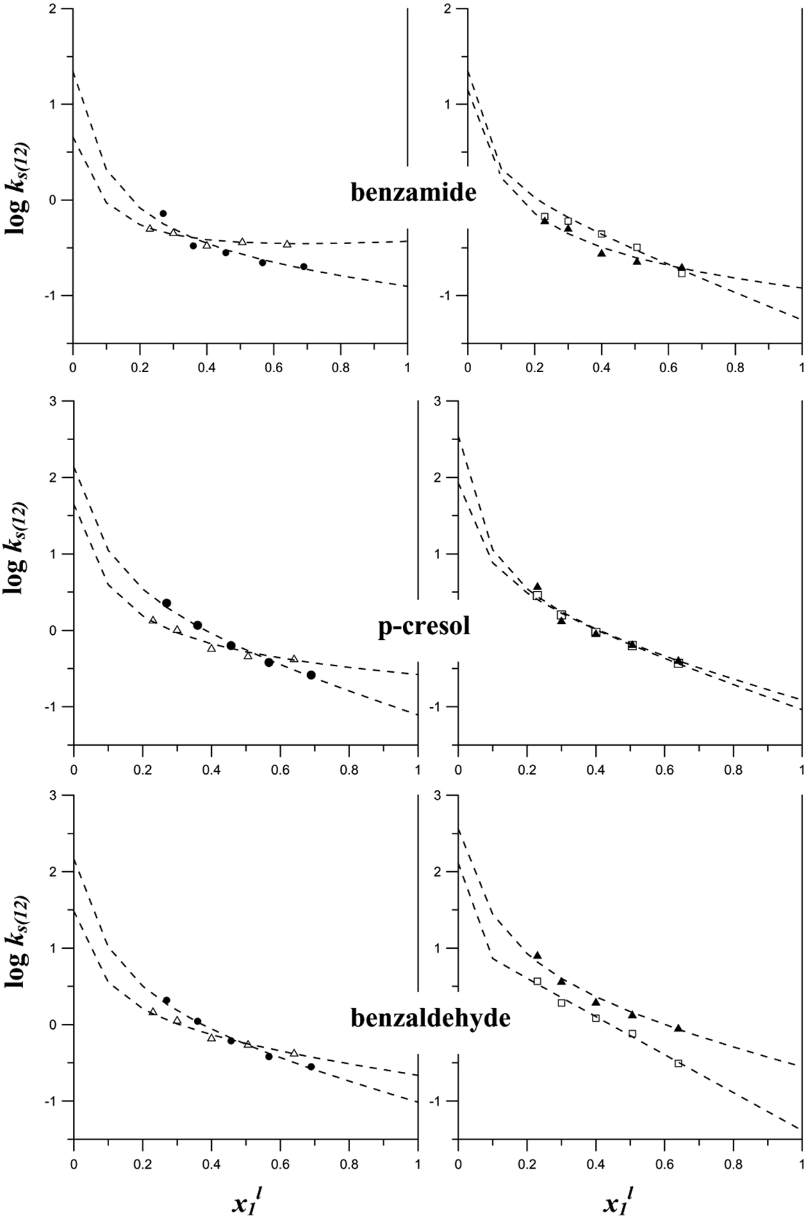
Figure 2. a. Theoretical (lines) and experimental (points) $\log k_{s(12)}$ values obtained for standards in different chromatographic systems: (●) RP-8/water-methanol; (Δ) RP-8/water-acetonitrile; (□) ODS/water-acetonitrile and (▲) PLRP-S/water-acetonitrile. b. Theoretical (lines) and experimental (points) $\log k_{s(12)}$ values obtained for standards in different chromatographic systems: (●) RP-8/water-methanol; (Δ) RP-8/water-acetonitrile; (□) ODS/water-acetonitrile and (▲) PLRP-S/water-acetonitrile.

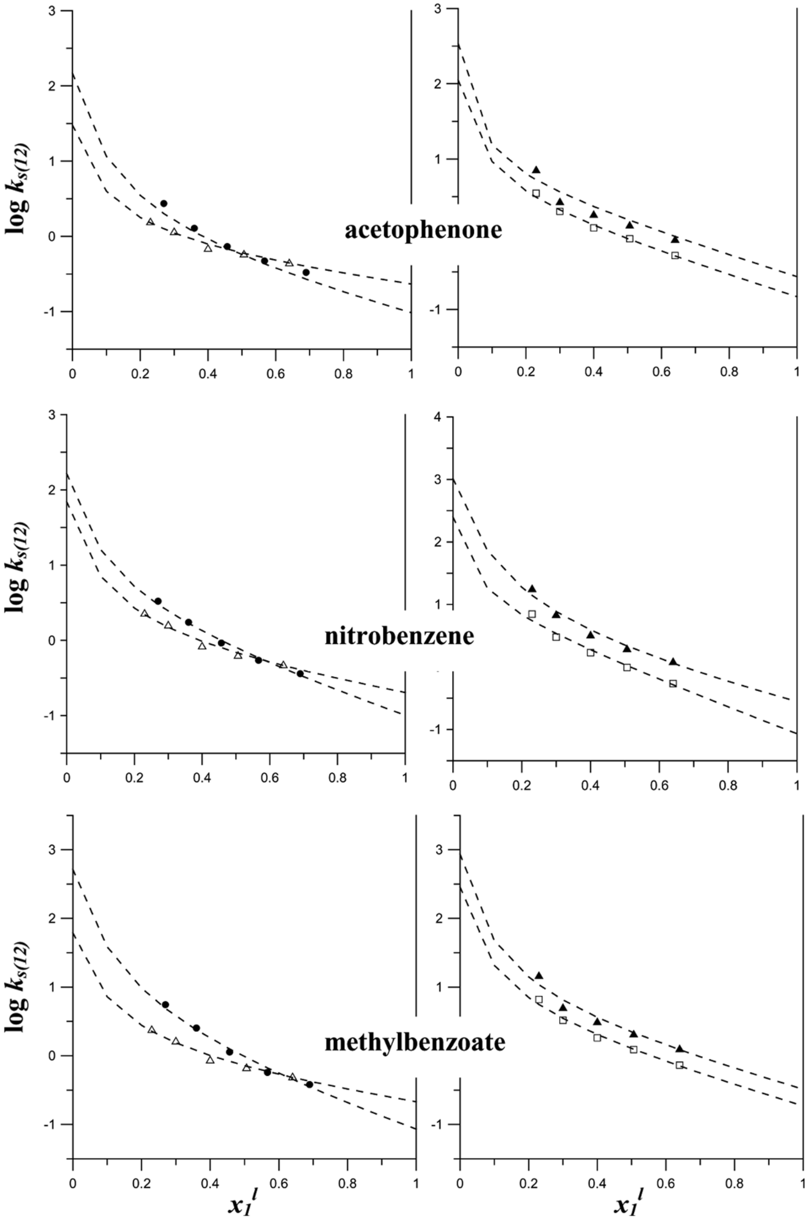


(b)

Figure 2. Continued.

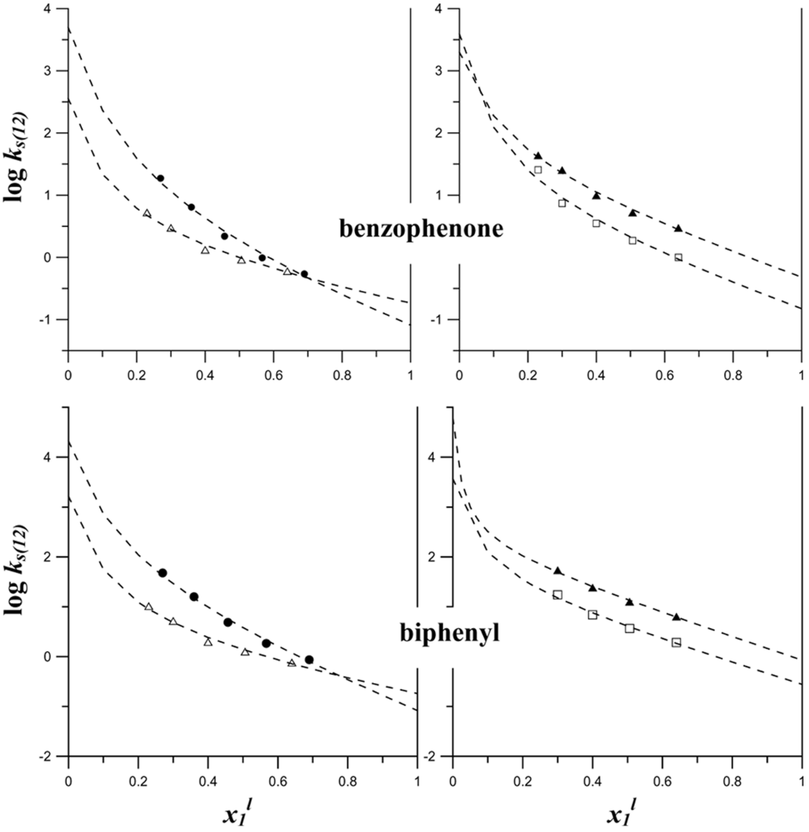
Figure 3. a. Theoretical (lines) and experimental (points) $\log k_{s(12)}$ values obtained for test substances in different chromatographic systems: (●) RP-8/water-methanol; (Δ) RP-8/water-acetonitrile; (□) ODS/water-acetonitrile and (▲) PLRP-S/water-acetonitrile. b. Theoretical (lines) and experimental (points) $\log k_{s(12)}$ values obtained for test substances in different chromatographic systems: (●) RP-8/water-methanol; (Δ) RP-8/water-acetonitrile; (□) ODS/water-acetonitrile and (▲) PLRP-S/water-acetonitrile. c. Theoretical (lines) and experimental (points) $\log k_{s(12)}$ values obtained for test substances in different chromatographic systems: (●) RP-8/water-methanol; (Δ) RP-8/water-acetonitrile; (□) ODS/water-acetonitrile and (▲) PLRP-S/water-acetonitrile.


benzamide
p-cresol
benzaldehyde
log $k_{s(12)}$
log $k_{s(12)}$
log $k_{s(12)}$
x_1^l
x_1^l
2
1
0
-1
3
0
0.2
0.4
0.6
0.8
1



(b)

Figure 3. Continued.



(c)

Figure 3. Continued.

were analyzed and intercorrelations between these parameters calculated from different systems are good, especially for the RP-8 stationary phase (Table 2).

K_{12} as well as $A_{s(12)}$ parameters were evaluated from linear $G(x_1^l)$ vs. x_1^l relationships (Figure 1) using Equations (7) and (8), respectively. It seems from data presented in Table 3 that calculated K_{12} values are in a high degree only fitting parameters. It is especially noticeable for benzaldehyde in the ODS/water-acetonitrile system where this value is enormously high. Finally, theoretical retention factors $\log k_{s(12)}$ were calculated from Equation (1) and the results are presented on Figures 2 and 3 separately for particular solutes. For each solute, independently of stationary or mobile phase, very good agreement between theoretical

Table 4. Experimental and calculated $\log P$ values for chromatographed solutes

Solute	$\log P_{exp}$	$\text{Alog}\,P_s$	$\text{AClog}\,P$	$\text{AB/log}\,P$	COSMO Frag	Kow Win	$\text{xlog}\,P$	$\text{milog}\,P$
Standards								
Toluene	2.73	2.56	2.30	2.63	2.59	2.54	2.46	2.39
Ethyl benzene	3.15	3.27	2.65	3.10	3.07	3.03	2.92	2.85
Propyl benzene	3.69	3.86	3.12	3.59	3.56	3.52	3.49	3.24
Butyl benzene	4.38	4.34	3.58	4.07	4.07	4.01	4.06	3.80
Hexyl benzene	5.52	5.27	4.51	5.04	5.11	5.06	5.02	4.81
Test compounds								
Benzamide	0.64	0.51	0.96	0.59	−0.09	0.74	0.91	0.76
p-cresol	1.94	1.95	2.00	2.00	1.72	2.06	2.05	1.91
Benzaldehyde	1.48	1.60	1.67	1.52	1.37	1.71	1.72	1.73
Acetophenone	1.58	1.65	1.90	1.67	1.52	1.67	1.86	1.84
Nitrobenzene	1.85	1.89	1.99	2.00	1.92	1.81	1.91	1.90
Methylbenzoate	2.12	1.98	1.96	1.94	2.02	1.83	1.96	2.11
Benzophenone	3.18	3.03	3.25	2.95	2.91	3.15	3.58	3.39
Biphenyl	3.98	4.02	3.66	3.89	3.78	3.76	3.96	3.73

and experimental $\log k_{s(12)}$ values is observed in the whole range of organic modifier concentration used in experiments.

Retention factors in water, $\log k_{s(2)}$, calculated by the numerical method were examined as a hydrophobicity index and compared with $\log P$ parameters (Table 4), experimental and calculated from solutes structures.[27] The correlation matrix (R and sd values) evaluated for these correlations is presented in Table 5 and, in any case, numerical $\log k_{s(2)}$ parameters create good linear relationships with experimental and calculated $\log P$ values. However, the best, hydrophobicity indices in comparison to $\log P_{exp}$, seem to be $\log k_{s(2)}$ parameters calculated from RP-8/water-acetonitrile system-only a little worse are these calculated from the RP-8/water-methanol system. It should be noticed that inter correlations obtained for different $\log P$ values are also diverse (Table 6). The best relationships between experimental $\log P_{exp}$ and calculated values are observed for $\text{Alog}\,P_s$, COSMOFrag, KowWin and $\text{AB/log}\,P$, while somewhat worse for $\text{AClog}\,P$, $\text{xlog}\,P$, and $\text{milog}\,P$. Simultaneously, the best inter correlations are found in these two groups of calculated $\log P$ parameters, i.e., for $\text{Alog}\,P_s$, COSMOFrag, KowWin and $\text{AB/log}\,P$ as well as for $\text{AClog}\,P$, $\text{xlog}\,P$, and $\text{milog}\,P$. These observations suggest that $\log P$ values calculated from the structures, though a valuable source of information, should be compared preferably with additional experimental data. Reversed phase liquid chromatography seems to be an especially attractive technique applied for the purpose.

Table 5. Correlation matrix obtained for calculated $\log k_{s(2)}$ and $\log P$ parameters

	$\log P_{exp}$	$\text{Alog}\,P_s$	$\text{AClog}\,P$	$\text{AB/log}\,P$	COSMOFrag	KowWin	$\text{xlog}\,P$	$\text{milog}\,P$
$\log k_{s(2)}$ RP-8 Water-methanol	$R = 0.9854$ $sd = 0.175$	$R = 0.9801$ $sd = 0.198$	$R = 0.9813$ $sd = 0.198$	$R = 0.9754$ $sd = 0.227$	$R = 0.9695$ $sd = 0.253$	$R = 0.9802$ $sd = 0.204$	$R = 0.9856$ $sd = 0.174$	$R = 0.9906$ $sd = 0.141$
$\log k_{s(2)}$ RP-8 Water-acetonitrile	$R = 0.9962$ $sd = 0.088$	$R = 0.9947$ $sd = 0.105$	$R = 0.9846$ $sd = 0.178$	$R = 0.9966$ $sd = 0.084$	$R = 0.9931$ $sd = 0.119$	$R = 0.9931$ $sd = 0.119$	$R = 0.9850$ $sd = 0.175$	$R = 0.9882$ $sd = 0.156$
$\log k_{s(2)}$ ODS Water-acetonitrile	$R = 0.9587$ $sd = 0.269$	$R = 0.9570$ $sd = 0.275$	$R = 0.9276$ $sd = 0.354$	$R = 0.9518$ $sd = 0.290$	$R = 0.9548$ $sd = 0.281$	$R = 0.9541$ $sd = 0.283$	$R = 0.9407$ $sd = 0.321$	$R = 0.9497$ $sd = 0.296$
$\log k_{s(2)}$ PLRP-S Water-acetonitrile	$R = 0.9386$ $sd = 0.341$	$R = 0.9512$ $sd = 0.305$	$R = 0.9388$ $sd = 0.340$	$R = 0.9565$ $sd = 0.288$	$R = 0.9648$ $sd = 0.260$	$R = 0.9348$ $sd = 0.351$	$R = 0.9233$ $sd = 0.379$	$R = 0.9399$ $sd = 0.337$

Table 6. Correlation matrix obtained for log P parameters

	Alog P_s	AClog P	AB/log P	COSMOFrag	KowWin	xlog P	milog P
log P_{exp}	$R = 0.9953$ $sd = 0.137$	$R = 0.9829$ $sd = 0.262$	$R = 0.9962$ $sd = 0.124$	$R = 0.9894$ $sd = 0.207$	$R = 0.9954$ $sd = 0.136$	$R = 0.9867$ $sd = 0.232$	$R = 0.9877$ $sd = 0.223$
Alog P_s		$R = 0.9791$ $sd = 0.285$	$R = 0.9981$ $sd = 0.085$	$R = 0.9923$ $sd = 0.173$	$R = 0.9952$ $sd = 0.137$	$R = 0.9834$ $sd = 0.255$	$R = 0.9833$ $sd = 0.255$
AClog P			$R = 0.9820$ $sd = 0.194$	$R = 0.9743$ $sd = 0.232$	$R = 0.9877$ $sd = 0.161$	$R = 0.9976$ $sd = 0.070$	$R = 0.9968$ $sd = 0.082$
AB/log P				$R = 0.9943$ $sd = 0.137$	$R = 0.9951$ $sd = 0.124$	$R = 0.9838$ $sd = 0.221$	$R = 0.9848$ $sd = 0.228$
COSMOFrag					$R = 0.9856$ $sd = 0.242$	$R = 0.9737$ $sd = 0.327$	$R = 0.9817$ $sd = 0.273$
KowWin						$R = 0.9924$ $sd = 0.154$	$R = 0.9901$ $sd = 0.176$
xlog P							$R = 0.9965$ $sd = 0.102$

CONCLUSIONS

The assumption of mixed, i.e., partition displacement mechanism of chromatographic process and Ośćik's Equation for description of solute retention in reversed phase liquid chromatography was a reasonable resolution giving satisfactory results. Very good accordance between theoretical and experimental retention factors for all solutes tested was obtained, independently of stationary and mobile phase properties. Moreover, retention factors in water, $\log k_{s(2)}$, calculated numerically using the linear form of Ośćik's Equation are good hydrophobicity indices, giving linear correlations with experimental and calculated $\log P$ values.

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