A Comparative Study Concerning the Lipophilicity of Some Synthetic Dyes Estimated by Thin Layer Chromatography and Different Computation Methods

DORINA CASONI, CODRUTA SIMONA COBZAC, COSTEL SARBU*
Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos Str., 400028, Cluj-Napoca, România

The retention behaviour of some selected synthetic dyes have been investigated on RP-18F$_{254S}$, RP-18W/UV$_{254}$ and CNF$_{254S}$ plates using methanol–water mixture in different volume proportions as mobile phases. The R_M values of the compounds decreased linearly with increasing concentration of methanol in the mobile phase in all cases. On the basis of the linear relationship between retention (R_M) values and volume fraction of methanol, values of R_{M0} corresponding to 100% water were obtained by extrapolation using five isocratic R_M values. The regression determination coefficients obtained for all stationary phases were excellent (higher than 0.99 in all cases). The good regularities of profiles of retention indices (R_M and PC1/R_M) indicated that the same mechanism (lipophilic interactions) is dominant in all cases and all types of stationary phases (RP-18, RP-18W and CN) appear to be suitable for estimating the lipophilicity of selected synthetic dyes. The chromatographic lipophilicity values (expressed by R_{M0}) estimated on three different stationary phases were not highly correlated between them and also with computed log P values. The best correlations were founded with lipophilicity parameters calculated by Dragon 5.4 software. By using PC1/R_M or φ_0 values as estimators for lipophilic character of synthetic dyes, the correlation between these values obtained on that three stationary phases were significantly improved, correlation coefficient being higher than 0.92 in some cases.

Keywords: lipophilicity, synthetic dyes, computed log P, RP-HPTLC, PCA

During the past decades an increasing number of quantitative structure-activity (QSAR) models have been using different molecular descriptors for predicting toxicological [1, 2] properties of chemicals.

Lipophilicity, defined as tendency of a chemical compound to distribute between an immiscible non-polar organic solvent and water, is one of the molecular parameters most frequently used for the assessment of the relationship between biological activity and physicochemical characteristics[3]. The most widely used measure of lipophilicity is the partition coefficient in the 1-octanol/water system denoted in few different ways (log P, log K_{ow}). The reference procedure to measure log P is the classical shake-flask method, which however is time-consuming, limited in range and limited to extremely pure compounds [4]. Measurement by use of equilibration methods is frequently made difficult, or even impossible, by the instability of compounds in some cases, by preference of a compound for one of the two phases of the system, by the formation of stable emulsions after shaking or by difficulties in solubility limits. For this reason the suitability of experimental and theoretical approaches for determination and estimation of the lipophilicity of organic compounds remains a focus of scientific interest.

Due to their advantageous application parameters, various reversed phase lichid chromatographic methods have been used for determination of lipophilicity [5, 6]. These techniques require only a small amount of compounds and they do not need to be very pure because their impurities are readily separated during the chromatographic process. Moreover, the lipophilicity values estimated by high-performance liquid chromatography (HPLC) and high-performance thin-layer chromatography (HPTLC) are generally well correlated [7]. In recent years, HPTLC technique has been used to estimate lipophilicity of a considerable number of chemicals and the relationship of this property with biological activity has been assessed [8-13]. The use of R_{M0} values obtained from different types of reversed-phase thin-layer chromatography (RP-TLC) is based on the assumed linear relationship between R_M and the concentration of organic modifier in the mobile phase:

$$R_M = R_{M0} + bC \quad (1)$$

$$R_M = log\ (1/R_F\text{-}1) \quad (2)$$

where R_M values are derived by the retention factor (R_F) according to the Eq. (2), R_{M0} is the R_M value extrapolated to 100% water, *C* is the concentration of organic modifier and *b* is the slope of regression function associated with specific hydrophobic surface area and it is considered an alternative measure of lipophilicity [14-19]. R_F is the retention factor calculated on the basis of migration distance of compound/migration distance of solvent front.

Recently, another retention related parameter (the isocratic chromatographic lipophilicity index), φ_0, have been introduced. It is defined as the volume fraction of the organic solvent in the mobile phase for which the amount of solute in the mobile phase is equal to that in the stationary phase when the retention factor (k) is 1 [20]. In thin layer chromatography φ_0 is described by equation (3):

$$\varphi_0 = R_{M0}/b \quad (3)$$

In addition, a new lipophilicity scale may be obtained by applying Principal Component Analysis (PCA) directly to the R_F and/or R_M values corresponding to different fractions of organic modifier and, as a direct consequence, the scores corresponding to the first principal component can be used as an alternative lipophilicity scale. Much more,

* *email: csarbu@chem.ubbcluj.ro*

the scatter plots of scores onto the plan described by the first two principal components offers the possibility to get a lipophilcity chart [21, 22].

A wide variety of synthetic dyes have been used in food processing and in a variety of modern industrial processes. Over the last few years a lot of concern has been expressed in the media over the safety of food additives generally and the synthetic food dyes in particular. Many synthetic food dyes used today have been proven to cause cancer, hyperactivity, inattentiveness, asthma, and in rare cases death [23]. Moreover, many of the water-soluble azo dyes are known to be degraded by intestinal microorganisms and some of their degradation products may have mutagenic properties [24-26]. Because of their commercial importance many analytical procedures has been established and used for quality control of dyes and for evaluation of their impact on human health or environmental pollution. The most relevant internationally agreed testing methods used by government, industry and independent laboratories to assess the safety of chemical products takes in consideration its lipophilicity parameters. Unfortunately, experimental lipophilicity data are not available in literature for the compounds investigated in this paper. The classical experimental procedure using shake-flask method seems to be difficult for some of structurally dyes because of the large difference between water solubility and anticipated solubility in octanol.

In the light of the above considerations, we found it interesting to carry out a comparative study concerning the chromatographic lipophilicity of several synthetic dyes on different stationary phases. Because most of the considered compounds are easily ionizing, the purpose of this paper was also the elucidation of the mechanism of retention on different types of stationary phase and the use of RP- TLC technique to assess the lipophilicity of this kind of compounds.

Experimental part

Thin-Layer Chromatography

The chromatographic behaviour of sixteen synthetic dyes listed in table 1 was studied on different stationary phases: RP-18 F_{254s} (20 X 20cm, Merck Darmstadt-Germany), RP-18W/UV_{254} (20 X 10cm, Macherey-Nagel) and CN F_{254s} (10 X 10cm, Merck, Darmstadt-Germany). The standards of analytical grade were purchased from Merck or Fluka.

Analytical-grade methanol was purchased from Chimopar (Bucharest, Romania). The standard solutions (1 mg mL^{-1}) of dyes were separately prepared in methanol and 2 µL from them were separately applied manually on the plates by means of a 10 µL Hamilton (Switzerland) microliter syringe. Chromatography was performed in a normal developing chamber (saturated for 15 min with solvent vapors) at room temperature (~22°C), using different proportion mixtures of methanol-water as mobile phase (from 20 to 60% methanol in steps of 10% for all types of stationary phases). The developing distance was 8 cm in all cases. After development the plates were dried in air at room temperature and the spots of dyes were apparent from their colours.

Theoretical Partition Coefficients

It is well known that many software and internet modules are able to calculate lipophilicity values by different algorithms. All of them require a previously molecule drawing that is usually performed by Hyperchem and optimized using the MM+ molecular mechanics force field [27]. On the basis of obtained geometry, different software allowing theoretical calculations of various lipophilicity descriptors. One of the log P values was calculated using fragmental and atomistic methods by Chem3D Ultra 8.0 [28], ($ClogP^{CD}$), four values (MLOGP, MLOGP2, ALOGP, ALOGP2) were calculated using topological descriptors by the software Dragon 5.4 [29] and six Log P values (ALOGPs, AC logP,, miLogP, $logP_{KOWWIN}$,

Table 1
THE COMMON AND IUPAC NAME OF THE SYNTHETIC DYES

No. Compound	Common name	IUPAC name
1	Quinoline Yellow WS	Sodium 2-(1,3-dioxoindan-2-yl)quinolinedisulfonate
2	Tartrazine	Trisodium (4*E*)-5-oxo- 1-(4-sulfonatophenyl)- 4-[(4-sulfonatophenyl)hydrazono]--pyrazolecarboxylate
3	Sunset Yellow FCF	Disodium 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfononate
4	Ponceau 4R	Trisodium (8Z)-7-oxo- 8-[(4-sulfonaphthalen-1-yl)hydrazinylidene] naphthalene--,3-disulfonate
5	Azorubine	Disodium 4-hydroxy-2-[(*E*)-(4-sulfonato-1-naphthyl) diazenyl]naphthalene-1--sulfonate
6	Erythrosine	2-(6-hydroxy-2,4,5,7-tetraiodo-3-oxo-xanthen-9-yl)benzoic acid
7	Amaranth (dye)	trisodium (4E)-3-oxo-4-[(4-sulfonato-1-naphthyl)hydrazono]naphthalene-2,7--disulfonate
8	Brilliant Blue FCF	Disodium2-[[4-[ethyl-[(3-sulfonatophenyl)methyl]amino]phenyl]-[4-[ethyl -[(3-sulfonatophenyl)methyl]azaniumylidene]-1-cyclohexa-2,5-dienylidene] methyl]benzenesulfonate
9	Patent Blue V	Sodium 4-[[4-(diethylamino)phenyl]-(4-diethylazaniumylidenecyclohexa-2,5--dien-1-ylidene)methyl]benzene-1,3-disulfonate
10	Methyl orange	4--dimethylaminoazobenzene-4'-sulfonic acid sodium salt
11	Congo red	Sodium 3,3'-(1E,1'E)-biphenyl-4,4'-diylbis(diazene-2,1-diyl)bis (4aminonaphthalene-1-sulfonate)
12	Cresol red	4-[3-(4-hydroxy-3-methylphenyl)-1,1-dioxobenzo[c]oxathiol-3-yl]-2 methylphenol
13	m-Cresol purple	4-[3-(4-hydroxy-2-methylphenyl)-1,1-dioxobenzo[c]oxathiol-3-yl]-3-methylphenol
14	Bromocresol purple	4,4'-(1,1-Dioxido-3H-2,1-benzoxathiole-3,3-diyl)- bis(2-bromo-6 methylphenol)
15	Bromocresol green	2,6-Dibromo-4-[7-(3,5-dibromo- 4-hydroxy-2-methyl-phenyl)- 9,9-dioxo-8-oxa-9λ6- thiabicyclo[4.3.0]nona- 1,3,5-trien-7-yl]-3-methyl-phenol
16	Azo violet	4-(p-Nitrophenylazo)resorcinol

Table 2

Log P VALUES CALCULATED BY DIFFERENT COMPUTING PROGRAMS (CHEMDRAW ULTRA 8.0, DRAGON 5.0 AND ALOGPS 2.1 [25-27])

No. Comp.	CLogP^{CD}	MLOGP	MLOGP2	ALOGP	ALOGP2	ALOGPs	AC logP	miLogP	KOWWIN	XLOGP2	XLOGP3
1	1.143	0.969	0.938	0.223	0.050	1.34	3.33	-3.47	-4.21	0.14	1.18
2	-0.843	0.056	0.003	0.897	0.805	2.36	3.23	-1.97	-6.74	2.37	2.35
3	1.187	1.369	1.874	2.100	4.408	-0.55	0.41	-1.02	1.40	2.05	2.09
4	0.389	1.086	1.179	1.638	2.682	2.14	6.02	-0.43	-1.74	3.56	3.65
5	2.361	2.173	4.720	3.008	9.048	-0.06	1.59	0.05	2.58	3.32	3.34
6	6.213	4.320	18.665	3.234	10.459	4.60	6.71	8.20	6.20	7.25	5.06
7	-0.409	1.086	1.179	-0.196	0.038	2.20	6.02	-0.43	-1.74	4.20	4.20
8	-0.857	3.630	13.176	2.796	7.820	1.95	6.26	-1.45	-2.74	6.12	5.76
9	-3.660	2.518	6.338	2.098	4.400	1.58	1.43	-1.62	-2.77	1.89	3.69
10	2.488	2.179	4.750	2.991	8.947	3.28	4.21	0.17	-0.66	3.45	3.09
11	4.856	2.805	7.868	6.338	40.165	4.85	9.04	3.90	2.63	6.29	6.78
12	3.277	3.002	9.012	4.445	19.757	3.27	2.40	2.89	0.97	2.03	4.47
13	3.277	3.002	9.012	4.445	19.757	3.36	3.43	4.03	4.30	3.94	3.75
14	5.037	3.915	15.326	5.942	35.304	4.42	4.82	6.02	6.08	5.11	5.13
15	5.961	4.327	18.721	6.952	48.334	5.20	6.22	7.50	7.86	6.71	6.51
16	3.265	1.366	1.867	0.971	0.944	3.31	3.74	3.32	4.25	3.22	2.82

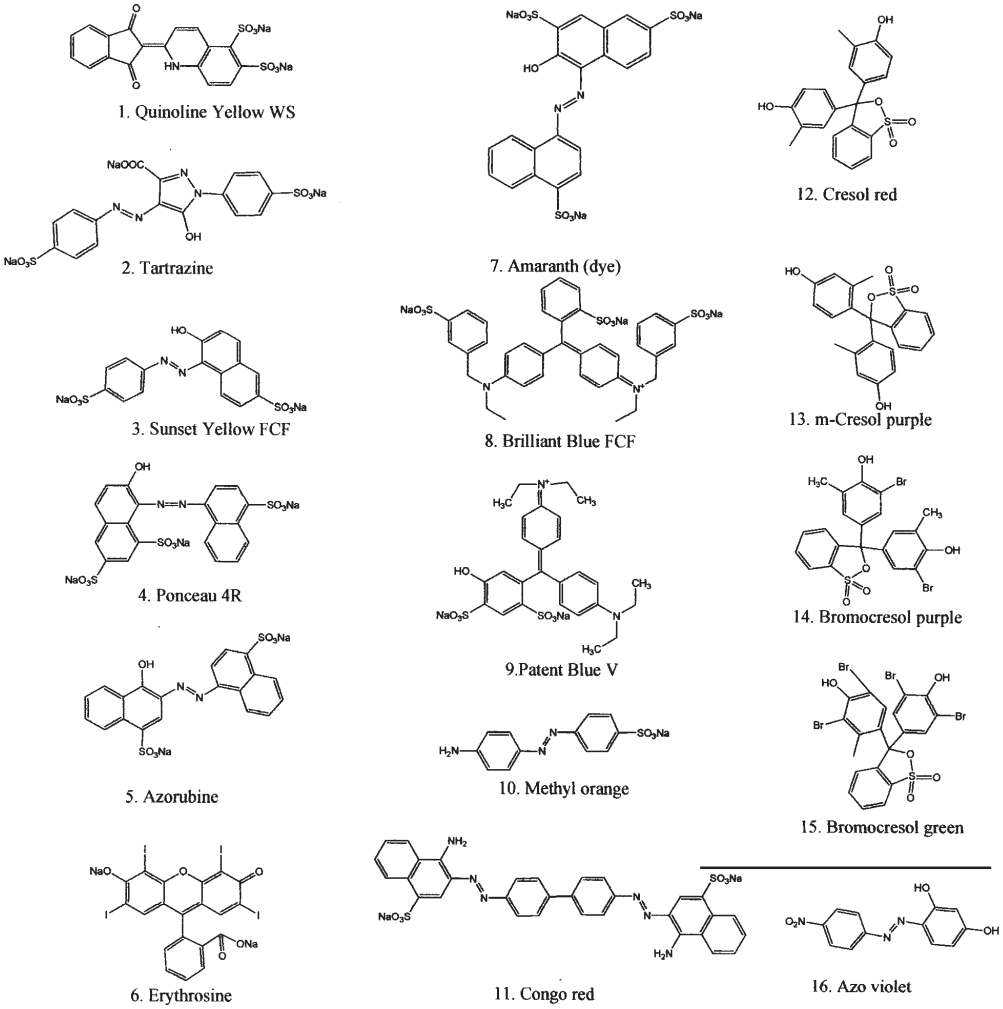

Fig. 1. The structures of the dyes investigated

XLOGP2, XLOGP3) based on different computation methods (electrotopological state descriptors, fragmental method and atom additive model) were obtained by using ALOGPS 2.1-vcclab free internet module [30]. All the calculated values are listed in table 2.

Results and discussions

The retention behaviour of several synthetic dyes (fig. 1) was investigated by systematic changing the amount of organic modifier in mobile phases. The R_f values obtained showed that the retention of the studied dyes regularly increased as the methanol content of the mobile phase was increased. Linear relationships characterized by high correlation coefficients were obtained between R_M values and volume fraction of methanol.

Because most of the studied compounds are easily ionizable, they could be susceptible to the secondary mechanisms of interactions with more or less non-polar stationary phase. The regular changes of the retention of dyes with changing water-methanol ratio can be observed by the profiles of retention indices (R_M) (fig. 2a-c).

These systematic regularities of retention observed for all three types of stationary phases might indicate that the same mechanism (lipophilic interactions) is dominant in all cases and no secondary mechanisms were highlighted. The extrapolated R_{M0} values and other experimental

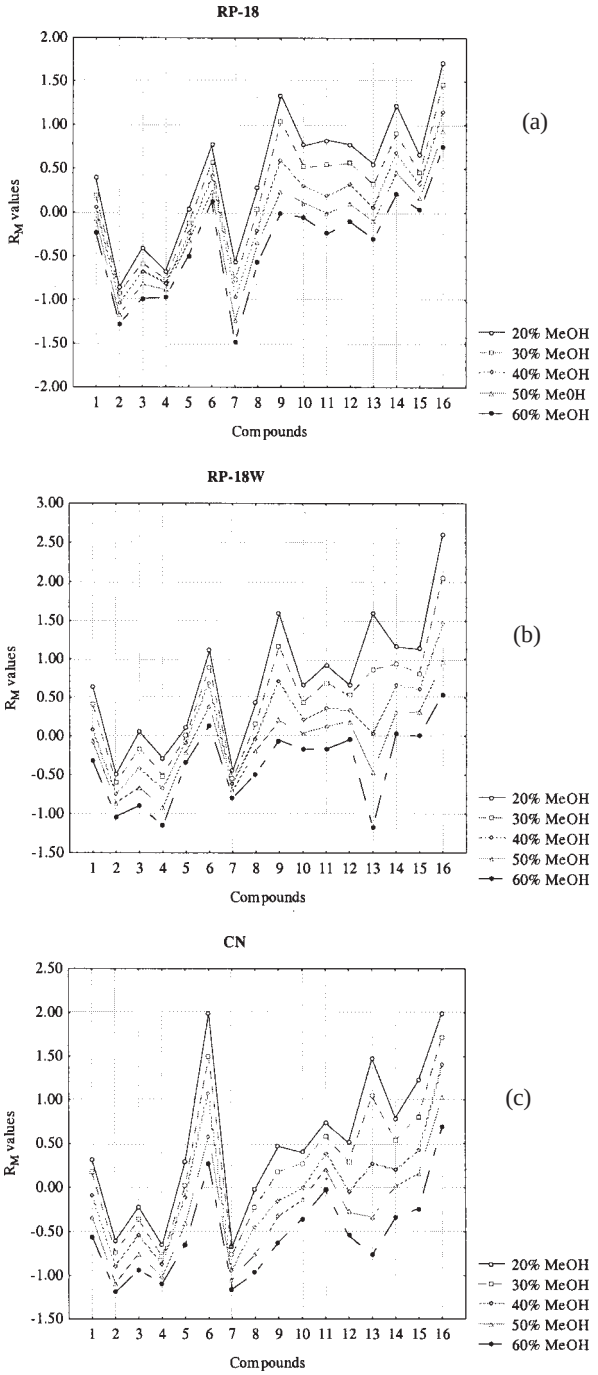

Fig. 2. The profiles of R_M values for all fraction of methanol: (a) RP-18; (b) RP-18W and (c) CN

lipophilicity indices obtained on the three stationary phases are summarized in table 3.

The similarity and/or differences between the lipophilicity parameters estimated from retention data obtained on the three stationary phases can be illustrated by representation of the profiles of R_{M0} values (fig.3.a) and profiles of scores obtained by applying PCA directly to the matrix of R_M values ($PC1/R_M$, fig. 3.b). Given the large number of existing stationary phases and their different properties, the problem is the choice of the most suitable stationary phases so that chromatographic results obtained to be comparable with the theoretical calculated values or obtained by established methods. In order to assess the experimental lipophilicity of the investigated compounds (estimated by R_{M0}, b, φ_0, scores corresponding to first principal component of R_f ($PC1/R_f$) and scores corresponding to first principal component of R_M ($PC1/R_M$)), the obtained results were compared with the different computed Log P values. The correlation matrix (table 4) illustrates a low compatibility between chromatographic indices of lipophilicity and computed Log P values for the investigated dyes.

The best correlations were obtained with the values calculated by using topological descriptors (Dragon 5.4 software). The weak correlation may be attributed to the fact that many computer programs do not recognize the potentially ionic character of molecules. Unfortunately, for the compounds considered in this study, the experimental lipophilicity determined by the classical shake-flask method are missing from the literature, probably, because of the large difference between water solubility and anticipated solubility in octanol.

By using $PC1/R_M$ or φ_0 values as estimators for lipophilic character of synthetic dyes, the correlation between these values obtained on the all three stationary phases were significantly improved, correlation coefficient being higher than 0.92 in some cases. These fairly high correlation between φ_0 parameters on three stationary phases may be further evidence that secondary retention mechanisms are absent in all cases.

Most of statistical algorithms do not require normalized input data but in some cases (linear regression) normalization is a recommended step. In statistics, normalization refers to the division of multiple sets of data by a common variable in order to allow data on different scales to be compared, by bringing them to a comparable scale. Lipophilicity charts (fig. 4a-c) obtained by scatter plots of normalized data for experimental lipophilicity

Table 3
EXPERIMENTAL LIPHOPHILICITY INDICES ESTIMATED BY DIFFERENT RP-HPTLC STATIONARY PHASES

No	RP-18					RP-18W					CN				
	R_{M0}	b	φ_0	Scores $PC1/R_f$	Scores $PC1/R_M$	R_{M0}	b	φ_0	Scores $PC1/R_f$	Scores $PC1/R_M$	R_{M0}	b	φ_0	Scores $PC1/R_f$	Scores $PC1/R_M$
1	0.665	-0.015	-44.04	1.012	0.179	1.120	-0.024	-46.09	0.914	0.490	0.798	-0.022	-35.63	1.172	-0.084
2	-0.622	-0.011	57.06	2.029	-2.321	-0.211	-0.013	15.63	1.856	-1.544	-0.288	-0.015	18.70	1.938	-1.899
3	-0.141	-0.014	10.14	1.818	-1.515	0.545	-0.024	-22.61	1.525	-0.746	0.167	-0.018	-9.18	1.679	-1.129
4	-0.535	-0.007	74.31	1.922	-1.813	0.153	-0.022	-7.08	1.793	-1.401	-0.444	-0.011	40.36	1.941	-1.881
5	0.282	-0.013	-22.20	1.364	-0.469	0.338	-0.011	-30.45	1.222	-0.154	0.749	-0.023	-32.57	1.256	-0.245
6	1.060	-0.016	-66.25	0.618	0.978	1.622	-0.024	-66.20	0.444	1.571	2.829	-0.044	-64.74	0.264	2.628
7	-0.121	-0.022	5.47	1.973	-2.190	-0.282	-0.008	33.18	1.777	-1.299	-0.410	-0.013	32.54	1.952	-1.938
8	0.674	-0.021	-32.25	1.268	-0.299	0.851	-0.022	-39.04	1.101	0.103	0.497	-0.024	-20.37	1.569	-0.912
9	2.034	-0.035	-58.62	0.488	1.540	2.426	-0.043	-56.95	0.475	1.873	0.973	-0.027	-36.58	1.163	-0.051
10	1.149	-0.021	-55.78	0.719	0.785	1.049	-0.020	-51.42	0.815	0.650	0.796	-0.019	-41.68	1.031	0.182
11	1.334	-0.027	-49.78	0.797	0.661	1.497	-0.028	-54.04	0.669	1.042	1.139	-0.019	-59.95	0.656	0.932
12	1.226	-0.022	-54.73	0.713	0.804	1.049	-0.018	-58.93	0.699	0.858	1.054	-0.027	-39.33	1.077	0.116
13	0.956	-0.021	-44.88	0.957	0.298	2.915	-0.069	-42.49	0.953	0.845	2.678	-0.059	-45.70	0.802	1.076
14	1.683	-0.025	-68.14	0.408	1.623	1.779	-0.029	-61.13	0.482	1.544	1.352	-0.028	-48.46	0.807	0.681
15	0.936	-0.015	-61.18	0.714	0.763	1.684	-0.028	-60.79	0.506	1.449	1.909	-0.036	-53.18	0.613	1.249
16	2.206	-0.025	-87.89	0.156	2.751	3.609	-0.052	-69.27	0.142	3.690	2.696	-0.033	-80.96	0.123	3.192

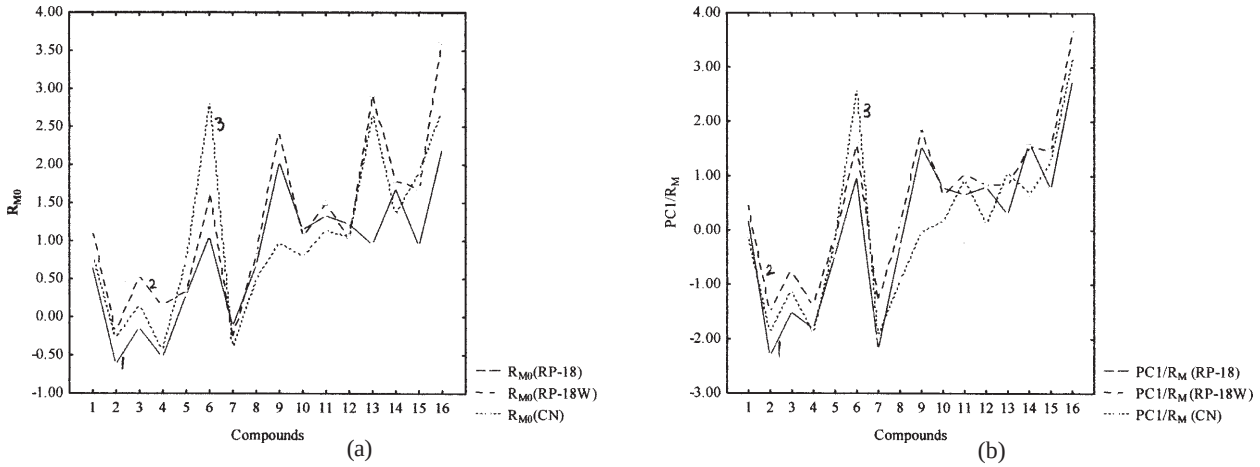

Fig. 3. The profiles of lipophilicity indices R_{M0} (a) and $PC1/R_M$ (b) of the investigated dyes

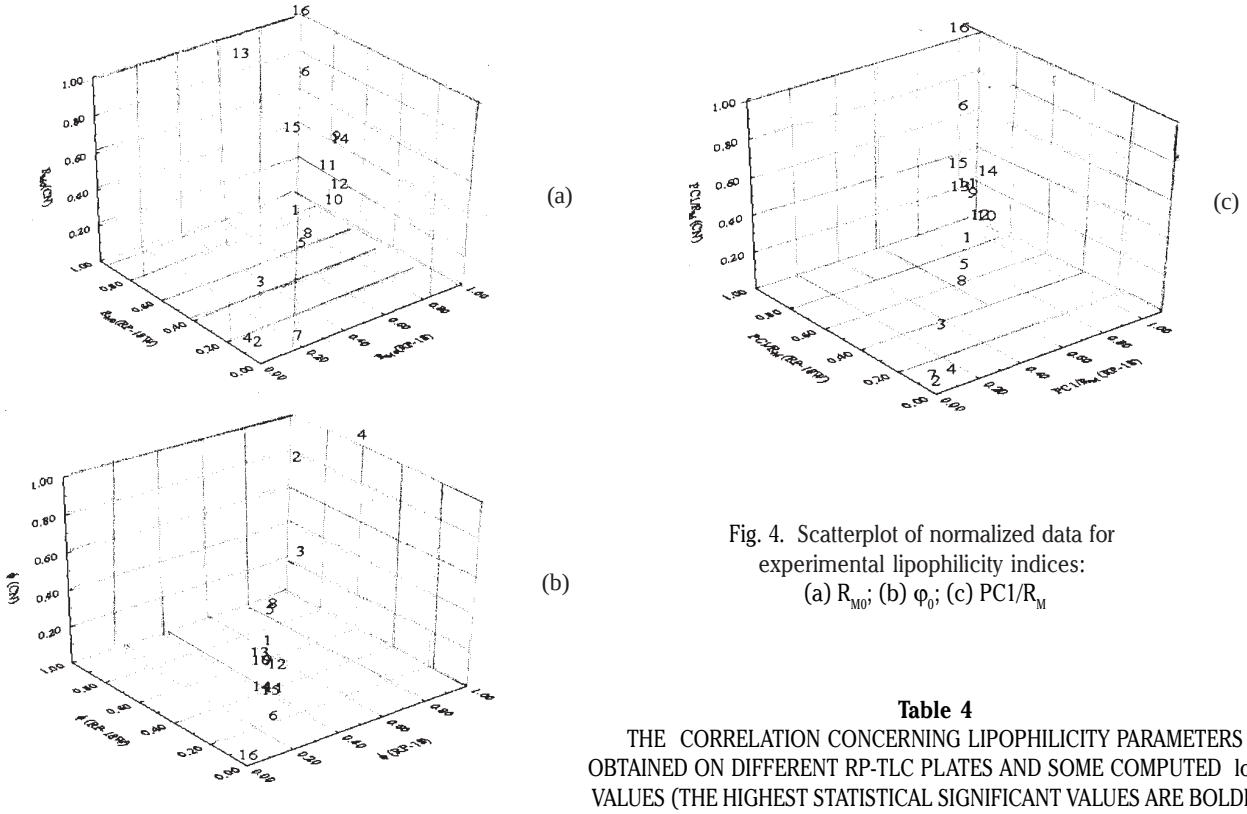

Fig. 4. Scatterplot of normalized data for experimental lipophilicity indices: (a) R_{M0}; (b) φ_0; (c) $PC1/R_M$

Table 4

THE CORRELATION CONCERNING LIPOPHILICITY PARAMETERS OBTAINED ON DIFFERENT RP-TLC PLATES AND SOME COMPUTED log P VALUES (THE HIGHEST STATISTICAL SIGNIFICANT VALUES ARE BOLDED)

	RP-18					RP-18W					CN				
	R_{M0}	b	$PC1/R_f$	$PC1/R_M$	φ	R_{M0}	b	$PC1/R_f$	$PC1/R_M$	φ	R_{M0}	b	$PC1/R_f$	$PC1/R_M$	φ
R_{M0}(RP-18)	1.00	**-0.81**	**-0.97**	**0.97**	**-0.91**	**0.85**	-0.57	**-0.95**	**0.95**	**-0.85**	**0.71**	-0.48	**-0.81**	**0.78**	**-0.85**
b (RP-18)	**-0.81**	1.00	0.64	-0.64	0.66	-0.60	0.44	0.61	-0.62	0.44	-0.33	0.22	0.41	-0.37	0.48
$PC1/R_f$(RP-18)	**-0.97**	0.64	1.00	**-0.99**	**0.93**	**-0.84**	0.53	**0.99**	**-0.96**	**0.92**	**-0.80**	0.56	**0.89**	**-0.86**	**0.91**
$PC1/R_M$ (RP-18)	**0.97**	-0.64	**-0.99**	1.00	**-0.92**	**0.87**	-0.56	**-0.98**	**0.98**	**-0.92**	**0.79**	-0.54	**-0.89**	**0.86**	**-0.91**
φ(RP-18)	**-0.91**	0.66	**0.93**	**-0.92**	1.00	**-0.76**	0.45	**0.94**	**-0.90**	**0.85**	**-0.79**	0.59	**0.86**	**-0.83**	**0.92**
R_{M0}(RP-18W)	**0.85**	-0.60	**-0.84**	**0.87**	**-0.76**	1.00	**-0.89**	**-0.83**	**0.91**	**-0.76**	**0.86**	-0.73	**-0.82**	**0.84**	**-0.80**
b (RP-18W)	-0.57	0.44	0.53	-0.56	0.45	**-0.89**	1.00	0.51	-0.62	0.48	-0.69	0.74	0.55	-0.58	0.51
$PC1/R_f$(RP-18W)	**-0.95**	0.61	**0.99**	**-0.98**	**0.94**	**-0.83**	0.51	1.00	**-0.97**	**0.94**	**-0.82**	0.57	**0.92**	**-0.89**	**0.94**
$PC1/R_M$(RP-18W)	**0.95**	-0.62	**-0.96**	**0.98**	**-0.90**	**0.91**	-0.62	**-0.97**	1.00	**-0.87**	**0.84**	-0.58	**-0.91**	**0.91**	**-0.91**
φ (RP-18W)	**-0.85**	0.44	**0.92**	**-0.92**	**0.85**	**-0.76**	0.48	**0.94**	**-0.87**	1.00	**-0.78**	0.56	**0.86**	**-0.83**	**0.92**
R_{M0}(CN)	**0.71**	-0.33	**-0.80**	**0.79**	**-0.79**	**0.86**	-0.69	**-0.82**	**0.84**	**-0.78**	1.00	-0.89	**-0.94**	**0.95**	**-0.87**
b (CN)	-0.48	0.22	0.56	-0.54	0.59	**-0.73**	**0.74**	0.57	-0.58	0.56	**-0.89**	1.00	0.69	**-0.71**	0.64
$PC1/R_f$(CN)	**-0.81**	0.41	**0.89**	**-0.89**	**0.86**	**-0.82**	0.55	**0.92**	**-0.91**	**0.86**	**-0.94**	0.69	1.00	**-0.99**	**0.95**
$PC1/R_M$(CN)	**0.78**	-0.37	**-0.86**	**0.86**	**-0.83**	**0.84**	-0.58	**-0.89**	**0.91**	**-0.83**	**0.95**	**-0.71**	**-0.99**	1.00	**-0.92**
φ (CN)	**-0.85**	0.48	**0.91**	**-0.91**	**0.92**	**-0.80**	0.51	**0.94**	**-0.91**	**0.92**	**-0.87**	0.64	**0.95**	**-0.92**	1.00
$CLogP^{CD}$	0.31	0.09	-0.48	0.45	-0.49	0.33	-0.14	-0.52	0.44	-0.54	0.66	-0.48	**-0.73**	0.69	-0.62
ALOGPs	0.47	-0.28	-0.56	0.50	-0.47	0.42	-0.25	-0.56	0.49	-0.45	0.56	-0.42	-0.64	0.59	-0.48
AC logP	0.04	-0.03	-0.08	0.04	-0.07	-0.03	0.11	-0.11	0.05	-0.04	0.11	0.01	-0.22	0.18	-0.06
miLogP	0.45	-0.14	-0.57	0.53	-0.53	0.48	-0.30	-0.61	0.55	-0.55	**0.75**	-0.63	**-0.75**	**0.73**	-0.60
KOWWIN	0.47	-0.13	-0.56	0.55	-0.58	0.53	-0.36	-0.61	0.58	-0.59	**0.75**	-0.62	**-0.75**	**0.74**	-0.65
XLOGP2	0.15	-0.06	-0.21	0.17	-0.25	0.12	-0.00	-0.27	0.20	-0.22	0.37	-0.31	-0.39	0.37	-0.27
XLOGP3	0.29	-0.30	-0.30	0.25	-0.32	0.13	0.01	-0.35	0.24	-0.30	0.26	-0.21	-0.33	0.27	-0.28
MLOGP	**0.77**	-0.56	**-0.77**	**0.77**	**-0.70**	**0.74**	-0.55	**-0.75**	**0.77**	-0.67	0.68	-0.53	**-0.72**	0.69	-0.69
MLOGP2	**0.77**	-0.56	**-0.77**	**0.77**	**-0.70**	**0.74**	-0.55	**-0.75**	**0.77**	-0.67	0.68	-0.53	**-0.72**	0.69	-0.69
ALOGP	**0.75**	-0.62	**-0.73**	**0.72**	-0.69	**0.70**	-0.52	**-0.71**	**0.72**	-0.59	0.62	-0.49	-0.66	0.63	-0.62
ALOGP2	**0.75**	-0.62	**-0.73**	**0.72**	-0.69	**0.70**	-0.52	**-0.71**	**0.72**	-0.59	0.62	-0.49	-0.66	0.63	-0.62

Table 5
THE NORMALIZED DATA FOR EXPERIMENTAL LIPHOPHILICITY INDICES ESTIMATED BY DIFFERENT RP-HPTLC STATIONARY PHASES

No	RP-18					RP-18W					CN				
	R_{M0}	b	Scores PC1/R_f	Scores PC1/R_M	φ_0	R_{M0}	b	Scores PC1/R_f	Scores PC1/R_M	φ_0	R_{M0}	b	Scores PC1/R_f	Scores PC1/R_M	φ_0
1	0.455	0.711	0.457	0.493	0.270	0.360	0.745	0.450	0.389	0.226	0.379	0.762	0.574	0.361	0.374
2	0.000	0.861	1.000	0.000	0.894	0.018	0.925	1.000	0.000	0.829	0.048	0.908	0.992	0.008	0.821
3	0.170	0.754	0.887	0.159	0.604	0.213	0.748	0.807	0.152	0.455	0.187	0.850	0.851	0.158	0.592
4	0.031	0.993	0.943	0.100	1.000	0.112	0.790	0.963	0.027	0.607	0.000	1.000	0.994	0.011	1.000
5	0.320	0.796	0.645	0.365	0.405	0.159	0.965	0.630	0.266	0.379	0.364	0.750	0.619	0.330	0.399
6	0.595	0.679	0.247	0.650	0.133	0.489	0.742	0.176	0.595	0.030	1.000	0.319	0.077	0.890	0.134
7	0.177	0.461	0.970	0.026	0.576	0.000	1.008	0.954	0.047	1.000	0.010	0.967	1.000	0.000	0.936
8	0.458	0.504	0.594	0.399	0.343	0.291	0.787	0.560	0.315	0.295	0.288	0.721	0.791	0.200	0.499
9	0.939	0.000	0.177	0.761	0.180	0.696	0.440	0.194	0.653	0.120	0.433	0.675	0.569	0.368	0.366
10	0.626	0.514	0.301	0.612	0.198	0.342	0.810	0.393	0.419	0.174	0.379	0.831	0.496	0.413	0.324
11	0.692	0.293	0.342	0.588	0.235	0.457	0.688	0.307	0.494	0.149	0.484	0.833	0.291	0.559	0.173
12	0.653	0.450	0.297	0.616	0.204	0.342	0.853	0.325	0.459	0.101	0.458	0.671	0.522	0.400	0.343
13	0.558	0.489	0.428	0.516	0.265	0.822	0.000	0.473	0.456	0.261	0.954	0.000	0.371	0.588	0.291
14	0.815	0.368	0.135	0.778	0.122	0.530	0.665	0.198	0.590	0.079	0.549	0.648	0.374	0.511	0.268
15	0.551	0.704	0.298	0.608	0.165	0.505	0.688	0.212	0.572	0.083	0.719	0.481	0.268	0.621	0.229
16	1.000	0.354	0.000	1.000	0.000	1.000	0.282	0.000	1.000	0.000	0.959	0.535	0.000	1.000	0.000

indices for three different stationary phases (table 5) are more easily to use for looking of trends, groupings or outliers. By careful visual examination of the "lipophilicity space" (fig. 4a-c), it is apparent that the chromatographic behavior of the investigated dyes is firstly in agreement with the number of ionic groups; the normalized values of φ_0 and PC1/R_M parameters associate the compounds in better way than R_{M0} values.

Conclusions

Retention behaviour of sixteen synthetic dyes was investigated by reverse phase thin-layer chromatography on RP-18F_{254S}, RP-18W/UV_{254} and CNF_{254S} plates using methanol–water mixtures as mobile phases. Systematic regularities of retention revealed by the profiles of retention indices (R_M) no highlighted secondary mechanisms of interaction with studied stationary phases. In addition, fairly high correlation between φ_0 parameters on three stationary phases may be further evidence that secondary retention mechanisms are absent. The low correlation between chromatographic indices of lipophilicity and computed Log P values might be attributed to the strong ionic character of investigated dyes. The results obtained indicate that descriptors for molecular properties computed by Dragon software are the best parameters for estimating the lipophilicity of this kind of compounds. The φ_0 and PC1/R_M values of synthetic dyes estimated on the three stationary phases seem to be the most suitable and appropriate estimators.

Acknowledgement: The financial support of the Ministry of Education and Research of Romania (CNCSIS, IDEI 560/2007) is gratefully acknowledged.

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Manuscript received. 28.10.2009