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Spectrophotometric Study of the Prototropic Equilibrium of Methyl Red in Organic Solvents

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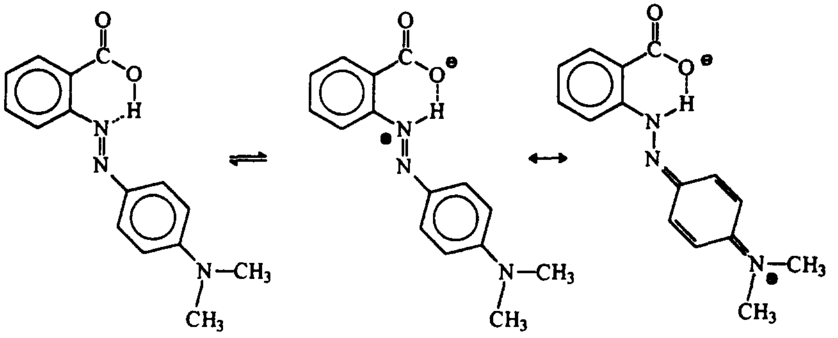
ABSTRACT

The electronic spectra of Methyl Red were evaluated in a diverse range of solvents. Solvatochromic characteristics of the dye are related to an acid–base equilibrium between azo and azonium chelated configurations. Correlations are reported between a variety of established solvent parameters and this equilibrium.

INTRODUCTION

In the course of our studies on the dyeing behaviour of some azo dyes derived from 2-aminobenzoic acid we were faced with the problem of their remarkable solvatochromism. Some studies[1,2] have already pointed out this behaviour of dyes derived from anthranilic acid, and others[3–5] have established that Methyl Red (2-[4-(dimethylamino)phenylazo]benzoic acid) exists in solution in the equilibrium forms I and II (Fig. 1), where the proton of the carboxyl group is transferred to the β-nitrogen of the azo group.

We consider that the solvatochromism of the anthranilic acid based dyes is a consequence of the variation of this equilibrium, and the object of this work is to study it in non-aqueous solvents. Only a few systematic studies[5,6] of the prototropic equilibria in organic solvents have been made and few quantitative data are available on the effect of the solvent properties. Knowledge of this equilibrium is important to more fully understanding the coloristic properties of dyes derived from anthranilic acid, and to elucidate what solvent parameters are responsible for the protonation equilibria.



I IIa IIb

Fig. 1. Intramolecular protonation equilibrium of Methyl Red.

EXPERIMENTAL

Materials

Methyl Red (MR) was prepared according to the method reported in the literature.[8] The dye was purified by repeated crystallizations and purity was checked by elemental analysis and thin layer chromatography.

Spectra

Absorption spectra in 49 selected organic solvents were carried out at 25 (±0·1)°C on a Varian Cary 5 spectrophotometer using 10 mm cells held in a thermostatted cell block. Dye concentration was about 10^{-3} M. The solvents used were either of commercial HPLC or spectrophotometric grade, or where these were not available, solvents were redistilled. All the solvents were dried according to the usual methods.[9]

Spectra analysis

Experimental absorption spectra were considered to be a linear combination of two component bands corresponding to the azo (I) and azonium (II) forms; hence the curves were resolved in two Gaussian bands using a regression method (see Fig. 2). The intensities (H_1 and H_2) and positions (λ_1 and λ_2) of these bands are reported in Table 1. Table 2 reports the values of the solvent parameters taken by several compilations and used throughout this work. The absorption spectra recorded in some haloaliphatic solvents showed a fine structure with two closely spaced peaks. For homogeneity with the other solvents, a smooth curve was traced over these peaks before the deconvolution.

TABLE 1

λ_{max} and Intensities of the Component Bands of the Absorption Spectra together with the Logarithm of the Proton Transfer Constant

Number	*Solvent*	*Type*	λ_1 *(nm)*	λ_2 *(nm)*	H_1	H_2	*log* K_{PT}[a]
1	Butyl acetate	HBA	436	490	0·440	0·904	0·313
2	Ethyl acetate	HBA	446	493	0·712	1·077	0·180
3	Methyl acetate	HBA	446	495	0·612	1·017	0·220
4	Acetone	HBA	440	498	0·462	1·212	0·418
5	*n*-Propyl acetate	HBA	436	490	0·502	1·111	0·345
6	Ethyl benzoate	NHB	445	499	0·460	1·222	0·425
7	Benzyl alcohol	HBD	455	505	0·610	1·022	0·224
8	1-Chlorobutane	NHB	452	492	0·813	0·862	0·025
9	Butyronitrile	HBA	445	499	0·480	1·237	0·411
10	1-Butanol	HBD	442	498	0·505	0·680	0·130
11	2-Butanol	HBD	448	500	0·524	0·737	0·148
12	2-Butanone	HBA	444	497	0·559	1·297	0·366
13	Carbon tetrachloride	NHB	446	484	0·488	0·368	−0·122
14	Dioxane	HBA	438	490	0·723	0·943	0·115
15	*N*,*N*-Dimethyl acetamide	HBA	417	499	0·626	0·324	−0·213
16	*N*,*N*-Dimethyl formamide	HBA	421	501	0·601	0·488	−0·090
17	Dimethyl sulfoxide	HBA	422	483	0·655	0·376	−0·241
18	1-Hexanol	HBD	453	501	0·531	0·804	0·180
19	Cyclohexanol	HBD	456	503	0·607	0·808	0·125
20	1,2-Dichloroethane	NHB	443	496	0·529	1·378	0·415
21	1,1,2,2-Tetrachloroethane	NHB	447	501	0·503	1·403	0·445
22	Trichloroethylene	NHB	448	492	0·638	0·886	0·142
23	Tetrachloroethylene	NHB	448	485	0·509	0·350	−0·162
24	Diethyl ether	HBA	439	485	0·850	0·907	0·028
25	Ethanol	HBD	409	482	0·521	0·424	−0·081
26	Formamide	HBD	420	470	0·736	0·274	−0·429
27	*N*-Methylformamide	HBD	411	459	0·776	0·268	−0·461
28	1,2 Dimethoxy ethanol	HBA	439	496	0·621	0·926	0·174
29	Diethylene glycol	HBD	411	458	0·674	0·308	−0·339
30	*iso*-Butanol	HBD	447	499	0·613	0·868	0·151
31	Acetonitrile	HBA	441	496	0·452	1·374	0·488
32	Dichloromethane	NHB	450	498	0·587	1·162	0·297
33	Chloroform	NHB	457	497	0·392	0·469	0·078
34	Methanol	HBD	405	441	0·580	0·259	−0·350
35	1-Pentanol	HBD	454	501	0·593	0·820	0·141
36	2-Pentanol	HBD	444	497	0·514	0·813	0·199
37	Cyclopentanone	HBA	444	502	0·395	1·066	0·431
38	Benzene	NHB	437	489	0·651	1·369	0·323
39	Dichlorobenzene	NHB	447	500	0·425	1·185	0·445
40	*p*-Xylene	NHB	441	489	0·648	1·117	0·236
41	Chlorobenzene	NHB	446	496	0·598	1·316	0·362
42	Benzonitrile	NHB	445	503	0·398	1·394	0·544
43	Cumene	NHB	441	489	0·650	1·160	0·251
44	Toluene	NHB	437	487	0·505	1·055	0·320
45	Anisole	NHB	443	498	0·458	1·280	0·447
46	Propionitrile	HBA	432	499	0·413	0·865	0·320
47	2-Propanol	HBD	415	495	0·326	0·400	0·088
48	1-Propanol	HBD	413	494	0·517	0·513	−0·003
49	Tetrahydrofuran	HBA	436	495	0·577	0·801	0·143

[a] $K_{PT} = H_2/H_1$.

TABLE 2
Physical Constants of the Solvents Used together with Some Empirical Parameters

Number	ε^a	n^a	μ^a *D*	π^{*b}	α^b	β^b	$\delta^{a,c}$	$\delta_d{}^d$	$\delta_p{}^d$	$\delta_h{}^d$	$DN_N{}^e$	$ET_N{}^f$	AN^g
1	5·01	1·3942	1·87	0·46	0	0·45	17·4	7·7	1·8	3·1	0·39	0·241	9·16
2	6·02	1·3724	1·82	0·55	0	0·45	18·6	7·7	2·6	3·5	0·44	0·228	8·61
3	6·68	1·3614	1·72	0·60	0	0·42	19·6	7·6	3·5	3·7	0·42	0·287	11·08
4	20·56	1·3587	2·69	0·71	0·08	0·48	20·5	7·6	5·1	3·4	0·44	0·355	13·92
5	6·00	1·3844	1·78	0·58	0	0·45	18·8				0·41	0·210	7·86
6	6·02	1·5057	1·99	0·74	0	0·41	19·9				0·39	0·228	8·61
7	13·10	1·5404	1·66	0·98	0·60	0·52	24·8	9	3·1	6·7	0·59	0·608	24·49
8	7·39	1·4023	1·90	0·39	0	0	17·1	8	2·7	1	0·00		
9	24·83	1·3838	3·50	0·71	0·19	0·44	21·5	7·5	6·1	2·5	0·43	0·383	15·09
10	17·51	1·3993	1·75	0·47	0·84	0·84	23·3	7·8	2·8	7·7	0·75	0·602	24·24
11	15·80	1·3971		0·40	0·69	0·80	22·1	7·7	2·8	7·1		0·506	20·23
12	18·51	1·3788	2·76	0·67	0·06	0·48	19·0	7·8	4·4	2·5	0·45	0·327	12·75
13	2·23	1·4602	0·00	0·28	0	0·10	17·5	8·7	0·0	0·3	0·00	0·052	1·26
14	2·21	1·4224	0·45	0·55	0	0·37	20·7	9·3	0·9	3·6	0·38	0·164	5·94
15	37·78	1·4384	3·71	0·88	0	0·76	22·1	8·2	5·6	5	0·72	0·401	15·84
16	36·71	1·4305	3·24	0·88	0	0·69	24·8	8·5	6·7	5·5	0·69	0·404	15·97
17	46·45	1·4793	4·06	1·00	0	0·76	24·5	9	8	5	0·77	0·444	17·64
18	13·30	1·4172	1·55	0·40	0·80	0·84	21·9					0·559	22·45
19	15·00	1·4648	1·86	0·45	0·66	0·84	23·3	8·5	2	6·6	0·64	0·500	19·98
20	10·37	1·4448	1·83	0·81	0	0·10	20·0	8·1	4	0·2	0·07	0·327	12·75
21	8·20	1·4940	1·71	0·95	0	0·00	20·5	9·2	2·5	4·6		0·269	10·33
22	3·42	1·4767	0·80	0·53	0	0·05	19·0	8·8	1·5	2·6		0·160	5·77
23	2·28	1·5058	0·00	0·28	0	0·05	19·0	9·3	3·2	1·4		0·037	0·63
24	4·20	1·3524	1·15	0·27	0	0·47	15·1	7·1	1·4	2·5	0·49	0·117	3·97
25	24·55	1·3614	1·66	0·54	0·86	0·75	26·1	7·7	4·3	9·5	0·82	0·654	26·42
26	111·00	1·4475	3·37	0·96	0·71	0·48	39·3	8·4	12·8	9·3	0·93	0·799	32·48
27	182·40	1·4319	3·86	0·90	0·62	0·80	20·3				1·26	0·722	29·26
28	7·20	1·3796	1·71	0·53	0	0·41	17·6				0·52	0·231	8·74
29	37·70	1·4318	2·31	0·92	0·91	0·52	29·1	7·98	4·7	6·62	0·52	0·790	32·10
30	17·93	1·3959	1·79	0·40	0·79	0·84	21·5	7·4	2·8	7·8		0·552	22·15
31	35·94	1·3441	3·53	0·75	0·19	0·40	24·8	7·5	8·8	3·0	0·36	0·460	18·31
32	8·93	1·4242	1·14	0·82	0·13	0·10	20·2	8·8	3	2·96	0·03	0·309	12·00
33	4·81	1·4459	1·15	0·58	0·20	0·10	19·4	8·7	1·5	2·8	0·10	0·259	9·91
34	32·66	1·3284	2·87	0·60	0·98	0·66	29·7	7·4	6	10·9	0·49	0·762	30·93
35	13·90	1·4100	1·70	0·40	0·84	0·86	22·3	7·8	2·2	6·8	0·64	0·568	22·82
36	13·71	1·4064	1·66				22·0					0·488	19·48
37	13·60	1·4375	2·86	0·76	0	0·52	21·3				0·46	0·269	10·33
38	2·27	1·5011	0·00	0·59	0	0·10	18·7	9	0	1	0·00	0·111	3·72
39	9·93	1·5515	2·14	0·80	0	0·03	20·6	9·4	3·1	1·6	0·08	0·225	8·49
40	2·27	1·4958	0·02	0·51	0	0·12	17·9	8·7	0·5	1·5	0·13	0·074	2·18
41	5·62	1·5248	1·62	0·71	0	0·07	19·8	9·3	2·1	1	0·09	0·188	6·94
42	25·20	1·5282	4·01	0·90	0	0·37	17·2	8·5	4·4	1·6	0·31	0·333	13·00
43	2·38	1·4917	0·39	0·41	0	0·17	17·6	8·3	0·09	0·07	0·15		
44	2·38	1·4969	0·31	0·55	0	0·11	18·2	8·8	0·7	1	0·00	0·099	3·22
45	4·33	1·5170	1·25	0·73	0	0·32	19·5	8·7	2	3·3	0·23	0·198	7·36
46	28·86	1·3658	3·50	0·71	0·19	0·37	22·1	7·5	7	2·7	0·41	0·401	15·84
47	18·30	1·3772	1·66	0·48	0·76	0·84	23·5	7·7	3	8	0·93	0·546	21·90
48	20·45	1·3856	3·09	0·52	0·84	0·90	24·3	7·8	3·3	8·5	0·52	0·617	24·87
49	7·58	1·4072	1·75	0·58	0	0·55	18·6	8·2	2·8	3·9	0·52	0·207	7·73

[a] Ref. 21.

[b] Kamlet–Taft solvatochromic solvent parameters for measuring polarity, acidity and basicity of solvents. Ref. 14.

[c] Solubility parameters ($J^{-1/2}$ $cm^{-3/2}$).

[d] Ref. 22.

[e] Normalized donor numbers. Refs 17, 18.

[f] Normalized ET values. Ref. 18.

[g] AN = acceptor numbers. Refs 18, 19.

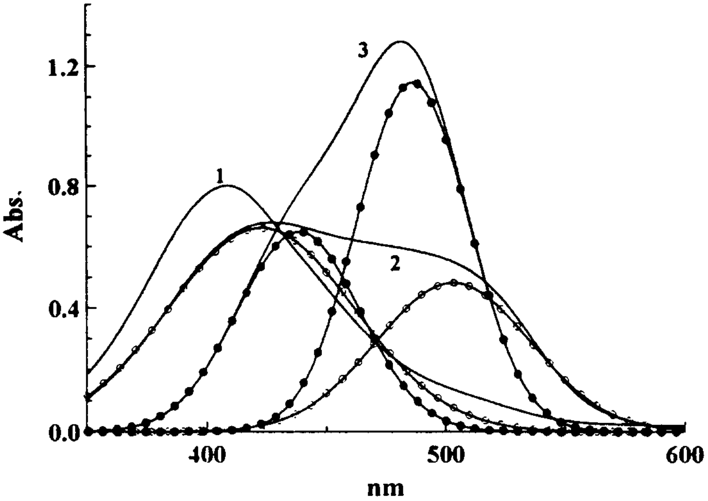


Fig. 2. Absorption spectra of MR in various solvents. 1 = methanol; 2 = DMF; 3 = *p*-xylene. Plain circles indicate the component curves of *p*-xylene spectra. Hollow circles indicate the component curves of DMF spectra.

RESULTS AND DISCUSSION

Aminoazo dyes are characterized by a positive solvatochromism,[10] i.e. with increasing solvent polarity a bathochromic shift of the absorption maximum is generally observed. From Fig. 2 it can be noted that MR seems not to obey this rule. In fact, in methanol it absorbs at 410 nm, whereas in less polar solvents such as dichloromethane or *p*-xylene it absorbs at 490 and 480 nm respectively.

Moreover the MR spectra are generally characterized by large bands sometimes with pronounced shoulders the intensities and positions of which are quite variable and solvent-dependent. Some absorption spectra are shown in Fig. 3 and it is apparent that all the curves exhibit a shoulder, in some cases very marked, and that some spectra even show two distinct absorption maxima.

Figure 4 shows the spectra of MR recorded in methanol/toluene solvent mixtures. The isosbestic point at 444 nm and analysis of the absorbance matrix[11] clearly indicate an equilibrium between at least two forms. This equilibrium is not restricted solely to these solvents, but has been observed in many other pairs of solvents. All these observations confirm that MR exists in solutions in two forms, differently affected by the solvents, and referable to the prototropic equilibrium of Fig. 1 between the undissociated form (I) and the ionic form (II) in which the carboxyl proton is bound to the β-azo nitrogen. Therefore, on the basis that the measured spectra

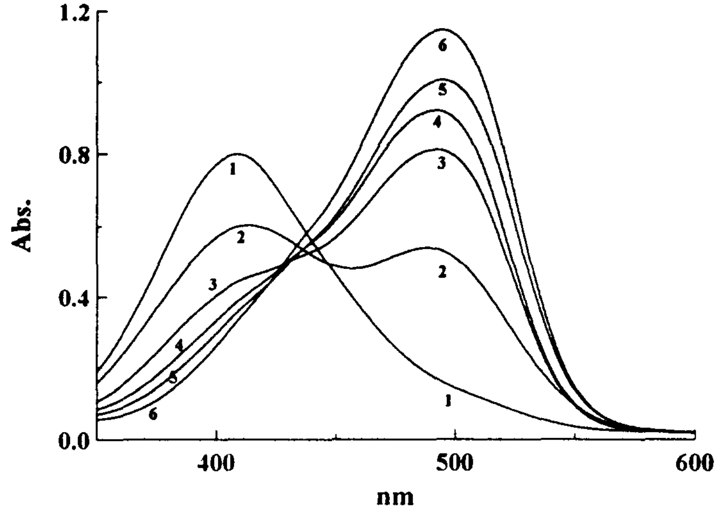


Fig. 3. Absorption spectra of MR in various alcohols. 1 = methanol; 2 = ethanol; 3 = 2-propanol; 4 = 1-butanol; 5 = 2-butanol; 6 = 1-pentanol.

comprise two overlapping bands, we deconvolved them into the component bands and, by analogy with aminoazobenzene dyes, have assigned the lower wavelength band to the azo form (I) and the higher wavelength band to the azonium form (IIa–b).

If we assume that the ratio of the heights of these component bands (H_2/H_1) is equivalent to an equilibrium quotient, the logarithm of this

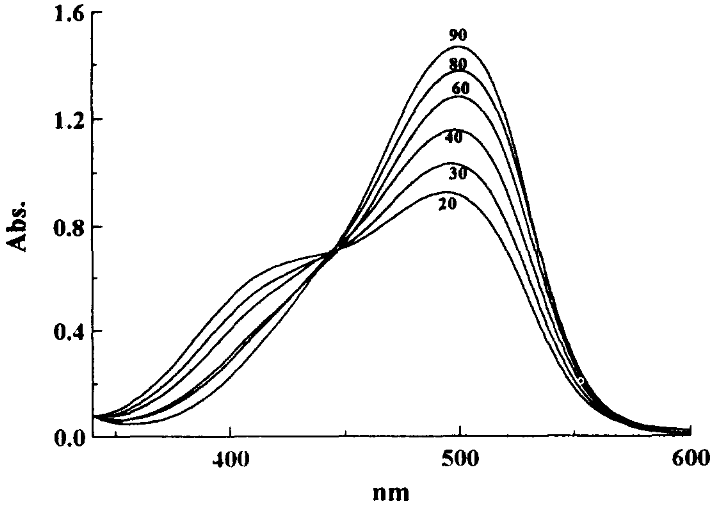


Fig. 4. Absorption spectra of MR in methanol/ethyl benzoate mixtures; the percentage (v/v) of methyl benzoate in the mixture is shown for each spectrum.

ratio (being proportional to the free energy for converting the azo to the azonium form) can be used to measure the solvent effect on the equilibrium.

Various studies on acid–base equilibria in organic solvents have always shown that the proton transfer equilibrium is shifted to the right as solvent polarity increases. Rospenk *et al.*,[7] on studying the intramolecular proton transfer reaction of 2,3,4,5-tetrachloro-6-[(diethylamino)methyl]phenol in six selected solvents, showed that a linear relationship exists between the logarithm of the proton transfer constant and the solvent polarity expressed by the Kirkwood function[12] $K = (\varepsilon - 1)/(2\varepsilon + 1)$.

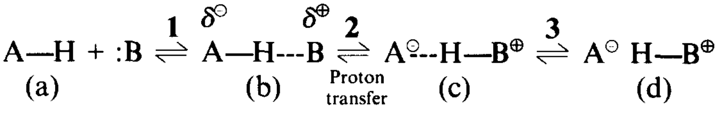
An inspection of the data reported in Table 1 shows, on the contrary, that high polar solvents with a high dielectric constant significantly decrease the logarithm of the proton transfer $K_{PT}(K_{PT} = H_2/H_1)$. In other words, the azonium form decreases as polarity increases. Additionally, the plot of log K_{PT} versus K shows no correlation (R = 0·1), and the points are widely scattered.

Use of the polarizability term[13] $P = (n^2 - 1)/(2n^2 + 1)$ in place of the Kirkwood parameter, or of both K and P in a two-variable equation, does not offer any definite advantage, the correlation remaining substantially unchanged.

This scattering of the points is not surprising owing to the simplification made in choosing only two solvent parameters (polarity and polarizability) for describing this equilibrium and neglecting the non-electrostatic and specific solute–solvent interactions. In fact from a study of the data of Table 1 it is evident that among the solvents with high dielectric constant those with fair basicity and capable of specific interactions shift the reaction equilibrium more toward the left side.

On excluding solvents with high dielectric constant (ε > 20) from the analysis, the correlation with K and P improves remarkably (R = 0·50) and, except for some particular solvents, log K_{PT} in general increases as solvent polarity increases. A further improvement of the correlation is obtained by omitting from the analysis the family of halogenated solvents, and this will be discussed later.

This correlation with K and P only for solvents of weak dielectric constant is not surprising if we consider the equation (Scheme 1) for generic proton transfer from an acid to a base.



$$\underset{(a)}{\text{A—H} + \text{:B}} \overset{1}{\rightleftharpoons} \underset{(b)}{\overset{\delta\ominus}{\text{A}}\text{—H---}\overset{\delta\oplus}{\text{B}}} \underset{\text{Proton transfer}}{\overset{2}{\rightleftharpoons}} \underset{(c)}{\text{A}^{\ominus}\text{---H—B}^{\oplus}} \overset{3}{\rightleftharpoons} \underset{(d)}{\text{A}^{\ominus}\ \text{H—B}^{\oplus}}$$

Scheme 1 Acid–base equilibrium.

The solvent can influence all the steps of the reaction and determine the position of the acid–base equilibrium by differential solvatation of the equilibrating species. Ionizing solvents should promote step 2, whereas dissociating solvents should promote step 3. Solvents with high dielectric constant, which have a high ability to separate the electrical charges and orientate the dipoles, could influence both steps 2 and 3. Solvents could also act themselves as an acid or a base, and hence influence the equilibrium by solute–solvent specific interactions. The breakdown of the correlation of log K_{PT} with K and P for solvents of high dielectric constant may be then due to the fact that in solvents with ε higher than 20 the dissociated form **d** in Scheme 1 should be predominant, and because these solvents are also good EPDs (electron pair donors) they participate in an acid–base equilibrium, with the azonium form shifting the equilibrium to the left.

In order to analyse these solute–solvent specific interactions, we then considered some of the previously proposed sets of empirical solvent parameters, viz.

(1) The α, β, π^* parameters proposed by Taft *et al.*;[14] these measure, respectively, the hydrogen bond donating and hydrogen bond accepting power of the solvents and their polarity–polarizability aptitude.

(2) The Dimroth-Reichard parameter[15] $E_T(30)$; E_T is the molar transition energy expressed in kcal mol^{-1} for the CT absorption band of the 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide betaine dye, and essentially represents a measure of the Lewis acidity for protic solvents. In our case it could account for the probability of strong specific hydrogen bonding interactions between the solvents and the β-azo nitrogen of the azo tautomer.

(3) The Gutmann donor number[16–18] DN; this has been defined as the negative ΔH value for the 1:1 adduct formation between $SbCl_5$ and nucleophilic solvents, and is related also to the solvent basicity.

(4) The Guttmann acceptor number AN, which is derived by the measurement in solvents of various electron pair acceptivities of the ^{31}P NMR shift of triethylphosphane oxide, and is correlated with the solvent electrophilic properties.[18,19]

Therefore, considering the possibility of specific solute–solvent interactions, we then attempted to correlate the log K_{PT} calculated in high dielectric constant solvents with the above-mentioned solvent parameters. The best fit was obtained using eqn (1):

$$\log K_{PT} = 2{\cdot}03 - 0{\cdot}63\pi^* - 0{\cdot}53\beta - 0{\cdot}65\alpha \qquad (1)$$

$$n = 14;\ R = 0{\cdot}934;\ F = 23$$

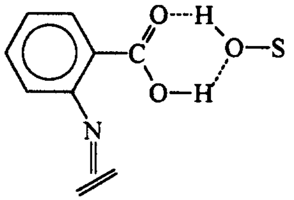


Fig. 5. Chelate hydrogen bonds between HBD solvents and the carboxyl group.

The equation shows that the azo form is favoured by polar solvents with fair donor character and able to form hydrogen bonds. The majority of highly polar solvents used were essentially amphoteric and acting as electron pair donors (EPD) or electron pair acceptors (EPA); therefore the equilibrium could be shifted left owing to the preferential solvation of the azo form by the formation of chelate hydrogen bonds (Fig. 5).

For the low dielectric constant solvents, log K_{PT} can be correlated with π^*, β and δ parameters:

$$\log K_{PT} = 1{\cdot}80\pi^* + 2{\cdot}23\beta - 1{\cdot}1\delta \qquad (2)$$
$$n = 34;\ R = 0{\cdot}940;\ F = 78{\cdot}1$$

Equation (2) clearly indicates that the proton transfer is favoured by basic polar solvents. In this correlation we have taken into account also the solvent cavity effects by using the δ parameter,[20] which is a measure of the work necessary to separate solvent molecules to create cavities suitable to accommodate solute molecules. This parameter also ranks the aptitude of the solvent molecule to form dispersion (δ_d), dipolar (δ_p) and hydrogen (δ_h) bonds. In this case, the inverse correlation between δ and log K_{PT} shows that highly structured solvents shift the equilibrium to the right.

Whilst these analyses have allowed the finding of statistically significant linear relationships, they also clearly demonstrate that for in-depth study of solvent effects it is necessary to take into consideration the specific features of every solvent family. Therefore, the analysis was repeated to classify, in accordance with Taft,[14] the solvents as hydrogen bond donors (HBD), hydrogen bond acceptors (HBA) and non-hydrogen-bonding (NHB).

In Fig. 6 the behaviour of HBA solvents is illustrated.

$$\log K_{PT} = 2{\cdot}37\mathrm{K} + 2{\cdot}02\mathrm{L} - 3{\cdot}6\mathrm{DN} \qquad (3)$$
$$n = 17;\ R = 0{\cdot}986;\ F = 156{\cdot}3$$

The regression equation (3), calculated for HBA solvents, shows that there is a direct correlation between log K_{PT} and the Kirkwood and Lorenz parameter, while an inverse correlation holds between log K_{PT} and DN which we know is a measure of the electron pair donation ability

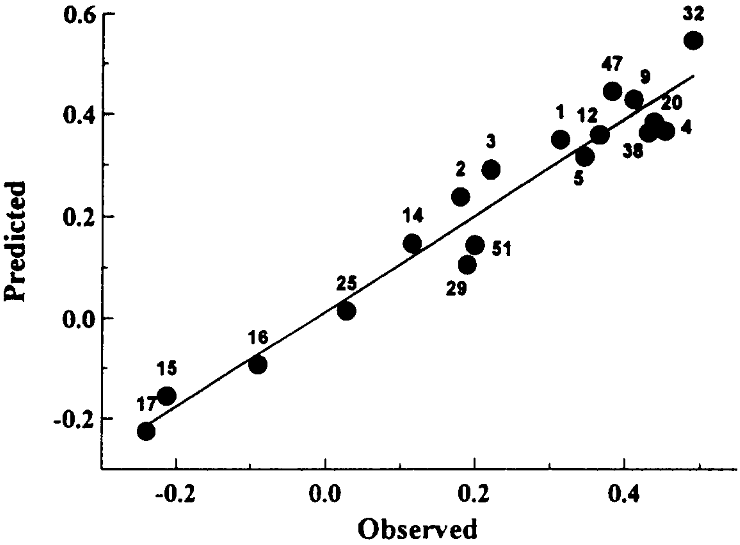


Fig. 6. Plot of the logarithm of the intensity ratios of the component bands of MR in HBA solvents.

or the ability to accept a hydrogen atom in the formation of a hydrogen bond. This correlation shows also that if these solvents act exclusively as polar ones, then the equilibrium is right-shifted, perhaps by the formation of a coordination bond between the positive β-azo or amine nitrogens and the electron pair of the solvent (Fig. 7). On the other hand, if basic behaviour prevails, the solvent can compete with the azo nitrogen to bond the carboxyl hydrogen, and the equilibrium is then left-shifted. However, in order for this to happen the solvent must also be a dissociating one, able to break the carboxyl–azo bond. Thus solvents with high DN and high dielectric constant (dimethylformamide, dimethylacetamide) shift the equilibrium to the left.

For HBD solvents (Fig. 8) the following correlation exists:

$$\log K_{\mathrm{PT}} = 5{\cdot}23 - 0{\cdot}70\mathrm{K} - 0{\cdot}31\mathrm{AN} \tag{4}$$

$$n = 15;\ R = 0{\cdot}980;\ F = 143{\cdot}1$$

From this it is shown that polar and electron pair acceptor solvents shift the equilibrium to the left. From Fig. 8 it is also evident that the HBD solvents which shift the equilibrium more to the left (methanol, glycol, formamide, *N*-methylformamide) are those with the highest dielectric constants and thus able to break the intramolecular bond and to form hydrogen bonds with the carboxyl moiety.

Halo-aliphatic, halo-aromatic and aromatic solvents are in general classified as NHB (non-hydrogen bonding) solvents even if the benzene

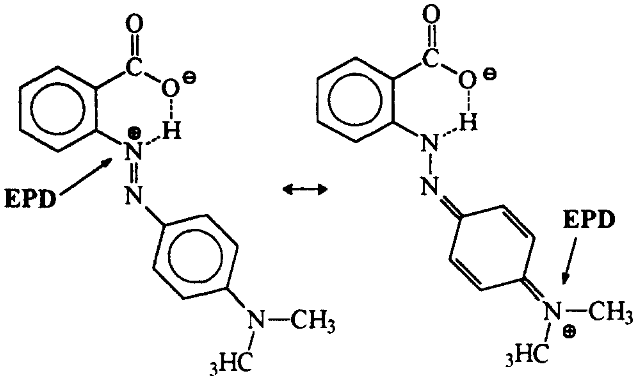


Fig. 7. Coordination bonds between MR cation and electron pair donor solvents.

ring exhibits a moderate donor aptitude. The regression equation for these solvents is:

$$\log K_{PT} = -0{\cdot}46 + 1{\cdot}37\pi^* + 0{\cdot}22\beta - 0{\cdot}59ET_N \qquad (5)$$

$$n = 15;\ R = 0{\cdot}964;\ F = 48{\cdot}1$$

This equation shows the participation of the β basicity parameter in stabilizing the positive charge of the azo nitrogen, and reveals also that the polarity–polarizability properties of the solvents are more important in stabilizing the polar protonated form. More statistically significant correlations can be obtained considering the two separate families of solvents: halogenated and aromatic.

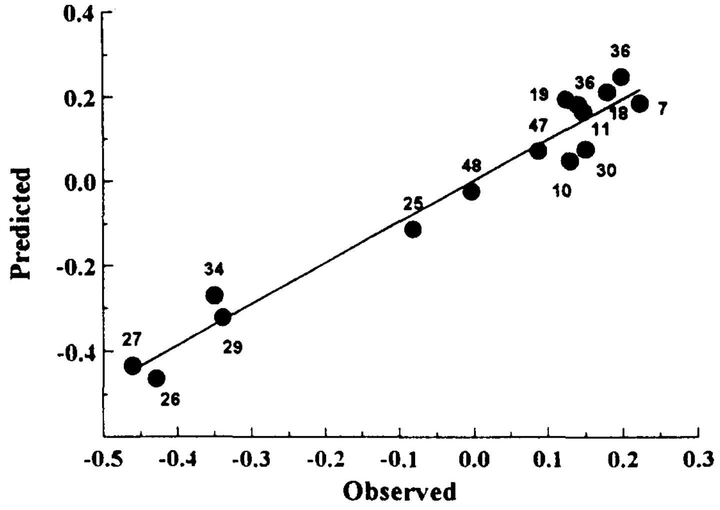


Fig. 8. Plot of the logarithm of the intensity ratios of the component bands of MR in HBD solvents.

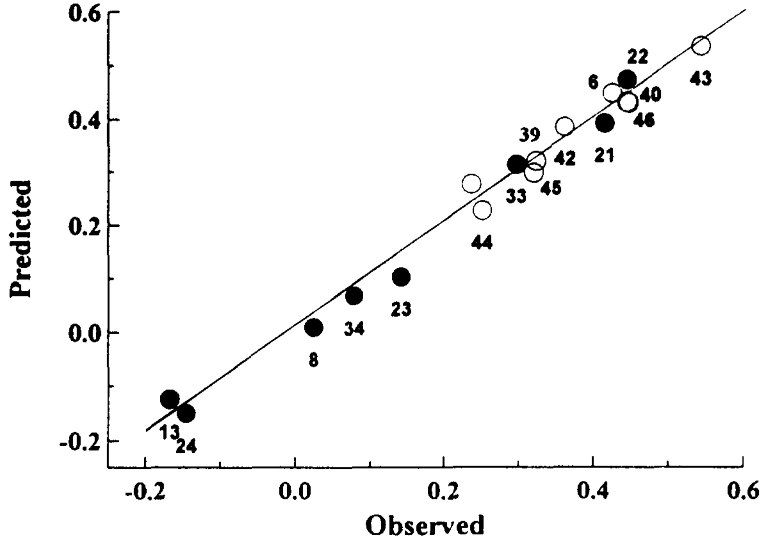


Fig. 9. Plot of the logarithm of the intensity ratios of the component bands of MR in halogenated aliphatic solvents (filled circles) and aromatic solvents (hollow circles).

For the halogenated solvents (Fig. 9, filled circles) the correlation equation (6) is applicable:

$$\log K_{PT} = 2{\cdot}22\pi^* - 0{\cdot}15\alpha - 1{\cdot}4\delta_D \qquad (6)$$
$$n = 8;\ R = 0{\cdot}997;\ F = 251{\cdot}6$$

This indicates that the more polar solvents (high π^*) enhance the solubility of the azonium form and shift the equilibrium to the right, while electron pair acceptors or more structured solvents shift the equilibrium to the left.

For these solvents the correlation may be also represented more simply and equally well by the single parameter equation (7):

$$\log K_{PT} = 0{\cdot}378 + 0{\cdot}974\pi^* \qquad (7)$$
$$n = 8;\ R = 0{\cdot}974;\ F = 112$$

which emphasises the important role of the solvent polarity–polarizability in the determination of the equilibrium.

Finally the behaviour of the aromatic solvents (Fig. 9, hollow circles) may be described by an equation that correlates the log K_{PT} with the polarity–polarizability of the solvent and with the electron donating aptitude of the aromatic ring.

$$\log K_{PT} = 0{\cdot}915\pi^* + 0{\cdot}096\beta \qquad (8)$$
$$n = 9;\ R = 0{\cdot}998;\ F = 778$$

Thus polar and electron donating solvents stabilize the azonium form and shift the equilibrium to the right.

CONCLUSIONS

The solvatochromism of MR is a consequence of an acid–base equilibrium between an azo and an azonium chelated form. Due to the number and complexity of the intermolecular interactions between MR and solvents it is impossible to describe in a quantitative way the effect on the equilibrium of the whole solvent used. The analysis is additionally complicated by the fact that the most solvent properties are intrinsically correlated and many solvents are amphoteric. Notwithstanding this, when separate solvent families are considered, a good and statistically significant relationship was found between the proton transfer equilibrium and solvent properties. The results show that in absence of specific interactions between solute and solvents, the intramolecular hydrogen bond between the carboxyl group and the azo nitrogen is preferred and, in general, polar solvents shift the equilibrium towards the azonium form. On the other hand, polar solvents with good dissociating capability and fair basicity break this intramolecular hydrogen bond and shift the equilibrium toward the azo form by forming an acid–base bond with the carboxyl group.

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