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**THE EFFECT OF SURFACTANTS ON THE ACID-BASE BEHAVIOUR OF METHYL RED. PART I. A SPECTROPHOTOMETRIC COMPARISON OF THE EFFECT OF CPB AND SDS**

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The effect of a cationic (CPB) and an anionic (SDS) surfactant on the bands in the absorption spectra of methyl red was studied. The interactions of methyl red with the two surfactants were monitored on the basis of the changes in the absorption curves that were mathematically deconvoluted into Gaussian shape absorption bands. The methyl red dissociation constants were determined in the presence of the two surfactants at sub- and supercritical micelle concentrations. The methyl red conditional dissociation constants changed by  $\Delta pK_a = -1.47$  for  $c(\text{CPB}) = 5 \text{ mmol l}^{-1}$  and  $\Delta pK_a = 0.81$  for  $c(\text{SDS}) = 4 \text{ mmol l}^{-1}$ . The contributions of the individual forms of methyl red to the interactions with CPB and SDS were discussed.

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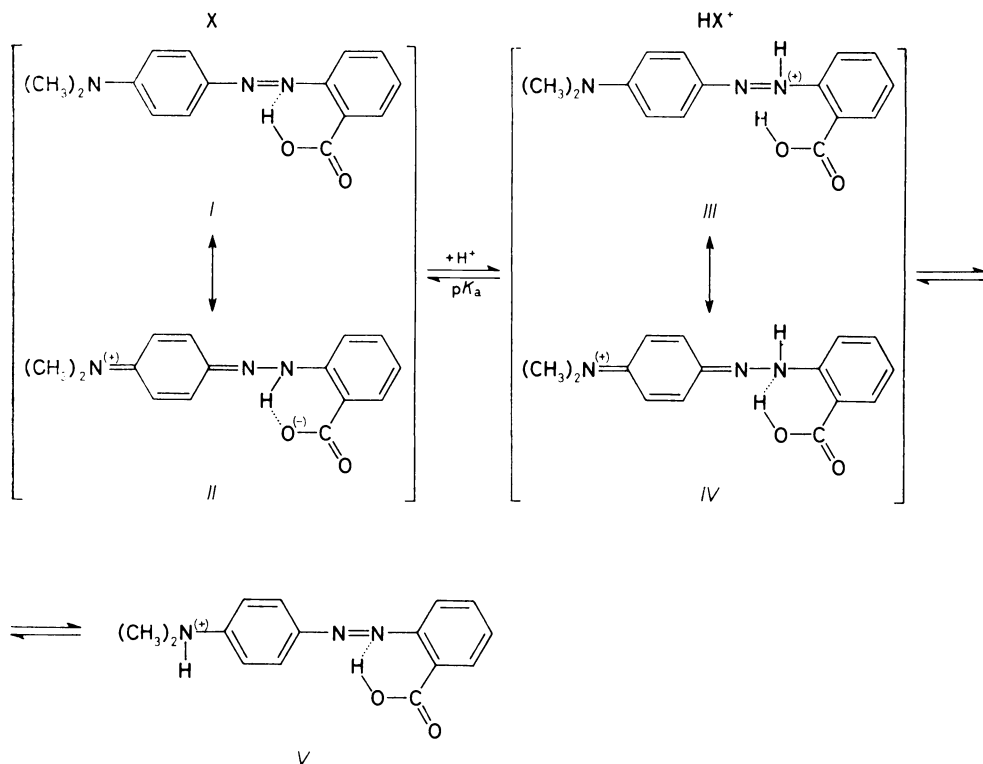
The extensive research carried out recently has confirmed the ability of surface active substances — surfactants — to affect the absorption electronic spectra of solutions of many dyes, including the triphenylmethane and azo dyes. This property has been utilized in spectrophotometric determinations of metal ions<sup>1-3</sup> and for an improvement of spectral characteristics of the coloured system<sup>4-7</sup>.

Whereas the principles of the complex formation in the metal-dye binary system and of ion association followed by micelle solubilization in the metal-dye-surfactant ternary system have been studied in detail, the study and description of the mechanism of the interaction between the dye and the surfactant is being further object of interests<sup>8-11</sup>. Therefore, we have studied the acid-base and spectral characteristics of some analytically important chromogenic reagents and indicators<sup>12-15</sup> in the presence of sub- and supercritical micelle concentrations of surfactants.

The present paper deals with the effects of the cationic surfactant cetylpyridinium bromide (CPB) and the anionic surfactant sodium laurylsulphate (SDS) on the acid-base behaviour of methyl red (MR). The MR interaction with the surfactants was evaluated from the change in the absorption electronic spectra in the visible region, on the basis of a mathematical treatment of the absorption curves obtained (a separation of the spectral bands into independent Gaussian bands)<sup>16</sup>. The magnitude of these changes in the MR-CPB and MR-SDS systems was determined from the con-

ditional dissociation constants of the dye in the presence of the surfactants and the dependences of the methyl red  $pK_a$  values on the surfactant concentrations in solution were measured.

Methyl red (C.I. 13 020) belongs among the best known and most widely used acid-base indicators<sup>17</sup> and the MR dissociation mechanism is shown in Scheme 1.



SCHEME 1

The solutions are yellow in the neutral region, corresponding to the MR forms *I* and *II* ( $\lambda_{max} = 430$  nm,  $\epsilon_{max} = 2.08 \cdot 10^4$  mol<sup>-1</sup> l cm<sup>-1</sup>). Machida et al.<sup>18</sup> assume that form *II* predominates in solution.

Protonation of the electroneutral form yields the conjugate acid  $HX^+$ . The azoform *V*, protonated on the nitrogen atom of the amine group, is assigned with an analytically unimportant band in the UV region ( $\lambda_{max} = 320$  nm) (ref.<sup>19</sup>). The absorption bands of the azonium form *III* and the quinoid form *IV* could be in the visible region. Various authors<sup>18,20</sup> assume that form *IV* predominates in solution. It can be concluded from analogy with methyl orange<sup>21</sup> that the low-frequency component of the band (LF form) is assigned to a  $\pi_1 \rightarrow \pi_1^*$  transition of a solvate

in which there is specific hydrogen bonding between the solvent ( $\text{H}_2\text{O}$ ) and the azo nitrogen, and the high-frequency component (HF form) to a  $\pi_1 \rightarrow \pi_1^*$  transition of solvate in which the interaction is absent. The mathematical separation of the absorption bands yielded the following  $\epsilon$  values: HF form –  $\epsilon_{522.5} = 4.72 \cdot 10^4 \text{ mol}^{-1} \cdot \text{l cm}^{-1}$ , LF form –  $\epsilon_{558} = 1.48 \cdot 10^4 \text{ mol}^{-1} \text{ l cm}^{-1}$ . The isosbestic point (ib) for the protonation equilibrium between X and  $\text{HX}^+$  lies at 464 nm and the values of the dissociation constant for this equilibrium, determined mainly spectrophotometrically and colorimetrically, are in the range,  $\text{p}K_a = 5.06$  to  $4.97$  (refs<sup>17,22,23</sup>). The  $\text{p}K_a$  value obtained from kinetic measurements is between 5.00 and 4.88 (refs<sup>24–26</sup>).

Double protonation of form X leads to the tautomeric forms that exist in strongly acidic media ( $\lambda_{\text{max}} = 515 \text{ nm}$ ,  $\epsilon_{\text{max}} = 4.9 \cdot 10^4 \text{ mol}^{-1} \text{ l cm}^{-1}$ ) (ref.<sup>27</sup>).

The present paper is primarily concerned with the forms X and  $\text{HX}^+$ , their equilibrium and the effects of the surfactants.

## EXPERIMENTAL

### Apparatus

The spectrophotometric measurements were carried out on an SP 800 and PU 8800 UV/VIS instruments (Pye Unicam, Cambridge, England), in 1 cm quartz cells. The solution pH was measured using a GK 2401B glass combination electrode and a PHM 64 pH-meter (Radiometer, Copenhagen, Denmark). The solutions were always thermostatted at  $25 \pm 0.5^\circ\text{C}$ .

### Chemicals

A  $1.0 \cdot 10^{-3} \text{ mol l}^{-1}$  stock solution of MR (4'-dimethylaminoazobenzene-2-carboxylic acid) was prepared from the purified and dried substance (Lachema, Brno, Czechoslovakia), by dissolving the weighed amount of the substance in 3 ml of  $0.2 \text{ mol l}^{-1}$  NaOH and diluting to 100 ml with redistilled water. MR was purified by repeated recrystallization from hot acetic acid and the purity was checked by elemental analysis and TLC.

A  $0.1 \text{ mol l}^{-1}$  aqueous stock solution of SDS was prepared by dissolution of the substance obtained from Sandoz (Switzerland).

A  $1 \cdot 10^{-2} \text{ mol l}^{-1}$  methanol–aqueous stock solution of CPB (Lachema, Brno, Czechoslovakia) was prepared by dissolving the purified and dried substance in 20% (v/v) methanol. CPB was purified on active charcoal and by multiple recrystallization from methanol. The purity was checked by elemental analysis. The investigations were carried out over the total methanol concentration regions of 0.1 to 10% (v/v).

### Procedure

In the determination of the conditional dissociation constants, the pH was adjusted by additions of NaOH and HCl only. The solution ionic strength was always maintained at  $I = 0.1 \text{ mol l}^{-1}$ , by adding  $1 \text{ mol l}^{-1}$  NaCl. The conditional dissociation constants of MR in the presence of CPB and SDS were obtained from the ascending parts of the sigmoidal  $A = f(\text{pH})$  dependences at a selected wavelength.

After adjusting the pH to a required value, the absorption spectra were measured for the dye alone and the dye in the presence of CPB or SDS. The curves obtained were treated mathematically<sup>16</sup>, by a separation into individual Gaussian shape absorption bands. Their parameters were obtained ( $A_{\max}$ ,  $\lambda_{\max}$ , halfwidth) and used in the discussion of the surfactant effects on the individual forms of the dye.

## RESULTS AND DISCUSSION

### *The Effect of CPB on the Absorption Spectra and the Change in the $pK_a$ Value*

In the MR-CPB binary system at pH = 3.93, when the  $HX^+$  form predominates in solution, pronounced changes occur in the dye absorption spectrum with increasing CPB concentration (Fig. 1). The wavelengths of the peaks for the HF and LF forms which most probably occur in the solution are not shifted much up to  $c_T \sim 1 \cdot 10^{-3} \text{ mol l}^{-1}$  corresponding roughly to the cmc value, but a hypochromic effect occurs. The evaluation of the changes after the separation of the absorption spectra into individual bands characteristic of forms HF and LF (Table I) confirms that for  $c_T < \text{cmc}$  the principal change is a decrease in the  $\epsilon$  value for both the forms of the dye.

On a subsequent increase in  $c_T$  above  $1 \cdot 10^{-3} \text{ mol l}^{-1}$ , when micelles are formed in the solution and the dye is solubilized, the absorption band peak position of the solubilized forms HF ( $\lambda_{\max} \sim 492 \text{ nm}$ ) and LF ( $\lambda_{\max} \sim 529 \text{ nm}$ ) are virtually unchanged. A hypochromic effect appears only with the form LF.

Fig. 1 also demonstrates the effect of CPB on the dissociation equilibrium of the dye: a gradual increase of  $c_T$  at sub- and supercritical values causes an appearance and increase of a band in a short-wave region, with  $\lambda_{\max} \approx 430 \text{ nm}$ , corresponding to the deprotonated form of the dye X. However, the hyperchromic effect is not pronounced with his band after exceeding the cmc.

It is also evident from Fig. 1 that the MR-CPB binary system exhibits a single isosbestic point in the dependence on  $c_T$ , at  $\lambda_{ib} = 468 \text{ nm}$ .

The absorption spectra of MR in the presence of CPB are similar to those of the dye alone, in dependence on the pH. Hence it is highly probable that, at subcritical CPB concentrations when neither form HF nor LF is preferred and both interact with the particles or pre-micellar aggregates of the surfactant in the same way, the acid-base equilibrium is shifted in favour of form X. At surfactant concentrations above the cmc, the trend is analogous, but less pronounced, as form LF is probably solubilized in the micelles (another decrease in  $\epsilon_{529}$ ). The overall change in the acid-base equilibrium due to the effect of  $c_T$  then results solely from equilibrium between forms HF and LF. This reasoning is also supported by the values of the conditional dissociation constants found in the MR-CPB binary system (Table II).

The  $c_T$  limit, above which the decrease in  $pK_a$  lies within experimental error, has been found from linear regression of the  $pK_a$  vs  $\log c_T$  dependence and equals

$c_T = 8.38 \cdot 10^{-4} \text{ mol l}^{-1}$ , which is comparable with the cmc value for CPB ( $6.2 \cdot 10^{-4} \text{ mol l}^{-1}$ ) (ref.<sup>28</sup>).

*The Effect of SDS on the MR Absorption Spectra and pK<sub>a</sub> Value*

When the concentration of the anionic surfactant is increased in the MR–SDS binary system, the absorption curves of the forms HF and LF of the dye change at pH =

TABLE I

The absorption bands of the  $\text{HX}^+$  form in the MR–CPB system

$c_T$ $\text{mol l}^{-1}$	Form HF		Form LF	
	$\lambda_{\text{max}}$ , nm	$\epsilon_{\text{max}} \cdot 10^{-4a}$	$\lambda_{\text{max}}$ , nm	$\epsilon_{\text{max}} \cdot 10^{-4a}$
—	522.5	4.71	558.0	1.47
$1 \cdot 10^{-4}$	521.1	3.86	556.8	1.12
$5 \cdot 10^{-4}$	519.8	3.16	556.8	0.58
$1.5 \cdot 10^{-3}$	491.4	2.03	528.5	1.08
$3 \cdot 10^{-3}$	492.6	2.07	529.6	0.98
$5 \cdot 10^{-3}$	491.1	2.05	528.5	0.91

<sup>a</sup>  $\epsilon_{\text{max}}$  in  $\text{mol}^{-1} \text{ l cm}^{-1}$ .

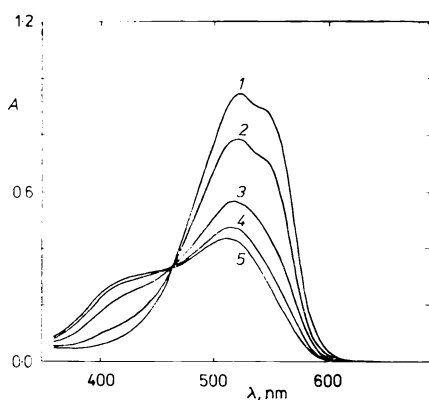


FIG. 1

Absorption spectra of the MR–CPB binary system. pH 3.93,  $c_{\text{MR}} = 2 \cdot 10^{-5} \text{ mol l}^{-1}$ ,  $I = 0.1 \text{ mol l}^{-1}$  (NaCl),  $c_{\text{CPB}}$  ( $\text{mmol l}^{-1}$ ) for curves: 1 0, 2 0.1, 3 0.5, 4 1.5, 5 5.0

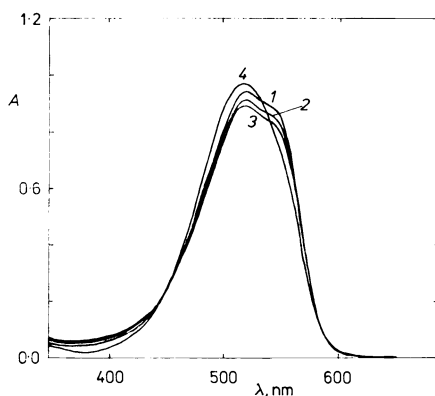


FIG. 2

Absorption spectra of the MR–SDS binary system. pH 3.93,  $c_{\text{MR}} = 2 \cdot 10^{-5} \text{ mol l}^{-1}$ ,  $I = 0.1 \text{ mol l}^{-1}$  (NaCl),  $c_{\text{SDS}}$  ( $\text{mmol l}^{-1}$ ) for curves: 1 0, 2 0.5, 3 1.0, 4 4.0

= 3.93 (Fig. 2). An analysis of the mathematically separated spectral curves indicates (Table III) that  $\lambda_{\max}$  values of the two absorption bands are unchanged by variation in  $c_T$ . The intensity of the band corresponding to form HF decreases with increasing  $c_T$ , up to  $c_T \sim 1.5 \cdot 10^{-3} \text{ mol l}^{-1}$  which corresponds to the surfactant cmc. Above this concentration limit, a hyperchromic effect appears with the absorption band of form HF, with simultaneous decrease in the absorbance for the band of form LF. No change occurs in the spectrum at low wavelengths.

It can be concluded from these data that, at  $c_T < \text{cmc}$ , the electropositive form of the dye LF, with strongly localized positive charge, is bound into an ion associate with the negatively charged SDS particles that is stronger than that between HF form and SDS, causing a shift in the equilibrium between forms HF and LF in favour of the latter. At supercritical micellar concentrations, the formation of SDS micelles prefers form HF that can be bound in the micelle through electrostatic interaction of the alkylsulphate anion of the surfactant and the electropositively charged form HF — the ion associate solubilized in the micelle interior. This changes the equilibrium between the two forms and the intensity of bands ( $\epsilon_{\max}$ ) of form LF strongly decreases in favour of that of the solubilized form HF. This conclusion is also supported by the fact that the character of the MR spectrum in the presence of a supercritical micelle concentration of SDS is analogous to the spectra of alcoholic solutions of MR. In the absorption spectra of ethanolic MR solution and in all MR solutions with lower relative permittivity, the absorption band at  $\lambda_{\max} = 522 \text{ nm}$  predominates, because hydrogen bonding, characteristic of form LF ( $\lambda_{\max} = 560 \text{ nm}$ ), does not occur in media of a low relative permittivities. Thus it can be assumed that the micromedium of the micelle interior exerts an analogous effect on the  $\pi$ -electron system of the dye as the medium of ethanolic solutions of MR. In contrast to CPB, SDS does not cause pronounced changes in the MR spectrum in the region of  $\lambda_{\max} \sim 430 \text{ nm}$ , which suggests a small solubilizing ability of the SDS micelles compared with the CPB micelles, for the deprotonated form of the dye. This conclusion also follows from Table IV.

Tables II and IV demonstrate very different effects of the anionic tensides SDS and the cationic tenside CPB.

At subcritical concentrations  $c_T$  of SDS  $< 2 \cdot 10^{-3} \text{ mol l}^{-1}$ , the conditional dissociation constants  $\text{p}K_a$  for SDS do not change much, but, on exceeding this concentration limit, the  $\text{p}K_a$  values increase (0.81 log unity). An increase by up to 2 units has been observed<sup>26</sup>. The concentration limit,  $c_T = 1.86 \cdot 10^{-3} \text{ mol l}^{-1}$  (cmc for SDS =  $1.42 \cdot 10^{-3} \text{ mol l}^{-1}$ ,  $I_{\text{NaCl}} = 0.1 \text{ mol l}^{-1}$ ,  $t = 25^\circ\text{C}$ , (ref.<sup>28</sup>)), was found from the regression dependence of  $\text{p}K_a$  vs  $\log c_T$ .

The absorption spectra and the changes in the conditional dissociation constants in the MR-CPB and MR-SDS binary systems suggest completely different types of interaction between the dye and the two surfactant types, at both sub- and supercritical concentrations of the tensides. During association of the monomeric form

TABLE II

The conditional  $pK_a$  values in the MR-CPB system

$c_T, \text{mol l}^{-1}$	$pK_a^a$
—	$4.95 \pm 0.02$
$5 \cdot 10^{-5}$	$4.43 \pm 0.02$
$1 \cdot 10^{-4}$	$4.25 \pm 0.03$
$4 \cdot 10^{-4}$	$3.86 \pm 0.02$
$8 \cdot 10^{-4}$	$3.60 \pm 0.03$
$1.2 \cdot 10^{-3}$	$3.57 \pm 0.03$
$3 \cdot 10^{-3}$	$3.48 \pm 0.04$
$5 \cdot 10^{-3}$	$3.48 \pm 0.04$

<sup>a</sup> Standard deviation obtained from 4 to 7 values.

TABLE III

The absorption bands of the  $HX^+$  form in the MR-SDS system

$c_T, \text{mol l}^{-1}$	Form HF		Form LF	
	$\lambda_{\text{max}}, \text{nm}$	$\epsilon_{\text{max}} \cdot 10^{-4}^a$	$\lambda_{\text{max}}, \text{nm}$	$\epsilon_{\text{max}} \cdot 10^{-4}^a$
—	522.5	4.71	558.0	1.47
$5 \cdot 10^{-4}$	522.2	4.61	557.7	1.31
$1 \cdot 10^{-3}$	521.4	4.47	557.2	1.31
$4 \cdot 10^{-3}$	521.1	4.86	557.7	0.63

<sup>a</sup>  $\epsilon_{\text{max}}$  in  $\text{mol}^{-1} \text{l cm}^{-1}$ .

TABLE IV

The conditional  $pK_a$  values of the MR-SDS system

$c_T, \text{mol l}^{-1}$	$pK_a^a$
—	$4.95 \pm 0.02$
$5 \cdot 10^{-4}$	$4.98 \pm 0.05$
$1 \cdot 10^{-3}$	$5.02 \pm 0.03$
$2 \cdot 10^{-3}$	$5.12 \pm 0.04$
$4 \cdot 10^{-3}$	$5.76 \pm 0.08$

<sup>a</sup> Standard deviation obtained from 4 to 8 values.

of CPB with the electropositive, protonated form of MR, it is understandable that cation  $CP^+$  and dye  $HX^+$  repulse each other electrostatically and thus the association constant in this system is lower than that in the system of  $CP^+$  and electro-neutral dye X. This leads to preference of one of the tautomeric forms of X. The result of these interactions is a strong shift of conditional dissociation constant  $K_a$  to higher values ( $\Delta pK_a \sim 1.35$ ). The character of these phenomena has been explained on the basis of a pseudophase ion-exchange model<sup>29</sup>, with a contribution from hydrophobic interactions<sup>30,31</sup>.

The hydrophobic character of the dye-micelle interaction in the MR-SDS binary system is suppressed at  $c_T < cmc$ , due to the formation of an ion associate between the positively charged dye  $HX^+$  and anion  $DS^-$ . At  $c_T > cmc$ , the electrostatic interaction of the two components is supplemented by a contribution from a hydrophobic interaction, as ion associate  $\{HX^+, DS^-\}$  is gradually solubilized in the hydrocarbon core of the micelle. This is also demonstrated in the character of the changes in the conditional dissociation constants in the MR-SDS system.

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