THE EFFECT OF SURFACTANTS ON THE ACID-BASE BEHAVIOUR OF METHYL RED. PART II. A SPECTROPHOTOMETRIC COMPARISON OF THE EFFECT OF TRITON X-100 AND β-CYCLODEXTRIN

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The effect of the non-ionogenic surfactant Triton X-100 (TX) and β-cyclodextrin (CD) on the absorption bands of methyl red was examined. The interactions of methyl red with the both substances were studied based on changes in the absorption curves after their resolution into Gaussian bands. The conditional dissociation constants of methyl red were determined at various concentrations of the additives (in the case of TX, both below and above its cmc value). At c_{TX} = 0.06 mol l^{-1} the change in the conditional dissociation constant of methyl red was $\Delta pK_a = -0.58$ and at c_{CD} = 6 mmol l^{-1} the ΔpK_a value was identical.

A continuation of our previous paper[1], this work deals with the effect of the non-ionogenic surfactant Triton X-100 (TX) on the acid-base behaviour of methyl red (MR). The effect of β-cyclodextrin (CD) on MR was also investigated with a view to comparing the results with those for another azo dye, viz. methyl orange[2]. The interactions of MR with TX and CD were again evaluated based on changes in the electronic absorption spectra in the visible region after resolving the curves into Gaussian bands by mathematical processing. The changes in the acid-base equilibrium of the dye were evaluated from the conditional dissociation constants pK_a of the MR–TX and MR–CD binary systems.

The acid-base properties of methyl red, one of the most widespread acid-base indicators, have been studied by many authors[3 – 8]. The mechanism of dissociation of MR according to the general scheme of dissociation of dimethylazobenzenes[9] can be found in ref.[1]. The values of the dissociation constant of the equilibrium $X + H^{(+)} \rightleftharpoons HX^{(+)}$ determined spectrophotometrically and colorimetrically differ within the range of pK_a = 5.06 – 4.97 (refs[3 – 5]), kinetic measurements gave values of pK_a = 5.00 – 4.88 (refs[6 – 8]).

EXPERIMENTAL

Apparatus

The spectrophotometric measurements were performed on SP 800 and PU 8800 UV-VIS recording spectrophotometers (Pye Unicam, Cambridge) using quartz cells 1 cm optical pathlength. The pH values were measured with a PHM 64 pH-meter (Radiometer, Copenhagen) equipped with a GK 2401B combined electrode. In all experiments, temperature was held constant at 25 ± 0.5 °C.

Chemicals

A stock solution of methyl red (4′-dimethylaminoazobenzene-2-carboxylic acid), $c = 1$ mmol l^{-1}, was prepared from the purified substance (Lachema, Brno); the corresponding amount was dissolved in 3 ml of NaOH solution (0.2 mol l^{-1}) and diluted with redistilled water to 100 ml in a volumetric flask. The purification of the chemical consisted in multiple crystallization from hot acetic acid. Purity was checked by elemental analysis and thin layer chromatography.

A stock solution of Triton X-100 (*p*-octylphenyl-poly(oxyethylene) containing 9.5 oxyethylene units; $M_r = 624.9$; TX) was prepared by dissolution of the chemical obtained from Serva (Heidelberg). Its cmc value is $1.6 \cdot 10^{-3}$ wt./vol.% (1 M $HClO_4$, 25 °C, refs[2,10]), or $1.41 \cdot 10^{-3}$ mol l^{-1} (0.5 M NaCl, 25 °C, ref.[11]).

A stock solution of β-cyclodextrin at $c = 10$ mmol l^{-1} was prepared by dissolving the chemical supplied by Chinoin (Budapest).

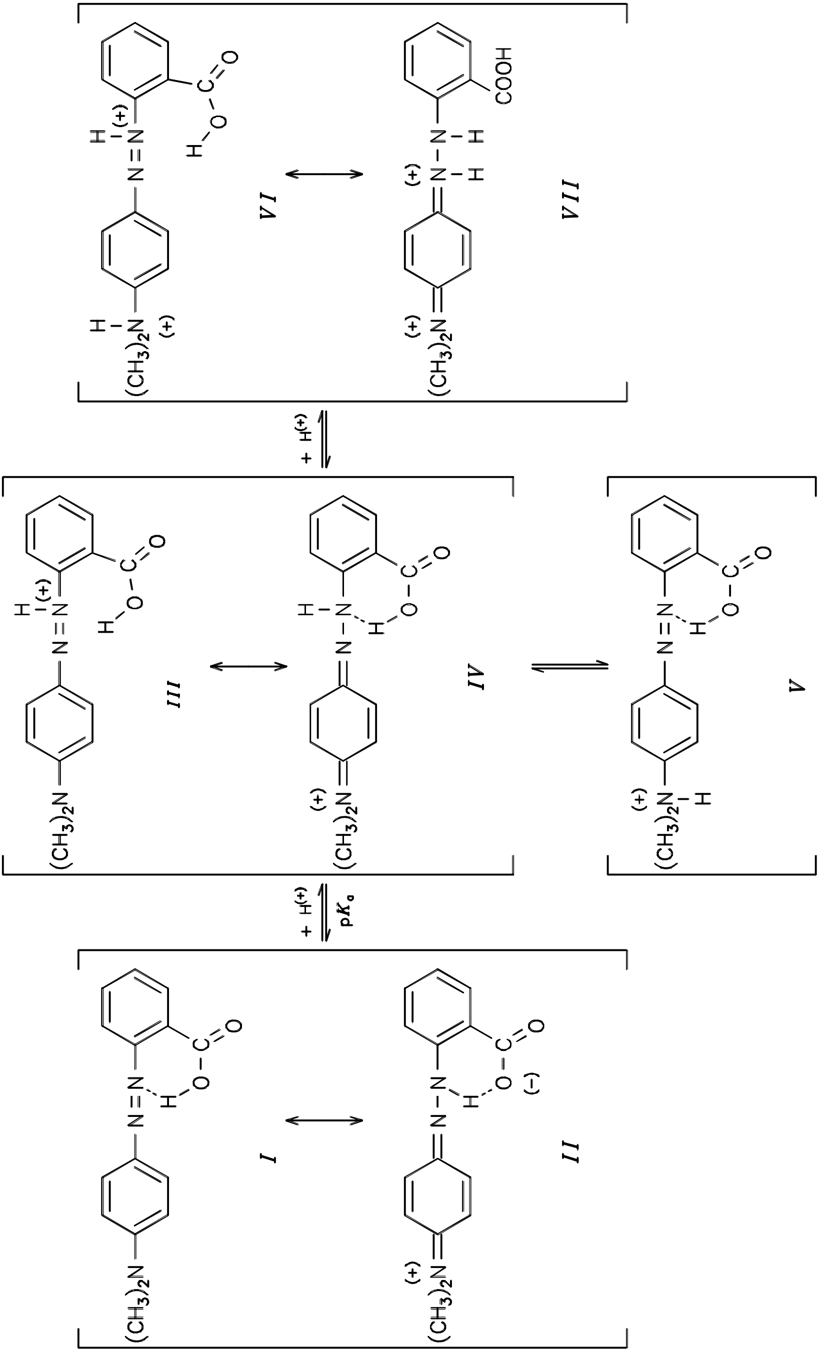
Procedure

The effect of TX and CD on the absorption spectra of MR was examined in acetate buffer. When the conditional dissociation constants were measured, the pH was adjusted by adding NaOH or HCl (0.2 mol l^{-1}) only. Ionic strength of the solutions was invariably held at $I = 0.1$ mol l^{-1} by adding 1 M NaCl. The conditional dissociation constants of MR in the presence of TX or CD were derived from the ascending segments of the sigmoid plots of A vs pH at λ_{max} of the given dye form.

After adjusting pH and ionic strength, the absorption spectra were recorded for the dye alone and in the presence of TX or CD. The absorption curves were resolved mathematically into Gaussian bands[12]. Their parameters (A_{max}, λ_{max}, half band width) were obtained and employed to discuss the effect of TX and CD on the dissociated dye species.

RESULTS AND DISCUSSION

The attention was paid to the individual species X and HX^+ of the dye MR, their mutual equilibrium and the effect of TX and CD on the equilibrium (changes in the pK_a value) and on the tautomeric equilibria of these two dissociated species (Scheme 1). The parameters of the absorption bands (λ_{max}, ε_{max}) of the species are given in Table I. The isosbestic point of the $X + H^+ \rightleftharpoons HX^+$ protonation equilibrium lies at 464 nm. The $HX^+ + H^+ \rightleftharpoons H_2X^{2+}$ equilibrium was not investigated.



SCHEME 1

The Effect of Triton X-100 on the Absorption Spectra and pK_a Values of Methyl Red

At pH 3.93, at which the HX^+ species predominates in the MR–TX binary system, increase in the concentration of TX brings about a hypochromic and hypsochromic effect in the spectrum of the dye (Fig. 1*a*). Table II demonstrates that the positions of the resolved bands of the HX^+ species, viz. the band of the high-frequency component HF and the band of the low-frequency component LF (ref.[1]), whose existence has been suggested[13], do not change appreciably for the red form of the dye up to $c_{TX} \approx 1 \cdot 10^{-3}$

TABLE I
Spectral parameters of the MR species

MR form			pH	λ_{max}, nm	$\varepsilon_{max} \cdot 10^{-4}$ l mol^{-1} cm^{-1}
X	*I, II*		≥ 7	430	2.08
HX^+	*III, IV*	HF	< 4	522	4.71
		LF		558	1.47
	V			320	0.29
H_2X^{2+}	*VI, VII*		2 M H_2SO_4	515	4.90

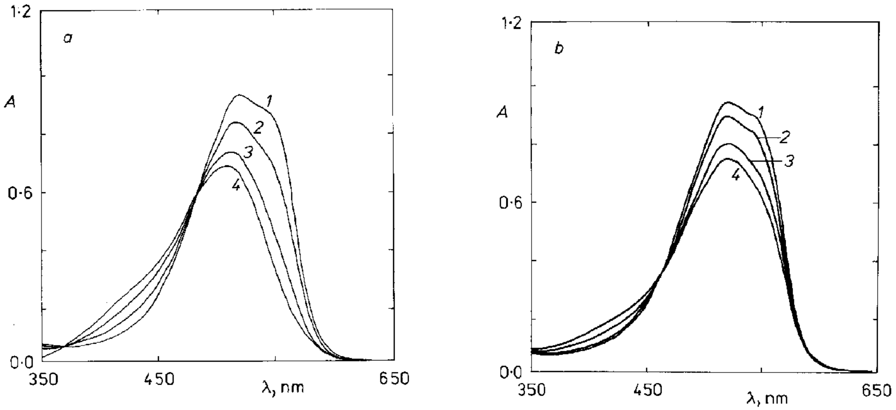


FIG. 1
Absorption spectra of the MR–TX (*a*) and MR–CD (*b*) binary systems; pH 3.93, I = 0.1 mol l^{-1} (NaCl), c_{MR} = 0.02 mmol l^{-1}, c_{TX} (mmol l^{-1}): *1* 0, *2* 1.0, *3* 5.0, *4* 30; c_{CD} (mmol l^{-1}): *1* 0, *2* 0.5, *3* 2.0, *4* 4.0

mol l^{-1} (which is roughly the cmc, ref.[11]), only the hypochromic effect mentioned takes place.

The character of the spectrum alters after the critical micellar concentration is surpassed. Micelles form in the solution, and the dye solubilizes. The absorption bands of LF and HF lie roughly at 517 and 509 nm, respectively.

The effect of TX on the dissociation equilibrium of the dye is apparent from Fig. 1*a*: the absorption band of the LF form of the micellized dye merges with that of the HF form to give a single band with $\lambda_{max} \approx 510$ nm (for LF, the difference in the λ_{max} values between the micellarly solubilized dye and the unaffected dye is $\Delta\lambda \approx 40$ nm). At the same time, as the concentration of TX in both the subcritical and supercritical regions is increased, the band in the short-wavelength spectral region with $\lambda_{max} \approx 430$ nm becomes more and more apparent; this band corresponds to the deprotonated dye species X. This effect deepens as the cmc is surpassed.

The absorption spectra of MR change in the presence of TX in a manner similar to that in the presence of CPB (ref.[1]). In the region of subcritical concentrations of TX, when neither of the HF and LF forms is preferred on the expense of the other, the two forms interact with the pre-micellar clusters of the surfactant in a similar way. As a

TABLE II
Parameters of the resolved absorption bands of the HX^+ species in the MR–TX and MR–CD binary systems

Concentration mmol l^{-1}	HF form		LF form	
	λ_{max}, nm	$\varepsilon_{max} \cdot 10^{-4}$ l mol^{-1} cm^{-1}	λ_{max}, nm	$\varepsilon_{max} \cdot 10^{-4}$ l mol^{-1} cm^{-1}
		Triton X-100		
–	522.5	4.71	558.0	1.47
1	520.6	4.15	557.1	0.87
5	515.2	2.77	516.5	0.81
30	509.4	2.32	517.1	1.05
50	508.4	2.22	517.1	1.01
		β-cyclodextrin		
–	522.5	4.71	558.0	1.47
0.5	522.1	4.37	557.7	1.08
2	523.3	3.88	558.0	0.83
4	522.5	3.08	558.3	0.70

result, the acid-base equilibrium shifts in favour of the yellow (basic) species X, whereupon the absorbance in the 430 nm range increases.

This process continues, and becomes even more pronounced, in the supercritical concentration region of the surfactant. The equilibrium between HF and LF is disturbed above cmc, and the electronic structure of LF is affected by its solubilization into micelles (the λ_{max} value decreases markedly). The pronounced decrease in the intensity of the HF band (its ε_{max} value) may be indicative of the fact that the HF species, which is most likely located in the outer layer of the micelles, is more inclined to dissociation and transforms in the species X. This is also borne out by the conditional dissociation constants of the MR–TX binary system (Table III).

The Effect of β-Cyclodextrin on the Absorption Spectra and pK_a Values of Methyl Red

The behaviour of the MR–CD system at pH 3.93 (HX^+ species) can be discussed with respect to its absorption spectra shown in Fig. 1*b*. As in the MR–CPB and MR–TX systems, increase in the CD concentration is accompanied by a hypochromic effect. However, the absorption spectrum of the HX^+ species retains its character in the presence of CD, two absorption bands being apparent. The λ_{max} values of the HF and LF forms, obtained by mathematical deconvolution, are not affected by the concentration of CD, only the intensity of the bands decreases with increasing c_{CD} and the absorbance in the spectral region corresponding to the yellow, dissociated form of the dye increases.

The dissociation constants of the MR–CD binary system are given in Table III. Addition of CD induces decrease in the pK_a value of methyl red. The change in the

TABLE III
Conditional dissociation constants pK_a in the MR–TX and MR–CD binary systems

c_{TX} mmol l^{-1}	pK_a[a]	c_{CD} mmol l^{-1}	pK_a[a]
–	4.95 ± 0.02	–	4.95 ± 0.02
0.5	4.77 ± 0.02	0.1	4.64 ± 0.04
1	4.73 ± 0.02	0.4	4.51 ± 0.05
5	4.54 ± 0.03	1	4.42 ± 0.05
10	4.45 ± 0.04	2	4.37 ± 0.06
40	4.35 ± 0.06	4	4.35 ± 0.06
60	4.33 ± 0.06	6	4.33 ± 0.06

[a] RSD determined from 4 to 7 measurements.

pK_a is highest in the region where c_{CD} is low and the dye is not bonded completely in the inclusion complex. Starting from c_{CD} > 2 mmol l^{-1}, the pK_a tends to a value of roughly 4.30.

The results for Triton X-100 can be interpreted as follows. At c_{TX} < cmc the pK_a value of the dye changes only negligibly. The decrease in the pK_a value is only more marked at c_{TX} > cmc, which indicates that a shift of the dissociation equilibrium takes place particularly in the micellar system. This can be explained so that owing to the low charge localization at its surface, the non-ionogenic surfactant in the monomeric form is incapable of any marked electrostatic interaction with the ionic species of the dye. Apparently, the hydrophobic interactions of the surfactant with a molecule of the dye are of minor importance as well, because the spectrum of the HX^+ species retains its character at c_{TX} < cmc. After surpassing the cmc, the micelles play a major role in the change in the acid-base properties of MR. In its interaction with MR, the bulky micelle[14] enables the dye molecule to be incorporated between oxyethylene chains of the surfactant, where the oxygen atoms affect, through their lone electron pairs, the electronic state of the dye molecule. Presumably, the LF form, which is solubilized more markedly, penetrates more closely to the hydrophobic micellar core, as indicated by the changes in the absorption band belonging to this form, in comparison with the HF form. Due to the effect of the hydrocarbon chains the relative permittivity in the medium of the micelle is probably different from that in the surrounding aqueous solution, and this change in the micro-environment will also contribute to the effect on the pK_a value of methyl red.

In its interaction with β-cyclodextrin, the molecule of methyl red is incorporated into a cavity with glycosidic oxygen atoms which possess lone electron pairs that affect appreciably the electronic state of MR. The decrease in the pK_a value can be explained in terms of the different stability of the inclusion complexes of the neutral and protonated dye species[15]. The stability of the inclusion complex increases with increasing polarizability of the guest molecule, which is proportional to the number of lone electron pairs in a molecule. The X species exhibits a higher polarizability and thus forms a more stable complex, and the dissociation equilibrium of MR, in interaction with CD, shifts in favour of that species. The two forms, HF and LF, form complexes of roughly identical stability, which, however, is lower than the stability of the complex of the X species. Their polarizability is lower due to the effect of the positive charge at the amino nitrogen atom. The decrease in the relative permittivity in the environment of the dye molecule after its inclusion into a hydrophobic cavity of cyclodextrin can also contribute to the change in the pK_a value of methyl red[16].

In conclusion, the interaction of Triton X-100 and of β-cyclodextrin with methyl red is similar as far as their effects on the acid-base equilibria of the dye are concerned. In the former case, the oxygen atoms of the oxyethylene chains affect, through the increased electron density, the electronic state of molecules of MR. In the latter case, the dye included is also affected by the lone electron pairs of the glycoside oxygens. It is, however, important that a difference in the behaviour of surfactants as compared to CD exists such that the changes in the absorption spectra of the dye in the presence of surfactants allow a more detailed evaluation of the interaction mechanism.

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