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Hydrophobicity, protolytic equilibrium and chromatographic behaviour of some monoazoic dyes

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Abstract

Reverse-phase thin layer chromatography (RP-TLC), water:octanol partition studies and spectrophotometric determinations of p*K*-values are reported for 8 monoazo derivatives of sulfanilic acid (3 of them having aromatic amino groups). The results are compared to previously published p*K* values for 7 derivatives of aminoazobenzene and R_{M0}-values for 11 azo dye derivatives of 4-aminobenzoic acid (5 of them having amino groups), in an attempt to study RP-TLC and partition results and to assess the relative importance in polar:lipophilic phase-partition processes of neutral, amphionic and ionic forms of these compounds. Calculated *C* log *P* and log P_{Suzuki} values are also reported. No correlation was found between R_{M0} and the apparent water:octanol partition coefficient, log P_{exp}-values for the first 8 azo dyes probably due to the different neutral and amphionic forms in the polar phases (water:methanol mixtures vs. water). Not only neutral, but amphionic and possibly ionic forms are important in assessing chromatographic R_{M0}-values for lipophilicity characterizations. Acceptable correlation between R_{M0} and log P_{Suzuki} was observed.

Keywords: Octanol:water partition coefficient (log *P*); Log *D*; RP-TLC hydrophobicity; Lipophilicity; Dyes

1. Introduction

Dye adsorption on a textile fibre is partially determined by hydrophobic interactions [1]. From this point of view, lipophilicity determinations for organic dyes used for natural fibres is relevant. Lipophilicity can be assessed from studies of water/hydrophobic solvent (usually *n*-octanol) partition equilibrium [2]. Reverse phase chromatography is often used to assess the lipophilicity of various molecular species [3]. As monoazo dyes contain ionisable groups, in the partition between water and a lipophilic medium, they are present in neutral, ionic and amphionic molecular forms.

This paper presents the reverse phase thin layer chromatography (RP-TLC) behaviour, water: octanol partition coefficient and protolytic equilibrium for a series of 8 monoazo dyes (Fig. 1a). Chromatographic R_{M0} values and octanol:water

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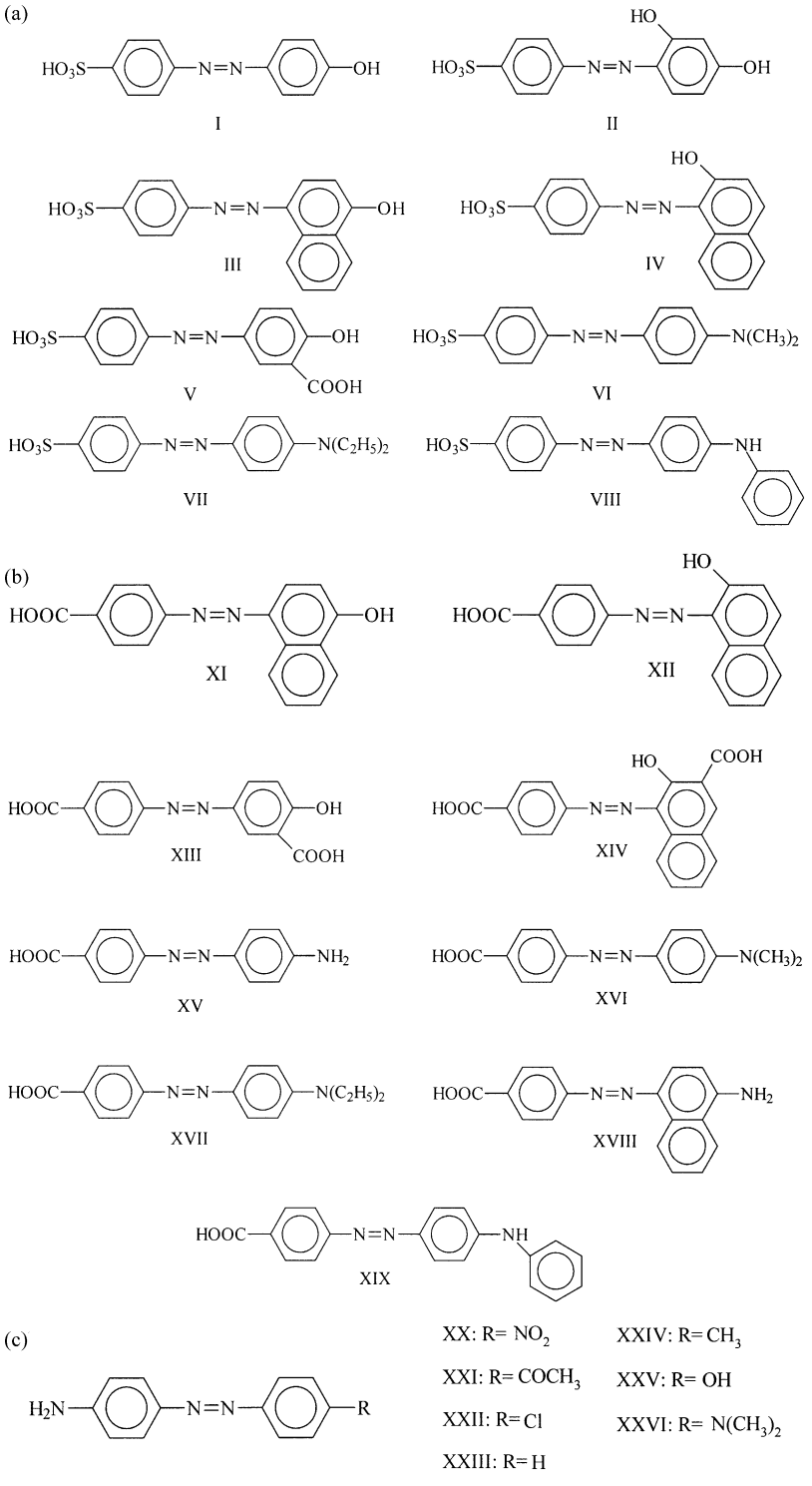

Fig. 1. Monoazoic derivatives with solubilizing (a) sulfonic acid group, (b) carboxylic acid group. (c) Aminoazobenzene derivatives (from [7]).

partition coefficients of the dyes are correlated and the importance in partition processes of both the ionic and amphionic forms are studied. Experimental pK values are used in this study and C log P [4] and log P_{Suzuki} [5] values are compared with chromatographic characteristics.

Data from previous work [6], especially the RP-TLC values for another series of monoazo dyes [7] (Fig. 1b) and earlier spectrophotometric pK determinations for aminoazobenzene derivatives [8] (Fig. 1c), are considered in various discussions and correlations attempted.

2. Experimental

A series of monoazo dyes (obtained from diazotized sulfanilic acid) were synthesized (Fig. 1a), according to the literature [9,10]. Dye purity was verified by TLC using Merck silica gel plates, with an isopropanol/methyl-ethyl-ketone/25% ammonium hydroxide solution as eluent.

The water-soluble dyes have a specific behaviour in aqueous solution due to their quasi-amphiphilic character (they contain an aromatic structure with extended conjugation and polar substituents such as OH, NH_2 and SO_3H groups).

Experimental determination of octanol:water partition coefficients was performed using a direct, classical method of extraction [11]. Centrifugation (15 min at 3000 rpm) gave good separation of the phases. To avoid dissociation of the sulfonic group, a pH of 0.4 in HCl solution was used for compounds **I**–**V**, while for compounds **VI**–**VIIII** a pH value of 2 was used. A Mettler AE-240 analytical balance (precision of 0.01 mg) was used; spectrophotometric determinations were recorded using a UV–VIS Perkin-Elmer Lambda 12 spectrofotometer, over the range 200–800 nm.

The experimental results are shown in the Table 1, together with the theoretical partition coefficients (calculated using C log P [4] and CHEMICALC-2 software [5]). As the variations of partition coefficient with temperature were insignificant, the experimental octanol:water partition coefficients were assessed in the range 15–20 °C and, thus, the apparent log D partition coefficient was obtained.

2.1. Chromatographic RP-TLC studies

Tomlinson and Rekker published some reviews concerning RP-TLC in relation to partition techniques [12,13]. Boyce and Millborrow pointed out the correlation between R_M values and the organic solvent concentration in the mobile phase for a chromatographic system [14]. The R_M values are defined by Eq. (1):

$$R_M = \log(1/R_f - 1) \quad (1)$$

As in RP-TLC, the R_M values are linearly correlated to the concentration of the organic component in the aqueous phase, and they can be extrapolated for 100% water, resulting R_{M0} as intercept. This, together with the regression slope of the RP-TLC equation leads to lipophilicity estimations [15,16].

To study dye lipophilicity, we used 20×20 cm silica gel plates of 0.25 mm layer thickness, predeveloped for 24 h with a hexane:paraffin oil (90:10) mixture. The hydrophobized plates exhibited an edge effect which was eliminated by cutting off 2 cm of the edges [17]. The mobile phase (saturated with paraffin oil) was a methanol:HCl 0.5 M mixture in which the methanol concentration varied between 30 and 60% using increments of 6 and 3%, respectively. At methanol concentrations under 30%, dyes **I**–**V** spots were deformed while

Table 1
Calculated and experimental water:octanol partition coefficient

Compound	log P_{exp}[a]	C log P[b]	log P_{Suzuki}[c]
I	1.60	3.73	1.32
II	1.90	3.30	0.50
III	2.35	3.27	2.51
IV	2.64	3.27	2.51
V	2.25	2.65	1.92
VI	1.31	2.63	2.30
VII	1.77	3.53	3.19
VIII	2.26	4.26	3.38

[a] Experimental octanol:water partition coefficient values log D at pH = 0.4 except compounds **VI**, **VII** and **VIII** determined at pH = 2.

[b] Theoretical values calculated by the CHEMICALC software [5].

[c] Values based on fragment contributions; calculated by the C log P software [4].

dyes **VI–VIII** could be found on the start line ($R_F = 0$). At concentrations above 60%, the dyes were found in the solvent front ($R_F = 1$). The dyes displayed different behaviour when the methanol concentration in the eluent (interval of 30–60%) was changed. Dyes **I**, **II** and **V**, obtained by coupling with phenols, had R_F values between 0.8 and 0.96 while those coupled with naphthols migrated over an interval, between 0.2 and 0.84. In these cases, the form of the spots changed with methanol concentration. Dyes **VI**, **VII**, **VIII**, obtained by coupling with *N*-substituted amines, had R_F values of between 0.06 and 0.85. The spot appearance change was not as obvious as for the naphthol derived dyes. In conclusion, it was very difficult to evaluate the maximum concentration of substance on the chromatogram.

In Table 2 the regression parameters values for the TLC equations concerning some monoazo dyes are shown.

For compounds **IX–XIX**, results are listed in Table 3.

As a linear correlation exists between the R_M values and the concentration of the organic component in mobile phase, R_{M0} may be considered as a measure of lipophilicity. The low correlation coefficients might be explained by the specific structure of this class of substances. In the case of **V** (diazotized sulfanilic acid coupled with salicylic acid) the smallest correlation coefficient was obtained, probably due to the presence of carboxylic groups. The polar molecule migrates close to the front resulting in low levels of determination.

Partial protonation of the substituted amino groups in compounds **VI**, **VII** and **VIII** may be another factor that reduces the accuracy of determination. Chromatographic behaviour suggests that the amino group protonation was low, compared to the classical partition of octanol:acidified aqueous solution. Table 2 points out a clear difference between the phenol-based dyes (**I**, **II**, **V**) and the naphthol-based dyes (**III**, **IV**). The presence of the benzene rings increased lipophilicity.

2.2. Spectrophotometric determinations of pK-values for NR_2 groups

The existence of an isosbestic point is an easy recognizable criteria for equilibrium between two ionic forms with overlapping absorption bands [18–21]. This condition was applied to compounds **VI–VIII** and compounds **IX–XV** in a previous publication [7] in order to obtain p*K* values for the amino group. The effect of the dissociation

$$-SO_3H \rightleftharpoons -SO_3^- + H^+$$

reaction [Eq. (1)] will be discussed later.

For compounds **VI–VIII** an aqueous solution compromising different buffers was used while for compounds **IX–XXVI** 1:1 (vol) methanol: water solution [7], due to solubility problems. The dye concentrations were 10^{-5} mol/l. The

Table 2
Regression parameters determined by TLC equations, compounds **I–VIII**

Compound	R_{M0}	b	n	r	r^2	F
	$R_M = R_{M0} + b$ (% methanol)					
I	0.12	−0.019	8	0.946	0.865	51.52
II	−0.19	−0.014	8	0.908	0.825	28.37
III	0.89	−0.028	8	0.935	0.875	42.37
IV	1.56	−0.038	8	0.925	0.856	35.72
V	−0.06	−0.021	8	0.879	0.774	20.58
VI	1.02	−0.031	8	0.890	0.792	22.92
VII	2.16	−0.044	8	0.904	0.818	27.08
VIII	2.71	−0.054	8	0.985	0.970	199.77

n—Number of the experimental determinations for each compound. *r*—Regression coefficient. *F*—Fisher test.

Table 3
Regression parameters determined by TLC equations, compounds **IX**–**XIX** [7]

Compound	R_{M0}	b	n	r	r^2	F
	$R_M = R_{M0} + b$ (% methanol)					
IX	0.64	−0.022	8	0.89	0.80	23.35
X	0.26	−0.015	8	0.91	0.83	30.57
XI	0.18	−0.017	8	0.87	0.79	19.44
XII	2.79	−0.046	6	0.99	0.99	226.20
XIII	−0.21	−0.009	8	0.83	0.77	13.30
XIV	1.23	−0.035	8	0.91	0.83	28.75
XV	0.63	−0.025	8	0.96	0.91	67.56
XVI	2.70	−0.018	8	0.94	0.87	46.33
XVII	3.29	−0.053	6	0.97	0.95	90.51
XVIII	1.91	−0.040	8	0.95	0.88	54.12
XIX	3.20	−0.041	8	0.98	0.97	255.18

buffers were disodic citrate, to which 0.1 N HCl solution was added [22, 23]. The spectra were recorded between pH = 0 and pH = 11.5, involving 10–11 samples within 1.0–1.5 pH units range around the pK-value considered. The calculation of pK values was performed using Eqs. (2a) and (2b)

$$pK = pH + \log\frac{d - d_N}{d_I - d}, \quad \text{for } d_I > d_N \tag{2a}$$

$$pK = pH + \log\frac{d_N - d}{d - d_I}, \quad \text{for } d_N > d_I \tag{2b}$$

where d_N, d_I and d are the optical densities at the analytic wavelength for the neutral, ionized form and respectively the mixtures.

A Mettler-Delta 350 pH-meter was used, with a combined Mettler Toledo U402-88TE-S7/120 electrode. Absorption spectra were recorded using a Perkin-Elemer-Lambda 12 UV–VIS spectrophotometer. The characteristic values are listed in Table 3, the pK-values for amino group protonation in Table 5—for compounds **VI**–**VIII** and Table 6 for compounds **XX**–**XXVI**.

2.3. Spectrophotometric determination of pK values for NR_2 and SO_3H groups

Compounds **VI**–**VIII** have two different groups attached to the phenyl moieties, one of them being the SO_3H group. Their neutral and ionized forms are:

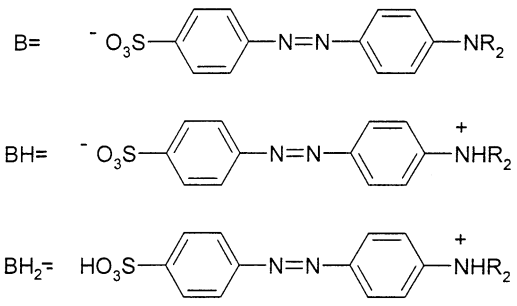

Table 4
Characteristics values for pK determination

Compound	pH domain	Number of determinations	λ Isosbestic nm	λ_{max} nm	λ_{max_I} nm	λ_{max_N} nm	pK medium
VI	2.76–4.00	10	469.04	508.04	464	484	3.28
VII	2.84–4.18	10	512.69	508.04	474	454.17	4.14
VIII	1.17–2.15	11	470.60	531.20	444.63	506.31	1.40

Table 5
(a) pK values for compounds **VI**, **VII** and **VIII**

Compound	pK_{amino}
VI	3.28
VII	4.14
VIII	1.40

Table 6
(b) pK values for compounds **XX**–**XXVI** [7]

Compound	pK
XX	1.88
XXI	2.16
XXII	2.24
XXIII	2.49
XXIV	2.56
XXV	2.74
XVI	pK_1 = 3.06 pK_2 = 1.78

Table 7
(c) pK_a values for compounds **VI**, **VII** and **VIII**

Compound	pK_{amino}	pK_{SO3H}
VI	3.29	0.27
VII	3.70	0.33
VIII	0.77	0.30

and the corresponding equilibria are:

$$B + H^+ \leftrightarrow BH \quad \beta_1 = \frac{[BH]}{[B][H^+]^2} \tag{3a}$$

$$BH + H^+ \leftrightarrow BH_2 \quad \beta_1 = \frac{[BH_2]}{[B][H^+]^2} \tag{3b}$$

If the dye concentration is constant and the pH values are varied, Eqs. (4) and (5) are obtained:

$$A = b\left(e_0 + e_1\beta_1 a + e_2\beta_2 a^2 + e_H a\right)l \tag{4}$$

$$E = \frac{A}{C} = \frac{e_0 + e_1\beta_1 a + e_2\beta_2 a^2}{1 + \beta_1 a + \beta_2 a^2} \tag{5}$$

where e_0, e_1, e_2, e_H are the molecular absorption coefficients of B, BH, BH_2 and respectively H^+ species ($e_H = 0$), "l" is the stratum length, "a" is the [H^+] concentration, "b" is the concentration of B species and "C" is the analytical dye concentration. The H^+ concentrations in high concentrated HCl solutions were corrected with the corresponding activity coefficients.

Compounds **VI**, **VII** and **VIII** were dissolved in water at 10^{-4}–10^{-5} mol/l concentration and the corresponding spectra were recorded with a CECIL CE 7200 spectrophotometer at 7 different pH values (Table 7)

$$pK_{amino} = \log \beta_1 \tag{6a}$$

$$pK_{SO_3H} = \log\frac{\beta_2}{\beta_1} \tag{6b}$$

For $C_6H_5SO_3H$, pK = 0.70, while for $C_6H_5N(CH_3)_2$, $C_6H_5N(C_2H_5)_2$ and $C_6H_5NHC_6H_5$ pK values of 5.15, 6.16 and 0.79 were obtained respectively [24]. For 4-anilinoazobenzene three different pK values, 1.52, 0.99 and 1.55 were found [20].

Octanol:water partition coefficients were calculated using $C\log P$ [4] and log P_{Suzuki} [5] software (Table 8).

It is generally considered that both neutral and also amphionic forms are present in water:octanol partitions. Therefore, for the 8 compounds for which RP-TLC and partition equilibrium were studied, the log P values corresponding to the neutral form were obtained from log P_{exp} values, and they were correlated with the chromatographic R_{M0}-values.

For compounds **I**–**V** partition equilibria were studied at a pH of 0.4, while a pH of 2 was used for compounds **VI**–**VIII**. The relation between log P_{exp} and log P and the quotient of the concentration of the neutral form [B_0], and the analytic concentration [C] is shown in Eq. (7)

$$\log P_{corr} = \log P_{exp} + \log([C])/[B_0] \tag{7}$$

For compounds **I**–**V**, the neutral form of B_0 is HO_3S–C_6H_4–N=N–C_6H_4–R. At pH 0.4 with p$K \approx 0.3$ for the SO_3H group (Table 5), about 50% of the SO_3H group will be undissociated.

For most compounds, the amino group will be protonated [Eq. (7)].

$$[C] \approx [BH_2] + [BH] \approx 2[BH_2] \tag{8}$$

Table 8
Experimental log P_{exp} and R_{M0} values, corrected log P_{corr}-values and calculated C log P and log P_{Suzuki} values

Compounds	R_{M0}	log P_{exp}	Log P_{corr}	log P_{Suzuki}	C log P
I	0.12	1.60	1.90	1.32	3.73
II	−0.19	1.90	2.20	0.50	3.30
III	0.89	2.35	2.65	2.51	3.27
IV	1.56	2,64	2.94	2.51	3.27
V	−0.06	2.25	2.55	1.92	2.65
VI	1.02	1.31	4.31	2.30	2.63
VII	2.16	1.77	5.40	3.19	3.53
VIII	2.71	2.26	3.10	3.38	4.26
IX	0.64			1.09	3.78
X	0.26			0.27	3.29
XI	0.18			2.28	4.95
XII	2.79			2.28	4.95
XIII	−0.21			1.69	4.27
XIV	1.23			1.86	5.44
XV	0.63			0.60	3.17
XVI	2.70			2.07	4.31
XVII	3.29			2.96	5.20
XVIII	1.91			1.80	4.35
XIX	3.20			3.15	5.93

At $pK - pH \geqslant 1$ the following correction [Eq. (9)] is required for compounds **VI–VIII**, which have also an amino group:

$$\log\frac{[C]}{[B_0]} \approx (pK_{amino} - pH) + (pH - pK_{SO_3H}) = pK_{amino} - pK_{SO_3H} \quad (9)$$

Thus, the value of $\log([C]/[B_0])$ is approximately 0.3, for compounds **I–V** while for compounds **VI**, **VII** and **VIII** values of 3.0, 3.6 and 0.8 are obtained if the mean values of pK_{amino} are considered (i.e. 3.3, 3.9 and 1.1, Table 5). The corrected log P_{corr}-values are listed in Table 9.

For the RP-TLC studies, the mobile phase was a solution of water:methanol 0.5 M HCl solution. The correction value of $\log([C]/[B_0])$ for chromatographic studies should also be about 0.3 for compounds **I–V**, but for compounds **VI–VII**, according to Eq. (10).

$$\log\frac{[C]}{[B_0]} \approx (pK_{amino} - pH) + \log\ 2 \quad (10)$$

The values approximate to 3.3, 3.9 and 1.1.

3. Results and discussions

Intercorelational coefficients (r) between various experimental and calculated lipophilicity and hydrophobiocity parameters are listed in Table 6.

For compounds **I–VIII** correlation between log P_{Suzuki} and R_{M0} gave $r = 0.91$. When compound **III** (sulfanilic acid coupled to 1-naphthol) and compound **V** (sulfanilic acid coupled to salicylic acid) were taken out from this subseries of compounds the value of r was 0.95.

For compounds **IX–XIX** the correlation between log P_{Suzuki} and R_{M0} gave $r = 0.72$. When compound **XI** (4-aminobenzoic acid coupled with 1-naphthol) and compound **XIII** (4-aminobenzoic acid coupled with salicylic acid) were removed from this subseries a value of $r = 0.95$ was obtained.

Protolytic equilibria play an important role in azo dyes. This aspect is clearly demonstrated by isomeric dyes Orange I (compound **III**) and Orange II (compound **IV**), the former being almost obsolete because its hue is affected by alkali. Above pH 8.2, it is mainly present as the dibasic anion, whilst Orange II does not lose its

Table 9
Intercorrelation coefficients (r) for compounds **I–XIX**[a]

r	R_{M0}	log P_{exp}	log P_{corr}	log P_{Suzuki}	C log P
R_{M0}	–	0.27	0.62	0.70	0.55
log P_{exp}	0.27	–	0.33	0.26	0.17
log P_{corr}	0.62	0.33	–	0.64	0.10
log P_{Suzuki}	0.70	0.26	0.64	–	0.40
C log$P$	0.55	0.17	0.10	0.40	–

[a] Intercorrelations between log P_{exp} and R_{M0}, log P_{corr}, C log P, log P_{Suzuki} are considered only for compounds **I–VIII**; intercorrelations between R_{M0} and C log P respectively log P_{Suzuki} are considered for compounds **I–XIX**; intercorrelations between C log P and log P_{Suzuki} are considered for compounds **I** to **XIX**: intercorrelations between log P_{corr} and C log P respectively log P_{Suzuki} are considered only for compounds **I** to **VIII**.

phenolic proton until the alkalinity is raised much higher. The constants K_2 which correspond to the acid dissociation of the phenolic groups, differ by more than 10^3, the cause being the intramolecular hydrogen bond in Orange II [25].

RP-TLC R_{M0} values are considered as measures for lipophilicity but for the 8 azo dyes concerned (compound **I–VIII**) there was no correlation between R_{M0} and logP_{exp} probably because of the differences between the phases used (water for partition determination and water:methanol mixture for RP-TLC determination). The reduced dielectric constant of the water:methanol solution probably disfavors the dissociation and the relative amount of neutral, amphionic and ionic forms of the dyes differ from those present in water. An attempt to correlate R_{M0} with log P_{corr}-values, corrected in the hypothesis that only neutral forms were involved in partition processes, failed. This fact and also the lack of correlation between log P_{corr} and C log P and respectively log P_{Suzuki} indicates that not only neutral but also amphionic, (possibly also ionic) forms contribute to the polar (water, water:methanol)–lipophilic partition process.

The RP-TLC method does not require purification of dyes. In the case of octanol:water partition, the purity of samples is extremely important.

The theoretic calculations of log P do not take into account the position of substituents but practically it was demonstrated that there was a significant difference between such compounds.

The only acceptable correlations are between R_{M0} and log P_{Suzuki}; possibly log P_{Suzuki} values have a more realistic calibration.

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