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LINEAR SOLVATION ENERGY RELATIONSHIPS FOR CHARACTERIZATION OF MLC SYSTEMS WITH SODIUM DODECYL SULPHATE MOBILE PHASES MODIFIED BY ALIPHATIC ALCOHOLS OR CARBOXYLIC ACIDS

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ABSTRACT. The Linear Solvation Energy Relationships (LSER) have been successfully used for the modeling of partition and retention of the set of test compounds in different systems. The properties of micellar chromatographic systems with the mobile phases on the basis of sodium dodecylsulphate modified (SDS) by additives of aliphatic alcohols (1-butanol, 1-pentanol) or aliphatic carboxylic acids (butanoic, pentanoic) were characterized on the basis of comparison of calculated LSER coefficients. Principal component analysis (PCA) was used for the classification of studied systems.

Keywords: *Linear Solvation Energy Relationships (LSER), partition, modeling, micelle bounding, Micellar Liquid Chromatography (MLC), Principal Component Analysis (PCA)*

INTRODUCTION

During several last decades Linear Solvation Energy Relationships (LSER) have been widely used for describing the different processes such as partitioning in two-phase systems, chromatographic retention, reactivity, solubility, toxicity etc. [1].

The variety of non-covalent interactions such as dispersion, dipole-dipole, dipole-inducted dipole, forming of hydrogen bonds are the main factors, which are responsible for the partition of solutes in two-phase systems and their chromatographic retention. The attempts to apply thermodynamic equations for describing the potential energies of unspecific interactions and treating the partition processes when a limited number of congeneric solutes is used for modeling. Unfortunately, the strict thermodynamics cannot be used for the

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prediction of chemical properties and is useful only for understanding the relationships between them. Thermodynamics gives more “physical” information than “chemical” that prevents the analysis of the relationships between the molecular structure and the physical-chemical properties. Linear solvation energy relationships are extrathermodynamic free energy relationships which connect some physical-chemical properties with descriptors describing the molecules. In general, the relationship between the dependent variable such as partition constant or retention factor and independent variables (descriptors) can be represented by equation (1):

$$SP = const + eE + sS + aA + bB + vV \quad (1)$$

where *SP* is the dependent variable; *E,* the excess molar refraction; *S*, the polarity/polarizability; *A,* the hydrogen bond donor acidity; *B,* the hydrogen bond acceptor basicity; *V,* the McGowan volume. The notations *e, s, a, b,* and *v* represent the LSER coefficients.

Descriptors *S*, *A*, *B* are historically related with the solvatochromic parameters of the solvents (*π*, α, β*) (polarity, acidity and basicity) proposed by Camlet and Taft [2] and later converted to molecular descriptors by Abraham [3]. Excess molar refraction of a solute is its polarizability above that of alkane (often hypothetic) of the same molar volume. McGowan volume is related with molecular size. The validity of LSER has been many times proofed for different systems. Recently several works on re-evaluation of LSER coefficients for different two-phase systems have been published [4-8]. LSER are also successfully used for the investigation of the properties of gas and liquid chromatographic systems.

Micellar liquid chromatography (MLC) is a mode of reversed-phase high-performance liquid chromatography (RP-HPLC) in which the mobile phases are solutions of surfactants above the critical micelle concentration with small additives of organic solvents. The aliphatic alcohols are often used as mobile phase modifiers in this chromatographic mode. The pioneering work on the characterization of MLC systems and their comparison with aqueous-organic RP-HPLC systems has been published in 1995 by Yang and Khaledi [9]. The authors have obtained LSER coefficients by using the data on retention in MLC (mobile phases on the basis of SDS and tetradecyltrimethylammonium bromide modified by 1-propanol) and RP-HPLC mode (mobile phases on the basis of methanol or 2-propanol). MLC systems with C8 and C18 stationary phases and mobile phases based on sodium dodecylsulphate (SDS) and cetyltrimethylammonium bromide solutions modified by methanol, 1-propanol or 1-butanol were characterized by Garcia et al. [10-12]. In the work [13], the MLC systems with micellar mobile phases and aqueous-organic mobile phases were thoroughly compared by Torres-Lapasio et al. Authors concluded that the solute dipolarity/polarizability and hydrogen donor basicity decrease

the retention and solute volume increases the retention [10]. The data obtained in biopartitioning micellar chromatographic (BMC) mode (mobile phases on the basis of polyoxyethylene(23)lauryl ether (Brij35) were modeled by using LSER with addition term mean net charge per molecule by Lu et al. [14]. Recently Tian and Row have obtained the LSER coefficients for SDS mobile phases modified by methanol, 1-propanol or 1-butanol [15]. The BMC systems using monolithic column were characterized by Lu et al. [16] and compared with other physicochemical and biological processes. The similarity between BMC systems and biomembrane transport process was observed [16].

In our previous works aliphatic carboxylic acids have been proposed and successfully used as modifiers of micellar eluents [17, 18]. After the comprehensive investigation of the effect of aliphatic carboxylic acids on retention and efficiency it was concluded that they can be used as successful alternative to alcohols and provide the different selectivity in comparison with alcohols [17]. As we know there are no works on the characterization of MLC systems with new modifiers in terms of any free-energy relationships.

Thus, the main aim of this research is the characterization of the MLC systems with SDS micellar mobile phases modified by additives of aliphatic carboxylic acids or alcohols and their comparison with different two-phase and pseudophase systems.

RESULTS AND DISCUSSION

Thermodynamics of partition in two-phase systems and chromatographic retention

In most partition and chromatographic experiments, the concentration of distributed compound is small enough and the activity coefficient (γ) tends to unity. In this case the partition constant is described by the equation (2):

$$K = \frac{[\mathrm{A}]^{I}\gamma_{A}^{I}}{[\mathrm{A}]^{II}\gamma_{A}^{II}} \cong \frac{[\mathrm{A}]^{I}}{[\mathrm{A}]^{II}} \tag{2}$$

where: [A] represents equilibrium concentration of A.

The retention factor, k, can be directly related with the partition constant and the volume ratio of mobile and stationary phases, being expressed by equation (3):

$$k = \frac{n(\mathrm{A})_{s}}{n(\mathrm{A})_{m}} = K\frac{V_{s}}{V_{m}} \tag{3}$$

As a result, the coefficients (except the intercept) of LSER for two-phase and chromatographic systems could be compared and analyzed.

The solubilization of solutes by surfactant micelles is often presented by binding constant or partition constant. The last one is the same as partition in "real" two-phase system. The binding constant is related with the chemical reaction that can be used for representing the solute (A) solubilization by micelles (Mic), as follows:

$$\mathrm{A+Mic=AMic}$$

The equilibrium constant of this reaction is called binding constant, K_b, and can be represented by the equation (4):

$$K_b = \frac{\left[\mathrm{A}_{Mic}\right]_{tot}}{\left[\mathrm{A}_{aq}\right]_{tot}\left(c_s - cmc\right)} \tag{4}$$

where $\left[\mathrm{A}_{Mic}\right]_{tot}$ and $\left[\mathrm{A}_{aq}\right]_{tot}$ are equilibrium concentrations of A in micellar and bulk aqueous phase related to the total volume of solution, c_s is the micellized surfactant concentration, *cmc* is the critical micelle concentration.

If the volume of micelles is much lower than the total volume of solution, the partition constant for micellar pseudophase-water system can be obtained by simple transformation expressed by equation (5):

$$K_{MW} = \frac{\left[\mathrm{A}\right]_{Mic}}{\left[\mathrm{A}\right]_{aq}} = K_b \upsilon_S^{-1} \tag{5}$$

where K_{MW} is the partition constant of solute in micellar pseudophase-water system; $\left[\mathrm{A}\right]_{Mic}$ and $\left[\mathrm{A}\right]_{aq}$ are the equilibrium concentrations of *A* in micellar and bulk aqueous phase related to the volume of each phase; υ_S is the molar volume of surfactant.

Data on partition and retention of test compounds in different systems and LSER descriptors

The set of test compounds that was used in this work is consisted of 33 aliphatic and aromatic compounds with different hydrophobicities. The data on chromatographic retention was obtained for 26 of these compounds. Also the set of aliphatic carboxylic acids which partition has been studied earlier was added to the test set [19]. In Table 1 the literature values of logarithms of partition constants of compounds in 1-octanol-water, heptane-water, chloroform-water, and SDS pseudophase-water system are presented. In the last case we have collected all our available data, because it is known that micelle-water partition constants can accept different values depending on

the method used for their determination [19]. As there is no commonly accepted procedure, in further work we have used the mean value of partition constant in SDS micelles-water system.

The partition constants are changed on five orders of magnitude: the minimum value of log K_{ow} is -0.17 (acetic acid), and the maximum value is 5.52 (hexylbenzene). The corresponding minimum and maximum values for heptane-water system are -3.14 (chloroacetic acid) and 4.11 (pentylbenzene). The data for hexylbenzene were not found in literature. The retention factors obtained for the test set of compounds in MLC mode with SDS based mobile phase modified by 1-pentanol, 1-butanol, butanoic or pentanoic acid are presented in Table 2 as well as the LSER descriptors.

The adequate LSER coefficients for each system could be obtained if there are no strong inter-correlations between the descriptors for the chosen set of compounds. As can be seen from Table 3 the statistically significant correlations were obtained only between the descriptors *E* and *S,* and *E* and *V*. These correlations could be explained by the relationship between the descriptors: *E* and *S* characterize the polarity of molecules, and *E* and *V* are functionally related [1, 20].

Table 1. Logarithms of partition constants of compounds from test set.

Compound	Log *K* (organic or micelle phase-water)			
	1-Octanol	SDS	Heptane	Chloroform
1,3,5-Trimethylbenzene	3.42 [21]	–	4.05 [22]	–
Monochloroacetic acid	–	–	-3.14 [23]	-1.35 [23]
1-Ethyl-4-nitrobenzene	2.94	2.63 [24]	–	–
2,3-Dichlorophenol	3.15 [25]	2.58 [26]; 2.52 [27] 2.57 [28]; 2.52 [29]	–	–
2,5-Dichlorophenol	3.06 [25]	2.52 [26]; 2.39 [27]; 2.46 [27]; 2.73 [29]	–	–
2,6-Dichlorophenol	2.64 [25]	2.33 [26]; 2.56 [29]	–	–
2-Nitroanisole	1.73 [30]	1.62 [31]	0.25 [22]	2.13 [32]
2-Nitrophenol	1.73 [21]	2.09 [33]; 2.17 [28]; 2.15 [28]	1.40[22]	2.54 [32]
3,4-Dichlorophenol	3.33 [25]	2.78 [26]; 2.70 [29]	–	–
3,5-Dichlorophenol	3.62 [25]	2.58 [26]; 2.60 [34]; 2.63 [35]; 2.59 [35]; 2.70 [27]; 2.82 [27]; 2.60 [29]	–	–
Trichloroacetic acid	–	–	-2.63 [22]	0.04 [36]
3-Chlorophenol	2.47 [21]	1.58 [37]	-0.08 [22]	1.02 [23]

Compound	Log *K* (organic or micelle phase-water)			
	1-Octanol	SDS	Heptane	Chloroform
3-Nitrophenol	2.00 [21]	2.07 [28]; 2.10 [28]	-1.40 [22]	0.41 [32]
4-Chlorophenol	2.44 [21]	2.10 [38]; 2.12 [34]; 2.35 [39]; 2.20 [35]; 2.09 [35]; 2.22 [27]; 2.28 [27]; 2.32 [40]; 3.03 [41]	-0.10 [22]	1.01 [23]
4-Nitrophenol	1.91 [21]	1.82 [42]; 1.45 [43]; 2.03 [33]; 1.89 [37]; 1.81 [34]; 1.89 [28]; 1.93 [28]	-2.00 [22]	0.17 [32]
Anisole	2.10 [21]	2.15 [40]; 1.49 [34]; 2.07 [44]; 2.15 [40]	2.10	1.33 [32]
Benzene	2.03 [21]	2.01 [38]; 1.93 [37]; 1.30 [45]; 1.99 [37]	2.22 [22]	2.80 [23]
Acetic acid	-0.17 [32]	–	-2.90 [23]	-1.56 [32]
Propanoic acid	0.33 [32]	1.00 [19]	-2.14 [23]	-0.79 [32]
Butanoic acid	0.79 [32]	1.28 [19]	-0.96 [23]	-0.27 [32]
Pentanoic acid	1.39 [32]	1.56 [19]	–	0.33 [32]
Hexanoic acid	1.92 [32]	2.02 [19]	0.24 [23]	0.95 [32]
Chlorobenzene	2.84 [46]	1.89 [45]; 2.52 [47]; 2.63[37]	2.92 [22]	3.46 [23]
Ethylbenzene	3.15 [46]	2.78 [38]; 2.23 [31]	3.43[22]	–
Fluorene	4.18[21]	3.11 [31]	–	–
Hexylbenzene	5.52 [46]	–	–	–
Naphtalene	3.59[21]	4.12 [48]; 2.53 [31]; 2.46 [45]	–	–
2-Nitroaniline	1.79 [21]	2.23 [24]	–	–
Pentylbenzene	4.90 [46]	3.96 [38]	4.11 [22]	–
Phenol	1.48 [21]	1.66 [40]; 1.64 [34]; 0.96 [45]; 1.60 [37]; 1.61 [49]; 1.51 [49]; 1.30 [34]; 1.47 [34]; 1.59 [44]; 1.78 [50]; 1.68 [51]; 1.60 [41]	-0.70 [22]	0.38 [32]
Phenanthrene	4.46 [21]	4.48 [34]; 3.79 [31]	–	–
p-Xylol	3.15 [21]	3.05 [34]; 2.27 [31]; 2.81 [39]	–	–
Toluene	2.73 [21]	2.42 [38]; 2.11 [34]; 1.85 [31]; 1.77 [45]; 2.48 [52]	2.75 [22]	3.41 [23]

Table 2. Logarithm of retention factors of test compounds and their LSER descriptors.

Compound	Log *k**	*E* / *S* / *A* / *B* / *V*	Ref.**
1,3,5-Trimethylbenzene	1.45 / 1.37 / 1.33 / 1.29	0.649 / 0.52 / 0 / 0.190 / 1.139	
Monochloroacetic acid	-	0.427 / 1.03 / 0.79 / 0.35 / 0.59	
1-Ethyl-4-nitrobenzene	1.09 / 1.04 / 0.96 / 0.94	-	
2,3-Dichlorophenol	0.73 / 0.80 / 0.65 / 0.66	0.96 / 0.94 / 0.480 / 0.20 / 1.02	[53]
2,5-Dichlorophenol	0.79 / 0.89 / 0.70 / 0.75	0.96 / 0.88 / 0.560 / 0.18 / 1.02	[53]
2,6-Dichlorophenol	0.72 / 0.78 / 0.62 / 0.65	0.90 / 0.90 / 0.380 / 0.24 / 1.02	[53]
2-Nitroanisole	0.54 / 0.44 / 0.43 / 0.36	0.97 / 1.42 / 0 / 0.360 / 1.09	[54]
2-Nitrophenol	0.72 / 0.67 / 0.64 / 0.59	1.015 / 1.05 / 0.05 / 0.37 / 0.949	[55]
3,4-Dichlorophenol	0.82 / 0.89 / 0.72 / 0.75	1.02 / 1.14 / 0.85 / 0.03 / 1.02	[53]
3,5-Dichlorophenol	0.90 / 1.00 / 0.82 / 0.85	1.02 / 1.10 / 0.83 / 0 / 1.02	
Trichloroacetic acid	-	0.524 / 1.21 / 1.01 / 0.26 / 0.83	[5]
3-Chlorophenol	0.64 / 0.71 / 0.56 / 0.59	0.91 / 1.06 / 0.69 / 0.15 / 0.898	[53]
3-Nitrophenol	0.36 / 0.45 / 0.30 / 0.36	1.05 / 1.57 / 0.79 / 0.23 / 0.949	[54]
4-Chlorophenol	0.62 / 0.67 / 0.55 / 0.55	0.915 / 1.08 / 0.67 / 0.2 / 0.898	[5]
4-Nitrophenol	0.35 / 0.42 / 0.25 / 0.31	1.07 / 1.72 / 0.82 / 0.26 / 0.949	[53]
Anisole	0.96 / 0.91 / 0.85 / 0.82	0.708 / 0.75 / 0 / 0.290 / 0.916	[54]
Benzene	1.05 / 1.02 / 0.95 / 0.93	0.61 / 0.52 / 0 / 0.14 / 0.716	[54]
Acetic acid	-	0.227 / 0.6 / 0.55 / 0.43 / 0.465	[57]
Propanoic acid	-	0.235 / 0.6 / 0.54 / 0.43 / 0.606	[57]
Butanoic acid	-	0.241 / 0.6 / 0.54 / 0.42 / 0.747	[57]
Pentanoic acid	-	0.247 / 0.6 / 0.54 / 0.41 / 0.887	[57]
Hexanoic acid	-	0.251 / 0.6 / 0.54 / 0.39 / 1.028	[57]
Chlorobenzene	1.34 / 1.28 / 1.23 / 1.19	0.718 / 0.65 / 0 / 0.07 / 0.839	[54]
Ethylbenzene	1.22 / 1.18 / 1.09 / 1.07	0.613 / 0.51 / 0 / 0.15 / 0.998	[5]
Fluorene	1.50 / 1.43 / 1.37 / 1.33	1.588 / 1.03 / 0 / 0.20 / 1.357	[56]
Hexylbenzene	1.64 / 1.49 / 1.58 / 1.47	0.591 / 0.50 / 0 / 0.150 / 1.562	[54]
Naphtalene	1.34 / 1.29 / 1.21 / 1.18	1.340 / 0.92 / 0 / 0.200 / 1.085	[54]
2-Nitroaniline	0.48 / 0.44 / 0.40 / 0.36	1.180 / 1.37 / 0.30 / 0.36 / 0.99	[16]
Pentylbenzene	1.57 / 1.46 / 1.50 / 1.42	0.594 / 0.520 / 0 / 0.14 / 1.421	[56]
Phenol	0.19 / 0.27 / 0.17 / 0.21	0.85 / 0.69 / 0.60 / 0.30 / 0.775	[54]
Phenanthrene	1.50 / 1.44 / 1.36 / 1.34	2.055 / 1.29 / 0 / 0.26 / 1.454	[56]
p-Xylol	1.37 / 1.31 / 1.24 / 1.21	0.613 / 0.52 / 0 / 0.16 / 0.998	[5]
Toluene	1.24 / 1.19 / 1.11 / 1.09	0.601 / 0.52 / 0 / 0.14 / 0.857	[58]

* log k (0.1 SDS 3% pentanoic acid) / log k (0.10 SDS 3% 1-pentanol) / log k (0.15 SDS 5% butanoic acid) / log k (0.15 SDS 5% 1-butanol).

** Reference to source of LSER descriptors.

Table 3. Correlation coefficients between the LSER descriptors of test compounds (the significant correlations are in bold).

Descriptors	Correlation coefficients
E – S	**0.62**
E – A	-0.19
E – B	-0.32
E – V	**0.55**
S – A	0.43
S – B	0.03
S – V	0.10
A – B	0.13
A – V	-0.45
B – V	-0.39

Literature data on LSER coefficients for selected systems

The interest to LSER results in a number of papers where the models of different processes are described in terms of LSER coefficients. In Table 4, the literature data on the coefficients for 1-octanol-water, SDS pseudophase-water, heptane-water, and chloroform-water systems are presented.

Table 4. Literature data on LSER coefficients for various systems.

Solvent or micellar mobile phase composition	log K = *const* + eE + sS + aA + bB + vV	*Ref.*
1-Octanol	log K^* = -0.03 + 0.49E - 1.05S - 0.028A - 4.23B +4.22V	[3]
SDS	log K = 0.54 - 0.58S - 0.37A - 1.65B + 3.02V	[59]
	log K = 1.20 + 0.54E - 0.40S - 0.13A - 1.58B + 2.79V	[42]
	log K = -0.62 + 0.32E - 0.57S - 0.08A - 1.84B + 3.25V	[60]
	log K = -1.87 - 0.25S - 0.16A - 1.79B + 4.00V	[61]
	log K = 1.327 + 0.37E + 0.41S - 0.13A - 1.98B + 2.98V	[8]
Heptane	log K = 0.325 + 0.67E - 2.06S - 3.32A - 4.73B + 4.54V	[3]
Chloroform	log K = 0.327 + 0.16E - 0.39S - 3.19A - 3.44B + 4.19V	[3]
SDS, 1-Pentanol (C18 Column)	log k^{**} = 0.20A - 0.50B + 0.26V	[62]
0.08 M SDS, 5% 1-Butanol (C18 Column)	log k = 0.46 + 0.27E - 0.49S - 0.44A - 1.38B + 1.18V	[11]
0.09 M SDS, 5% 1-Butanol (C18 Column)	log k = 1.25 + 0.17E - 0.88S - 0.22A - 0.73B + 1.05V	[15]
0.14 M SDS, 3% 1-Butanol (C8 Column)	log k = 0.91 + 0.53E - 0.40S - 0.28A - 0.81B + 0.67V	[10]

* Distribution constant
** Retention factor

It should be noted that our aim was not to bring all of the known coefficients of the LSER for each system. Only recent results for two-phase systems are shown except the SDS pseudophase-water system. The LSER

coefficients for MLC systems with SDS mobile phases which composition is close to the composition of mobile phases investigated in our work are also included in Table 5.

Description of experimental data by LSER

The application of LSER for the description of experimental data on the partition and retention of compounds in all studied systems results in high goodness-of-fit: squares of correlation coefficient are in the range 0.86-0.99. The prediction power of obtained models was examined by leave-one-out cross validation procedure. The lower values of R^2 and R^2_{cross} estimated for SDS pseudophase-water system could be explained by higher uncertainty in the values of partition constants.

Table 5. The LSER coefficients for various systems constructed on the basis of data presented in Table 1 and 2.

Solvent or micellar mobile phase composition	log *K* = *const* + *eE* + *sS* + *aA* + *bB* + *vV*	*n* / R^2 / R^2_{cross}
1-Octanol	log *K* = 0.17+ 0.51*E* - 0.92*S* + 0.09*A* - 4.36*B* + 3.84*V*	31 / 0.99 / 0.98
SDS	log *K* = 0.36+0.43*E* - 0.63*S* - 0.05*A* - 1.71*B* + 2.59*V*	26 / 0.89 / 0.75
Heptane	log *K* = 0.74 + 1.34*E* - 2.38*S* - 2.87*A* - 5.24*B* + 3.70*V*	20 / 0.98 / 0.91
Chloroform	log *K* = 1.01 + 0.12*E* - 0.57*S* - 2.33*A* - 5.85*B* + 3.68*V*	18 / 0.94 / 0.88
0.10 M SDS, 3% Pentanoic acid	log *k* = 0.94 + 0.20*E* - 0.18*S* - 0.80*A* - 2.37*B* + 0.68*V*	25 / 0.96 / 0.93
0.10 M SDS, 3% 1-Pentanol	log *k* = 0.97 + 0.28*E* - 0.26*S* - 0.58*A* - 2.31*B* + 0.57*V*	25 / 0.95 / 0.91
0.15 M SDS, 5% 1-Butanoic acid	log *k* = 0.79 + 0.18*E* - 0.23*S* - 0.71*A* - 2.17*B* + 0.72*V*	25 / 0.97 / 0.93
0.15 M SDS, 5% 1-Butanol	log *k* = 0.81 + 0.23*E* - 0.26*S* - 0.60*A* - 2.16*B* + 0.64*V*	25 / 0.96 / 0.91

The representativeness of chosen set of compounds for the estimation of LSER coefficients is also confirmed by comparing the LSER coefficients obtained in our work with literature data for the two-phase systems. The correlation coefficient between the literature values of LSER coefficients and those calculated are very high for 1-octanol-water and heptane-water systems and for most SDS pseudophase-water systems, excepting the data from paper [61]. The sign of the s coefficient presented in [8] differs from that presented in other works. The analysis of residuals shows no systematic dependences that indicates the adequacy of the constructed models.

Comparison of studied systems on basis of LSER coefficients

The principal component analysis (PCA) has been applied for the classification of the investigated systems. Figure 1 presents the projection of the first and second components obtained for literature data of LSER coefficients and the LSER coefficients estimated in our work for two-phase and chromatographic systems.

As can be seen from the Figure 1, the micellar chromatographic systems form a separate group that indicates their difference from “real” two-phase systems. The points related to SDS pseudophase-water systems have positive values of the first principal component and positive or negative values of the second principal component and they are distributed separately.

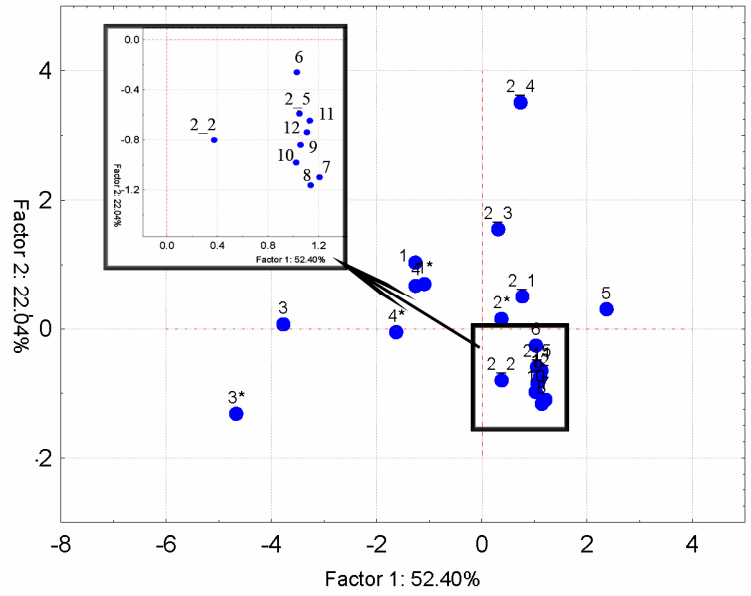

Figure 1. The projection of the first and second components on the surface. 1 – 1-octanol-water [3]; 2_1 – SDS-water [59]; 2_2 – SDS-water [42]; 2_3 – SDS-water [60]; 2_4 – SDS-water [61]; 2_5 – SDS-water [8]; 3 – heptane-water [3]; 4 – chloroform-water [3]; 5 – mobile phase SDS, 1-pentanol (Column C18) [62]; 6 – 0.08 M SDS, 5% 1-butanol (Column C18) [11]; 7 – 0.09 M SDS, 5% 1-butanol (Column C18) [15]; 8 – 0.14 M SDS, 3% 1-butanol (Column C8) [10]; 9 – 0.10 M SDS, 3% pentanoic acid; 10 – 0.10 M SDS, 3% 1-pentanol; 11 – 0.15 M SDS, 5% 1-butanoic acid; 12 – 0.15 M SDS, 5% 1-butanol; 1* – 1-octanol-water (our data); 2* – SDS-water (our data); 3* – heptane-water (our data); 4* – chloroform-water (our data); 5* – chloroform-water (our data); 10 – 0.10 M SDS, 3% pentanoic acid.

Figure 2 shows the histogram of LSER coefficients which could be used for comparing the properties of different systems. However, some points must be taken into account during the analysis of obtained coefficients. First, each coefficient shows the difference in the properties of two phases. Second, the coefficients *a* and *b* characterize the difference in basicity and acidity of phases correspondingly. The negative values of LSER coefficients indicate the shift of partition to aqueous phase.

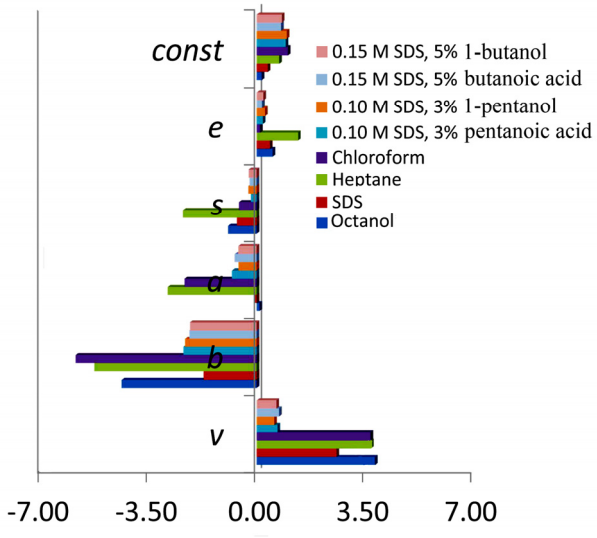

Figure 2. Histogram of LSER coefficients estimated in our work for the chromatographic systems: 1-octanol-water, heptane-water and SDS pseudophase-water.

As can be seen in Figure 2 the values of *s* are negative. This means that the polarity of 1-octanol, heptane, SDS pseudophase and C18 column modified by mobile phase components are lower in comparison with aqueous phase. The largest difference in polarity is observed for heptane-water. The difference in polarity of micellar mobile phase and dynamically modified stationary phase is lower than for SDS pseudophase-water system. This can be related with the formation of hemimicelles on the surface of stationary phases. Heptane has the lowest hydrogen bond donor (*b* = -5.24) and acceptor (*a* = -2.87) properties. Thus, the compounds with tendency to form hydrogen bonds are partitioned into the aqueous phase. The dynamically modified stationary phases and 1-octanol have low hydrogen bond donor capacity due to the absence of hydrogen bond donor groups in C18 bonded groups and SDS monomers. In contrast, each molecule of water has two hydrogen atoms which could form the hydrogen bonds. The less difference in the properties

of SDS pseudophase and water can be explained by the hydration of SDS micelles surface. Otherwise, hydrogen bond acceptor capacity of water, 1-octanol, and SDS pseudophase are almost equal. Such similarity of 1-octanol and SDS pseudophase properties can explain the correlation between partition constants in these systems for the congeneric compounds [25].

The size of the molecule has the largest contribution to the distribution of organic compounds into the non-aqueous phase and their retention. The *v* coefficient is related with the energy which is needed for forming the cavity inside the bulk phase. Intermolecular interactions are weaker in the heptane, 1-octanol and hydrophobic micelle core comparing with water which expels large hydrophobic molecules. The properties of mobile and stationary phase are less different in chromatographic systems due to the opportunity of direct partition of hydrophobic compounds into stationary phase from the micelles without transfer to the bulk aqueous phase.

The chromatographic systems with SDS mobile phases modified by acids show less difference in the polarity of mobile and stationary phases in comparison with mobile phases modified by alcohols. However the cavity formation in the stationary phase is energetically more favorable in the case of using of mobile phases modified by acids that result in stronger retention of highly hydrophobic compounds. Hydrogen bond donor properties of mobile and stationary phases modified by acid or alcohol with the same carbon chain length are quite similar. Despite the general similarity of MLC systems modified by acid or alcohol they provide different selectivity of compounds separation which is indicated by differences in coefficient values obtained for these MLC systems.

CONCLUSIONS

LSER is a useful tool for modeling the partition of two-phase and pseudophase systems and the retention in liquid chromatography with micellar mobile phases. The chosen set of test compounds allows obtaining adequate LSER coefficients and interpreting their chemical sense. The MLC chromatographic systems modified by different modifiers shows the similar properties in terms of LSER coefficients. However, the analysis of their absolute values differences can be used to move inside the mechanism of retention in MLC.

EXPERIMENTAL SECTION

Reagents

Mobile phases were prepared with sodium dodecylsulphate (≥97%, Fluka, Buchs, Switzerland or >98.5%, Sigma-Aldrich, L'Isle d'Abeau Chesnes, France), 1-butanol (>99%, Carlo Erba Reagents, Peypin, France), 1-butanoic

acid (>99%, for synthesis, Merck, Darmstadt, Germany), 1-pentanol (Aldrich), 1-pentanoic acid (99%, Janssen Chimica, Geel, Belgium). The standard buffer solution was prepared from NaH_2PO_4 (Prolabo, Paris, France) and H_3PO_4 (Fluka, Buchs, Switzerland).

The stock solutions of phenol from Prolabo (Paris, France) and 2,5-dichlorophenol (98%), 4-chlorophenol (99%), 2,3-dichlorophenol (98%), 3,4-dichlorophenol (99%), 3,5-dichlorophenol (97%), 3-nitrophenol (99%), 2-nitrophenol (98%), 4-nitrophenol (99%), 2,6-dichlorophenol from Aldrich, anisole (99%) from Janssen Chimica, benzene (99.5%), phenanthrene (97%) from Fluka, naphthalene (99%) from Aldrich, fluorene (97%) from Fluka, o-nitroaniline "pure" from Prolabo, hexylbenzene from Fluka, chlorobenzene (99%) from Merck, pentylbenzene (97%) from Fluka, ethylbenzene (99%) from Merck, p-xylol (99%) from Aldrich, 1,3,5-trimethylbenzene (99%) from Fluka, 1-ethyl-4-nitrobenzene (99%) from Fluka, 3-chlorophenol (98%) from Merck, toluene from Rectapur, and 2-nitroanisole (98%) from Fluka were prepared in methanol.

The working solutions of the test compounds were prepared by the dilution of standard solutions with micellar mobile phase.

Apparatus and chromatographic conditions

The Shimadzu HPLC system (Kyoto, Japan) was composed of a pump (model LC-10AS), a UV detector (model SPD-6A), a column oven (model CTO-6A) and an in-line Rheodyne 7010 valve with a 20 µl sample loop. The retention data were obtained by using isocratic conditions with the flow rate of 0.5 mL/min for the Zorbax Extend-C18 column (150 mm×3.0 mm i.d., 5 µm particle size diameter, Agilent, USA). After working with the micellar mobile phase, the columns were washed by water, water-acetonitrile (Prolabo, Paris, France) and water-methanol solutions and rinsed with pure methanol before storage. The two identical columns from the same batch were used for the collection of chromatographic data. The pH meter was a Mettler Toledo MP220 (Mettler, Virofly, France) equipped with a combination pH electrode which was calibrated with pH 4.0 and pH 7.0 standard buffer solutions. The Mettler Toledo AB204-S balance was used for the preparation of stock solution and phosphate buffer. An Elmasonic ultrasound bath (Elma Hans Schmidbauer GmbH & Co. KG, Stuttgart, Germany) was used for dissolution of samples.

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