

THE INTERACTION OF AZURE B WITH SURFACTANTS

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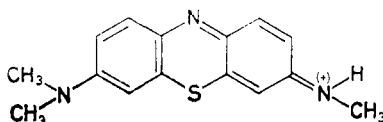
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Dedicated to Professor Václav Suk on the occasion of his 70th birthday.

A study was made of the effect of anionogenic, cationogenic and nonionogenic surfactants (tensides) on the absorption spectra of azure B. It was found that the change in the absorption spectra in solutions containing sodium lauryl sulfate are produced by change in the polymerization of the dye. At low tenside concentrations, dimers and higher dye aggregates are formed as a result of a decrease in the dye cation repulsion caused by interaction with tenside monomer anions. Above the critical micelle concentration, the dye is solubilized in the micelles, where the monomer form of azure B predominates. The cationogenic tenside does not affect dye polymerization; monomer formation is preferred in the nonionogenic tenside after micelle formation.

Azure B (3-methylamino-7-dimethylaminophenothiazine, AB) is a dye in the group of derivatives of phenothiazine that has so far been studied in the framework of a study of the general properties of the 3,7-derivatives of phenothiazine¹.



Of the dyes in this group, analytical use is made primarily of methylene blue (bis-3,7-dimethylaminophenothiazine) and thionine (3,7-diaminophenothiazine) as redox indicators². Methylene blue and azure A, B and C are used in extraction spectrophotometry, as they form ion associates with organic or complex inorganic anions, which can be extracted into organic solvents; this is used most often for the determination of anionogenic tensides^{3,4}. Thus, it is important to obtain all possible information on the types of interactions of these substances.

The effect of tensides has been studied primarily for photoredox reaction of thionine⁵. The fluorescence of methylene blue has been found to change in the presence of sodium lauryl sulfate⁶.

The effect of tensides on the properties of azure B solutions was studied in this work. Studies were carried out using the cationogenic tenside Septonex (1-carbethoxy-

pentadecyltrimethyl ammonium bromide), anionogenic tenside sodium lauryl sulfate (sodium dodecyl sulfate, NaLS) and nonionogenic tenside Triton X-100 (mono-octylphenyl polyethylene glycol ether with ten ethylene glycol units, TX).

EXPERIMENTAL

Instrumentation

The spectrophotometric measurements were carried out on a PU 8800 spectrophotometer from Pye-Unicam - Philips, Cambridge (Great Britain) with glass cuvettes with an internal thickness of 10 mm.

pH measurements were carried out using a PHM 26 pH-meter (Radiometer, Copenhagen) with a glass combined electrode.

Chemicals and Solutions

Azure B was prepared⁷ by extraction into CCl_4 from technical methylene blue (Lachema Brno), which contains about 10% of this substance, after transfer from a neutral medium to an alkaline medium, where azure B is present as a neutral molecule. A 2% solution was prepared from the commercial methylene blue substance, insoluble substances were removed by filtration and the pH was adjusted to about 12.0 using NaOH. The solution was transferred to a separating funnel and tetrachloromethane was added (in a ratio of 1 : 1). The mixture was shaken for 3 min, the phases were separated and the aqueous layer was filtered. Tetrachloromethane was again added to the filtrate and the mixture was again shaken for 3 min. Both extracts were joined. Azure B was transferred from this extract into aqueous phase by shaking with $4.5 \cdot 10^{-4} \text{ mol l}^{-1}$ HBr. Concentrated HBr was added to the solution obtained (2.5 ml to 97.5 ml of solution) and the solution was left in a refrigerator to crystallize. Decanting of the mother liquor yielded crystals that were dried over silica gel in a dessicator.

The efficiency of the purification was controlled by paper chromatography (Whatman No. 1 chromatographic paper, previously saturated with the vapours of the mobile phase: butanol-ethanol-water-glacial acetic acid in a ratio of 5 : 2 : 2 : 1)⁸. The dye yielded a single spot.

The absorption spectrum of a solution of purified azure B exhibits an absorption maximum at 644 nm, in agreement with the data given in the literature⁹.

The stock solution of $2.5 \cdot 10^{-3} \text{ mol l}^{-1}$ azure B ($M_r = 305.83$) was prepared by dissolving of purified dye in distilled water in a volumetric flask. The solution was stored in the cold and dark and was stable for at least 3 weeks. Its stability was monitored by measuring the absorption spectra in the visible region.

The stock solutions of $1 \cdot 10^{-2} \text{ mol l}^{-1}$ Septonex (Slovakofarma, Hlohovec; $M_r = 422.48$), sodium lauryl sulfate (Serva Heidelberg; $M_r = 288.38$) and Triton X-100 (Serva Heidelberg; $M_r = 624.90$) were prepared by dissolving the substances in distilled water. Septonex had been dried for several days in a dessicator over silica gel.

The ionic strengths of the solutions were adjusted using $1 \cdot 10^{-1} \text{ mol l}^{-1} \text{ NaNO}_3$.

The pH was adjusted using $1 \cdot 10^{-2} \text{ mol l}^{-1} \text{ NaOH}$ and $1 \cdot 10^{-2} \text{ mol l}^{-1} \text{ HCl}$. The chemicals were of p.a. purity.

RESULTS AND DISCUSSION

In aqueous solutions of pH 1–12 azure B is present in the form of the cation with

the above structure, with $\lambda_{\max} = 644$ nm and a shoulder at about 600 nm. In strongly acidic solutions, the heterocyclic nitrogen of the dye is protonated¹ and species with $\lambda_{\max} = 730$ nm is formed. The dye dissociates in alkaline solutions at $\text{pH} > 12$ (λ_{\max} of neutral molecule formed is 530 nm). At high dye concentrations ($> 1 \cdot 10^{-3} \text{ mol l}^{-1}$), a dimer with an absorption maximum at about 600 nm is formed, in analogy to other dyes of this structural type¹⁰.

Preliminary experiments demonstrated that the absorption spectrum and dissociation equilibrium of azure B were affected by the presence of surfactants. The ionic strength also play an important role. Therefore, these effects were studied in detail. The influence of surfactant on the acid-base properties of the dye will be reported elsewhere.

The effect of NaNO_3 on azure B solutions without surfactants was studied at concentrations of $0.02\text{--}1 \text{ mol l}^{-1}$. As the NaNO_3 concentration increased, the position of the absorption maximum of the monomer did not change, its height decreased somewhat and the absorbance at about 600 nm became more pronounced.

The Effect of the Anionogenic Surfactant

The effect of the concentration of the sodium lauryl sulfate on the dye spectrum was studied ($c_{\text{AB}} = 1 \cdot 10^{-4} \text{ mol l}^{-2}$) at $\text{pH} 7$. As it was found that, in the presence of the surfactant, even a small amount of salt greatly affects the absorption spectrum of the dye, measurements were carried out in solutions in the absence of NaNO_3 (Fig. 1) and at $I = 0.1 \text{ mol l}^{-1}$ (Fig. 2). The tenside concentration was varied from

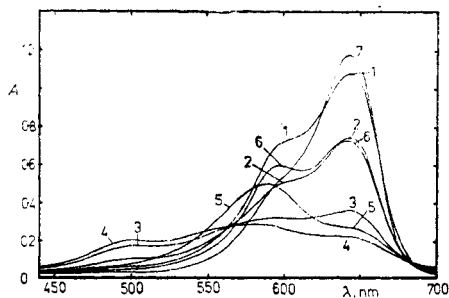


FIG. 1

The effect of the concentration of sodium lauryl sulfate on the absorption spectra of azure B in the absence of salts. $c_{\text{AB}} = 1 \cdot 10^{-4} \text{ mol l}^{-1}$; $\text{pH} 7$; $c_{\text{NaLS}} (\text{mol l}^{-1})$: 1 0, 2 $1 \cdot 10^{-4}$, 3 $3 \cdot 10^{-4}$, 4 $8 \cdot 10^{-4}$, 5 $3 \cdot 10^{-3}$, 6 $5 \cdot 10^{-3}$, 7 $1 \cdot 10^{-2}$

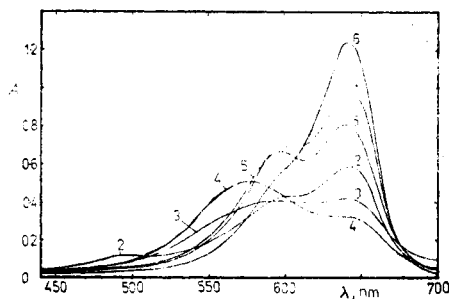


FIG. 2

The effect of the concentration of sodium lauryl sulfate on the absorption spectra of azure B in the presence of NaNO_3 ($I = 0.1 \text{ mol l}^{-1}$). $c_{\text{AB}} = 1 \cdot 10^{-4} \text{ mol l}^{-1}$; $\text{pH} 7$; $c_{\text{NaLS}} (\text{mol l}^{-1})$: 1 0, 2 $2 \cdot 10^{-4}$, 3 $4 \cdot 10^{-4}$, 4 $7 \cdot 10^{-4}$, 5 $1 \cdot 10^{-3}$, 6 $1 \cdot 10^{-2}$

$1 \cdot 10^{-4} \text{ mol l}^{-1}$ to $1 \cdot 10^{-2} \text{ mol l}^{-1}$ (the critical micelle concentrations are $7 \cdot 10^{-3} \text{ mol l}^{-1}$ in solutions without salt and $1 \cdot 3 \cdot 10^{-3} \text{ mol l}^{-1}$ at $I = 0 \cdot 1 \text{ mol l}^{-1}$)¹¹.

As can be seen from Fig. 1, with increasing sodium lauryl sulfate concentration up to $8 \cdot 10^{-4} \text{ mol l}^{-1}$ (curves 1–4) the monomer absorbance decreases ($\lambda_m = 644 \text{ nm}$), accompanied by the formation of a maximum at $\lambda_d = 580 \text{ nm}$, apparently corresponding to the dimer, and a maximum at a wavelength of 500 nm .

The formation of the dimer of a cationic dye with a similar structure (acridine orange, safranin) was explained in terms¹² of weakening of the electrostatic repulsion between the cations through interaction with the anions of the tenside. However, this interaction can simultaneously induce the formation of small pre-micelle aggregates of the tenside with the high solubilized dye contents^{12,13}. During this dye concentration process, azure B can form further oligomers (such as for example the trimer) with $\lambda_t = 500 \text{ nm}$.

At higher sodium lauryl sulfate concentrations, micelles are gradually formed with higher surfactant and lower dye contents, in which first the dimers predominate (up to a surfactant concentration of $3 \cdot 10^{-3} \text{ mol l}^{-1}$ – curve 5) and the amount of trimer decreases. As the number of micelles increases with an increasing tenside concentration at a given dye concentration, the dye molecules are distributed over an ever increasing number of micelles, so that the effect of concentration of the dye in the micelles is eliminated and monomers gradually come to predominate in the micelles (curves 6 and 7). The wavelength maximum for the monomer shifts from 644 nm to 640 nm . Changes in the contents of monomer and dimer have also been observed for methylene blue in the presence of montmorillonite¹⁴.

The monomer \rightleftharpoons dimer \rightleftharpoons trimer equilibrium for azure B in the micelles of sodium lauryl sulfate is shifted in favour of the monomer compared to the ratios in water alone (see curves 1 and 7).

At $I = 0 \cdot 1 \text{ mol l}^{-1}$ (Fig. 2) the decrease in amount of monomer absorbing at $\lambda_m = 644 \text{ nm}$ and formation of the trimer absorbing at $\lambda_t = 500 \text{ nm}$ appears already at very low NaLS concentration (up to concentrations of $c_{\text{NaLS}} = 3 \cdot 10^{-4} \text{ mol l}^{-1}$). At surfactant concentrations of $4 \cdot 10^{-4} - 7 \cdot 10^{-4} \text{ mol l}^{-1}$ (curves 3 and 4) both the monomer and trimer maxima decrease and the maximum of the dimer at $\lambda_d = 580 \text{ nm}$ increases. Up to a surfactant concentration of $c_{\text{NaLS}} = 1 \cdot 0 \cdot 10^{-3} \text{ mol l}^{-1}$ (curve 5) the micelles contain relatively large amounts of dimer (the trimer maximum disappears) and, from surfactant concentrations of $c_{\text{NaLS}} > 1 \cdot 10^{-3} \text{ mol l}^{-1}$ the micelles contain more monomer (the absorbance of the monomer increases to that at $1 \cdot 10^{-2} \text{ mol l}^{-1}$ NaLS – curve 6 – it is again greater than in water, curve 1). The wavelength of the monomer absorbance shifts from 644 nm to 640 nm .

The whole process of formation of pre-micelle aggregates and micelles is thus shifted to lower concentrations of sodium lauryl sulfate at $I = 0 \cdot 1 \text{ mol l}^{-1}$ because NaNO_3 decreases the critical micelle concentration of the surfactant.

Figure 3 depicts the changes in the monomer absorbance ($\lambda_m = 640-644$ nm) as the concentration of sodium lauryl sulfate increases at pH 7 in solutions without salt (curve 1) and at $I = 0.1 \text{ mol l}^{-1}$ (curve 2). As the tenside concentration increases, the amount of monomer first decreases in both cases and then rapidly increases above a concentration of $2 \cdot 10^{-3}$ for the solution without salt and of $7 \cdot 10^{-4} \text{ mol l}^{-1}$ at $I = 0.1 \text{ mol l}^{-1}$. This concentration values apparently correspond to the beginning of the formation of classical micelles, in which the number of dye molecules is far lower than the number of surfactant molecules, so that dye polymerization decreases. Above a higher surfactant concentration ($4 \cdot 10^{-3} \text{ mol l}^{-1}$ without salt and $7 \cdot 10^{-4} \text{ mol l}^{-1}$ for $I = 0.1 \text{ mol l}^{-1}$), the monomer absorbance attains a constant value, apparently corresponding to constant distribution of the dye molecules in the micelles. In the presence of inorganic salts, classical micelles are formed at smaller surfactant concentrations.

The Effect of the Ionic Strength

As the presence of a strong electrolyte thus basically affects the interaction between the dye and sodium lauryl sulfate, the effect of the ionic strength of the solution was studied in detail on the spectra of azure B in the range $I = 0.02-1 \text{ mol l}^{-1}$ ($c_{AB} = 1 \cdot 10^{-4} \text{ mol l}^{-1}$) in the presence of sodium lauryl sulfate at concentrations of $7 \cdot 10^{-4}$ and $2 \cdot 10^{-3} \text{ mol l}^{-1}$ (concentrations at which a change in the micelle formation occurs were selected from Fig. 3). These dependences are depicted in Figs 4 and 5.

At tenside concentrations of $c_{NaLS} = 7 \cdot 10^{-4} \text{ mol l}^{-1}$ (Fig. 4) in solutions in the absence of NaNO_3 and at low NaNO_3 concentrations (up to 0.04 mol l^{-1} , curves 1 and 2), dye-rich premicelle aggregates are formed, participating in the formation

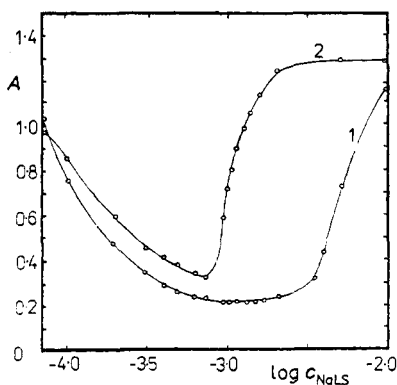


FIG. 3

The effect of the concentration of sodium lauryl sulfate on the absorbance of the monomer of azure B. $c_{AB} = 1 \cdot 10^{-4} \text{ mol l}^{-1}$; $\lambda_m = 640-644$ nm; pH 7; 1 solutions in the absence of salt; 2 solutions with adjusted ionic strength ($I = 0.1 \text{ mol l}^{-1}$)

of the dimer with $\lambda_d = 580$ nm and trimer with $\lambda_t = 500$ nm. The presence of the salt increases the aggregation ability of the tenside, so that larger micelle aggregates are formed as the NaNO_3 concentration increases; the trimer disappears in these aggregates and the dimer predominates (curve 3). At higher salt concentrations, the monomer of the dye begins to predominate in the micelles (curves 5, 6). Thus, an increase in the NaNO_3 concentration in solution with NaLS affects the absorption spectra of azure B similarly to an increase in the sodium lauryl sulfate concentration.

At higher tenside concentrations ($2 \cdot 10^{-3} \text{ mol l}^{-1}$, Fig. 5), micelles are formed at very low salt concentrations. For example, curve 5 ($I = 0.16 \text{ mol l}^{-1}$) in Fig. 4 ($c_{\text{NaLS}} = 7 \cdot 10^{-4} \text{ mol l}^{-1}$) is roughly comparable to curve 2 ($I = 0.02 \text{ mol l}^{-1}$) in Fig. 5.

The Effect of the Cationogenic Tenside

The effect of this tenside on the absorption spectrum of azure B (at constant dye concentration $c_{\text{AB}} = 1 \cdot 10^{-4} \text{ mol l}^{-1}$) was determined at Septonex concentrations below and above the critical micelle concentration (cmc), i.e. in the range $5 \cdot 10^{-5}$ to $5 \cdot 10^{-3} \text{ mol l}^{-1}$ (cmc = $7.74 \cdot 10^{-4} \text{ mol l}^{-1}$ in solutions without salt and $1.16 \cdot 10^{-4} \text{ mol l}^{-1}$ at $I = 0.1 \text{ mol l}^{-1}$)¹⁵. No changes occur in the absorption spectra for solutions without salt and for $I = 0.1 \text{ mol l}^{-1}$ as the Septonex concentration increases. Thus, the cationogenic tenside, which does not enter into any electrostatic interactions with the dye cation, does not affect the polymerization of azure B.

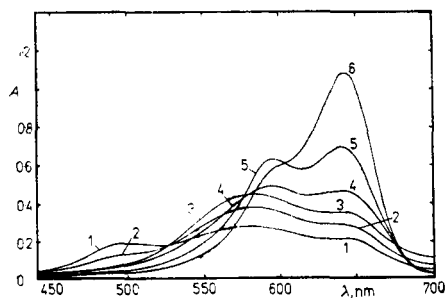


FIG. 4

The effect of the ionic strength on the absorption spectra of azure B in the presence of $7 \cdot 10^{-4} \text{ mol l}^{-1}$ sodium lauryl sulfate. $c_{\text{AB}} = 1 \cdot 10^{-4} \text{ mol l}^{-1}$; pH 6; I (mol l^{-1}): 1 0, 2 0.04, 3 0.1, 4 0.12, 5 0.16, 6 1.00

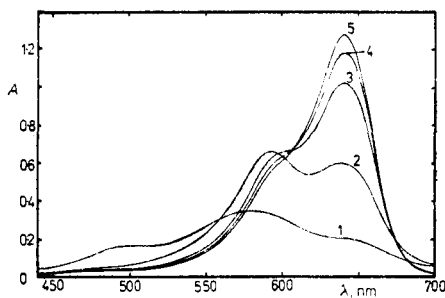


FIG. 5

The effect of the ionic strength on the absorption spectra of azure B in the presence of $2 \cdot 10^{-3} \text{ mol l}^{-1}$ sodium lauryl sulfate. $c_{\text{AB}} = 1 \cdot 10^{-4} \text{ mol l}^{-1}$; pH 6; I (mol l^{-1}): 1 0, 2 0.02, 3 0.04, 4 0.06, 5 1.00

The Effect of the Nonionogenic Tenside

An increase in the monomer absorbance occurs in azure B solutions ($c_{AB} = 1 \cdot 10^{-4} \text{ mol l}^{-1}$) in the presence of Triton X-100 ($c_{TX} = 1 \cdot 10^{-4} - 1 \cdot 10^{-2} \text{ mol} \cdot \text{l}^{-1}$), in solutions in the absence of salt, from a value of 1.10 for $c_{TX} = 0$ to 1.20 for $c_{TX} = 1 \cdot 10^{-2} \text{ mol l}^{-1}$, and at $I = 0.1 \text{ mol l}^{-1}$ for the same tenside concentrations, from a value of 1.00 to 1.20. Changes occur only at higher tenside concentrations. The dye is solubilized in the micelles primarily as the monomer.

REFERENCES

1. Chalvet O., Hoaran J., Jousot-Dubien J., Rayez J. C. J.: *J. Chim. Phys. Physicochim. Biol.* **69**, 630 (1972).
2. Němcová I., Zimová N., Němec I.: *Chem. Listy* **76**, 142 (1982).
3. Otsumi S., Ito S., Machida A., Isozaki A.: *Jpn. Analyst* **16**, 1213 (1967).
4. Wanga L. W., Panzardi P. J.: *Anal. Chem.* **47**, 1472 (1975).
5. Sakata T., Suda Y., Tanaka J., Tsubomura H.: *J. Phys. Chem.* **81**, 537 (1977).
6. Ghosh A. K.: *Indian J. Chem.* **12**, 313 (1974).
7. Marshall P. N., Lewis S. M.: *Stain Technol.* **50**, 375 (1973).
8. Löhr W., Grubhofer N., Sohmer I., Wittekind D.: *Stain Technol.* **50**, 149 (1975).
9. Taylor K. B.: *J. Histochem. Cytochem.* **8**, 248 (1960).
10. Lewis G. N., Goldschmid O., Magel T. T., Bigeleisen J.: *J. Am. Chem. Soc.* **65**, 1150 (1943).
11. Corrin M. J., Harkins W. D.: *J. Am. Chem. Soc.* **69**, 683 (1974).
12. Neumann M. G., Gehlen M. H.: *J. Colloid Interface Sci.* **135**, 209 (1990).
13. Diaz Garcia M. E., Sanz-Medel A.: *Talanta* **33**, 255 (1986).
14. Bergmann K., O'Konski G. T.: *Talanta* **30**, 617 (1984).
15. Čermáková L., Rosendorfová J., Malát M.: *Collect. Czech. Chem. Commun.* **45**, 210 (1980).

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