THE EFFECT OF TENSIDES ON THE DISSOCIATION OF AZURE B

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A study was carried out of the effect of an anionogenic and a cationogenic tenside on the dissociation of azure B. It was found that, in the presence of sodium lauryl sulfate, the pH value of the solution affects both the dissociation and the ratio of the contents of the monomer, dimer and higher aggregates of the dye at various concentrations of this tenside. The dependences of pK_a on the concentration of the given kind of tenside and its variation in the presence of an inorganic salt ($NaNO_3$) were found.

Azure B (3-methylamino-7-dimethylaminophenothiazine, AB) is one of the derivatives of phenothiazine. The dyes of this group (methylene blue, thionine, azure A) are utilized in analytical chemistry as redox indicators or in extraction spectrophotometry for the determination of inorganic or organic anions.

In an earlier work[1], we studied the interaction of azure B with tensides because it is known that tensides greatly affect the properties of organic dyes and thus also analytical methods in which these dyes are employed[2,3]. We found that the aggregation of molecules of azure B is favoured in solutions with low concentrations of the anionogenic tenside sodium lauryl sulfate. At tenside concentrations above the critical micelle concentration, the dye molecules are bonded to the tenside micelle, where they are gradually diluted, so that the monomer form of the dye once again predominates. This process is greatly affected by the presence of an inorganic salt. Cationic tensides do not affect the dye aggregation.

The effect of tensides on the dissociation of the hydrochlorides of phenothiazine derivatives has so far been studied[4,5] only for derivatives substituted on the heterocyclic nitrogen by an alkyl chain, terminated by a dialkylamine or piperazine group; these substances are employed as pharmaceuticals. A decrease in the pK_a value in the presence of a cationogenic tenside has been used in its alkalimetric determination.

Of the derivatives substituted in the 3 and 7 positions, azure B was selected, whose molecule contains one dissociable hydrogen atom and which is thus a very suitable simple model for study of the effect of the tenside on the acid-base properties of this group of substances.

The dissociation of azure B proceeds according to Scheme 1.

EXPERIMENTAL

Apparatus

Spectrophotometric measurements were carried out using a PU 8800 Pye Unicam–Philips, Cambridge spectrophotometer with glass cuvettes with an internal pathlength of 10 mm.

pH measurements were carried out using a PHM 26 pH-meter (Radiometer, Copenhagen) with a glass combined electrode GK 2401 C calibrated using buffers from the same company.

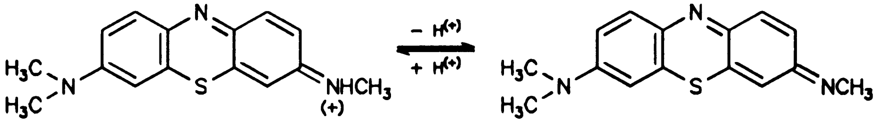
Chemicals and Solutions

The stock solution of 2.5 . 10^{-3} mol l^{-1} azure B (M_r = 305.83) was prepared by dissolving the purified[1] dye in water. The solution was stored in the cold and dark and was stable for at least 3 weeks. Its stability was controlled by measuring the absorption spectra in the visible radiation region.

The stock solution of 1 . 10^{-2} mol l^{-1} sodium lauryl sulfate, NaLS (Serva Heidelberg; M_r = 288.38) and the stock solution of 1 . 10^{-2} mol l^{-1} Septonex [1-(ethoxycarbonyl)pentadecyl]trimethylammonium bromide (Slovakofarma Hlohovec; M_r = 422.48) were prepared by dissolving the substances in water. Septonex was first dried for several days in a desiccator over silica gel.

The ionic strength was adjusted using a 1 . 10^{-1} mol l^{-1} solution of $NaNO_3$.

The pH was adjusted using solutions of NaOH, p.a. of various concentrations (max. 20%) and 1 . 10^{-2} mol l^{-1} HCl, p.a.



SCHEME 1

RESULTS AND DISCUSSION

In the absence of tensides and salts, azure B in slightly acidic and neutral medium yields an absorption curve with a monomer maximum[1] at λ_m = 644 nm and a slight dimer maximum at about 600 nm (Fig. 1). Dye dissociation occurs in the alkaline region, reflected in the appearance of a maximum at λ = 550 nm. At high pH values, the dye decomposes[6], so that the dissociation constant cannot be found exactly. The pK_a value was estimated from the inflection point on the dependence of the absorbance on the pH and is equal to about 11.8.

In the presence of $NaNO_3$ (I = 0.01 – 0.5 mol l^{-1}), the absorption curves of azure B at high pH values also do not pass through the isosbestic point and the dye once again decomposes. As the ionic strength increases, the estimated pK_a value increases to 12.4 at I = 0.5 mol l^{-1}.

The Effect of the Anionogenic Tenside Sodium Lauryl Sulfate

To determine the pK_a value in dependence on the tenside concentration, the effect of the pH on the absorption spectra of azure B was studied at concentrations of sodium lauryl sulfate varying in the interval $5 \cdot 10^{-4} - 1 \cdot 10^{-2}$ mol l^{-1}.

Solutions in the absence of NaNO$_3$. At a dye concentration of $c_{AB} = 1 \cdot 10^{-4}$ mol l^{-1} and tenside concentration of $c_{NaLS} = 5 \cdot 10^{-4}$ mol l^{-1} (Fig. 2) and at pH < 12, the monomer absorbance is decreased compared to solutions in the absence of tenside. Curves *1* and *2* exhibit moreover two clear maxima, corresponding[1] to the dimer and a higher oligomer (trimer) with λ_t = 500 nm. The formation of these dye aggregates is favoured by the presence of the anions of the tenside monomers (the critical micelle concentration of sodium lauryl sulfate *cmc* = $7 \cdot 10^{-3}$ mol l^{-1} in solutions in the absence of the salt)[7]. Association of the tenside anions with the dye cations suppresses their repulsion forces and favours dye polymerization[8]. The associates formed can then induce the formation of premicellar tenside aggregates[8 - 10].

On an increase in the pH to values above 11.5, a broad band appears between the wavelengths 550 – 600 nm on curves *3* and *4*, which can be assumed to correspond to the sum of the bands of the dimer and the deprotonated forms of azure B that are being formed. This assumption was confirmed by mathematical analysis[11] of absorption curve *4*. Gaussian curves were obtained with a maximum at 557.7 nm ($\varepsilon = 1.285 \cdot 10^4$ l mol^{-1} cm^{-1}), 599.5 nm ($\varepsilon = 0.032 \cdot 10^4$ l mol^{-1} cm^{-1}) and 655.7 nm ($\varepsilon = 0.113 \cdot 10^4$ l mol^{-1} cm^{-1}). The value of λ_{max} for the first two maxima is in good agreement with the position of the absorption bands of the dimer and the deprotonated dye forms.

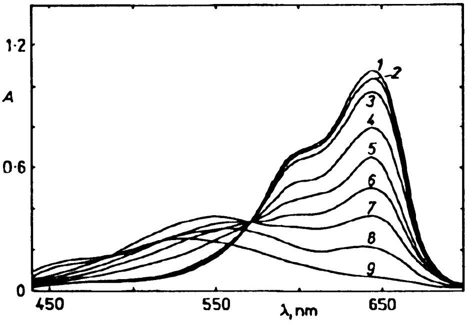


FIG. 1

The effect of the pH on the absorption spectra of azure B. $c_{AB} = 1 \cdot 10^{-4}$ mol l^{-1}; pH: *1* 7.05; *2* 9.86; *3* 10.14; *4* 11.47; *5* 11.92; *6* 12.06; *7* 12.32; *8* 12.65; *9* 13.15

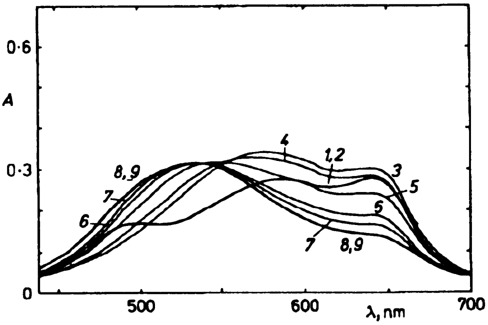


FIG. 2

The effect of the pH on the absorption spectra of azure B in the presence of $5 \cdot 10^{-4}$ mol l^{-1} sodium lauryl sulfate (without NaNO$_3$). c_{AB} = $1 \cdot 10^{-4}$ mol l^{-1}; pH: *1* 9.20; *2* 11.50; *3* 11.91; *4* 12.07; *5* 12.23; *6* 12.46; *7* 12.62; *8* 12.78; *9* 12.89

A further increase in the pH (curves *5* – *9*) leads to dissociation of the dye; the absorbances of the monomer and dimer decrease and the maximum of the deprotonated form increases.

On an increase in the concentration of NaLS to a value of 1 . 10^{-3} mol l^{-1}, the dimer predominates on the absorption curves up to pH 12.2. At higher pH values, the monomer maximum rapidly increases; however, above pH 12.8 it again rapidly decreases with simultaneous increase in the maximum of the dissociated form (the curves form an isosbestic point). No explanation has been found for this phenomenon.

At $c_{\mathrm{NaLS}} = 7 \cdot 10^{-3}$ mol l^{-1} (the critical micelle concentration of sodium lauryl sulfate) the monomer maximum predominates on the curves and is higher than in solutions in the absence of tenside (Fig. 3). As the pH increases to a value of 12.3, the maximum further increases (curves *1* – *7*) with a simultaneous decrease in the dimer maximum. It has been shown[1] that the increased amount of monomer is a consequence of micelle formation in solution. In contrast to the premicelle aggregates the real micelle have higher tenside content, the dye is diluted and its aggregation is suppressed.

At higher pH values, the dye is dissociated. However, in contrast to surfactant-free solutions , the dye is not decomposed even at the highest pH values.

At $c_{\mathrm{NaLS}} > 1 \cdot 10^{-2}$ mol l^{-1} and at all pH values, the monomer absorbance is high and constant up to the beginning of dye deprotonation. The absorption maximum exhibits a slight hypsochromic shift (λ_{max} = 640 nm).

The effect of time on the absorption spectra has been studied at various concentrations of sodium lauryl sulfate. At $c_{\mathrm{NaLS}} < 7 \cdot 10^{-3}$ mol l^{-1} (*cmc*), the absorption corresponding to the dimer gradually decreases and the monomer absorption increases (by about 10% in 30 min). At NaLS concentrations above the *cmc*, when the monomer maximum predominates on the curves, no time changes occurred on the spectra. Thus, the former changes are probably a consequence of the fact that the premicelle aggregates gradually form larger species, while the size of micelles formed at high tenside concentrations does not change with time.

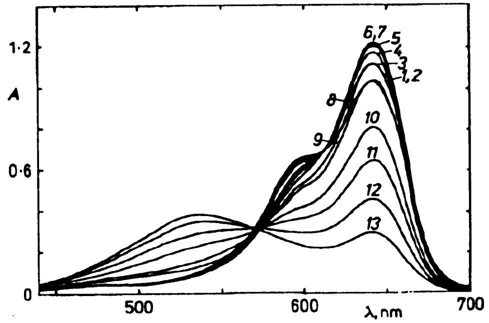


FIG. 3

The effect of the pH on the absorption spectra of azure B in the presence of 7 . 10^{-3} mol l^{-1} sodium lauryl sulfate (without $NaNO_3$). c_{AB} = 1 . 10^{-4} mol l^{-1}; pH: *1* 6.45; *2* 10.90; *3* 11.17; *4* 11.47; *5* 11.59; *6* 11.73; *7* 12.33; *8* 12.58; *9* 12.67; *10* 12.83; *11* 12.93; *12* 13.03; *13* 13.12

It is apparent from these results that the ratio of the amount of monomer and dimer of azure B is affected by both the tenside concentration (and partly also time), as well as by the pH value of the solution. These changes are depicted in Fig. 4, giving the dependence of the absorbance at the wavelengths of the monomer maximum (640 – 644 nm) on the pH for the solution in the absence of the tenside and at elevated tenside concentrations. In the solution without tenside (curve *1*) the monomer absorbance is constant to pH 9, and then slowly decreases as a result of deprotonation. At tenside concentrations below the *cmc*, where premicellar aggregates with concentrated dye molecules are formed in solution, the effect of the pH on the ratio of monomer and dimer is greatest. As it is known that the presence of the ions of a strong electrolyte decreases the *cmc* of the tenside, it is probable that Na^+ ions added in pH adjustment produce a decrease in the *cmc* value, micelles are formed in the solution and the amount of monomer is increased. At higher tenside concentrations (curve *6*), where the micelles are formed immediately in solution and the dye is present primarily as the monomer, whose concentration is greater than in aqueous solutions (cf. curve *1*), the absorbance is constant in the whole pH range up to the beginning of deprotonation.

Solutions in the presence of $NaNO_3$. Figure 5 depicts the dependence of the absorbance of the dye monomer on the pH at increasing tenside concentrations for I = 0.01 mol l^{-1}. The shape of the curve is analogous to that in Fig. 4 (with all the apparent

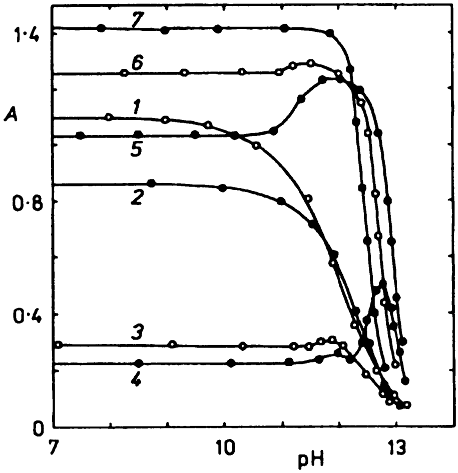


FIG. 4

The dependence of the absorbance of the azure B monomer on the pH in the presence of sodium lauryl sulfate (without $NaNO_3$). c_{AB} = 1 . 10^{-4} mol l^{-1}; λ_m = 640 – 644 nm; c_{NaLS} (mol l^{-1}): *1* 0; *2* 1 . 10^{-4}; *3* 5 . 10^{-4}; *4* 1 . 10^{-3}; *5* 7 . 10^{-3}; *6* 1 . 10^{-2}; *7* 5 . 10^{-2}

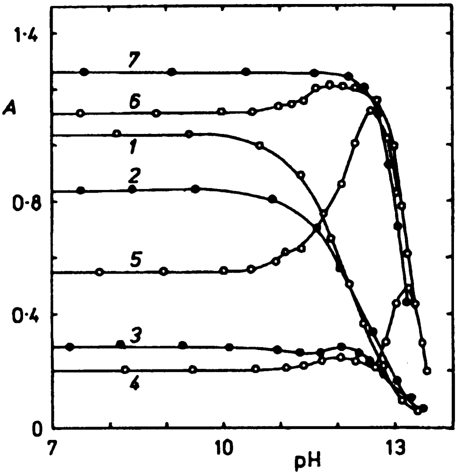


FIG. 5

The dependence of the absorbance of the azure B monomer on the pH in the presence of sodium lauryl sulfate and $NaNO_3$ (I = 0.01 mol l^{-1}). c_{AB} = 1 . 10^{-4} mol l^{-1}; λ_m = 640 – 644 nm; c_{NaLS} (mol l^{-1}): *1* 0; *2* 1 . 10^{-4}; *3* 5 . 10^{-4}; *4* 1 . 10^{-3}; *5* 3 . 10^{-3}; *6* 5 . 10^{-3}; *7* 1 . 10^{-2}

irregularities, which are completely reproducible); however, the tenside concentrations at which these changes occur on the absorption curves are different. While the monomer maximum predominates in solutions in the absence of $NaNO_3$ at $c_{NaLS} > 7 \cdot 10^{-3}$ mol l^{-1} (corresponding to micelle formation), this value decreased to $c_{NaLS} = 5 \cdot 10^{-3}$ mol l^{-1} at $I = 0.01$ mol l^{-1}. Up to this tenside concentration, the ratio of the monomer and dimer also depends on the pH of the solution, while at higher concentrations the amount of monomer in the micelles is pH-independent. In addition, from this concentration, the absorption curves for a further increase in the pH corresponding to the dissociation of the dye pass through a sharp isosbestic point and dye decomposition does not occur.

At $I = 0.1$ (Fig. 6), the dye monomer predominates at $c_{NaLS} = 1.3 \cdot 10^{-3}$ mol l^{-1}. At this ionic strength, the ratio of the monomer and dimer is not affected by the solution pH at any tenside concentration. The concentration of the ions of the salt employed is so high that the effect of the ions used for pH adjustment is negligible. The conditions are similar for $I = 0.5$ mol l^{-1}; the dye monomer begins to predominate in the micelles at $c_{NaLS} < 1 \cdot 10^{-3}$ mol l^{-1} and its amount is independent of the solution pH. The curves pass through a sharp isosbestic point and the dye does not decompose.

It can thus be summarized that, in acidic, neutral and weakly alkaline media, the formation of premicellar aggregates and NaLS micelles and the corresponding amounts of monomer and higher oligomers of azure B depends on the tenside concentration, ionic strength and solution pH. In strongly alkaline medium, azure B dissociates; however, in contrast to the aqueous phase, the dye bonded in the micelles does not decompose.

It is apparent from Figs 4 – 6 that the curves of the dependence of the absorbance on the pH are steeper at $c_{NaLS} = 0$ and especially at $c_{NaLS} > cmc$, i.e. for increased monomer

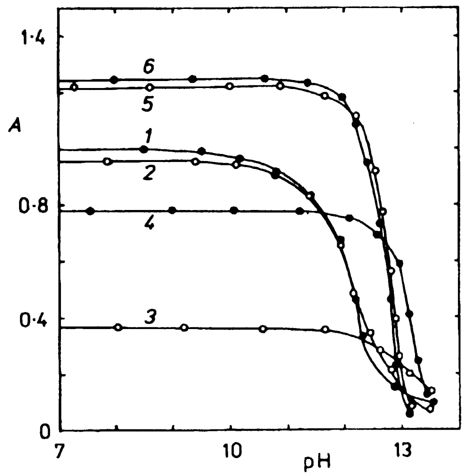


Fig. 6

The dependence of the absorbance of the azure B monomer on the pH in the presence of sodium lauryl sulfate and $NaNO_3$ ($I = 0.1$ mol l^{-1}). $c_{AB} = 1 \cdot 10^{-4}$ mol l^{-1}; $\lambda_m = 640 - 644$ nm; c_{NaLS} (mol l^{-1}): *1* 0; *2* $1 \cdot 10^{-4}$; *3* $5 \cdot 10^{-4}$; *4* $1 \cdot 10^{-3}$; *5* $5 \cdot 10^{-3}$; *6* $1 \cdot 10^{-2}$

contents, than the curves at NaLS concentrations corresponding to increased dimer (or trimer) contents in the premicellar aggregates. It thus follows that the pK_a values for the monomer and higher oligomers are somewhat different and the curves for the dependence $A = f(\text{pH})$ for $0 < c_{\text{NaLS}} < cmc$ are formed by the summation of the curves for the individual forms.

The pK_a values have not been calculated exactly, as the pH values measured in the strongly alkaline region cannot be considered completely accurate. However, it is apparent from Figs 4 – 6 that the pK_a value first increases with increasing tenside concentration (e.g. in solutions in the absence of $NaNO_3$ from p$K_a \approx 11.8$ for $c_{\text{NaLS}} = 0$ to p$K_a = 13$ for $c_{\text{NaLS}} = 7 \cdot 10^{-3}$ mol l^{-1}) and then again decrease slightly. The NaLS concentration at which the maximum pK_a value is attained, decreases with increasing ionic strength of the solution: in solutions in the absence of $NaNO_3$, this concentration equals $7 \cdot 10^{-3}$ mol l^{-1}; at $I = 0.01$ mol l^{-1}, $5 \cdot 10^{-3}$ mol l^{-1}; and at $I = 0.1$ mol l^{-1}, $1 \cdot 10^{-3}$ mol l^{-1}. It is apparent from comparison with the previous results that these are the concentrations at which micelles are formed in solution at the individual ionic strengths.

The effect of tensides on the dissociation constants of organic dyes has been studied in detail in a number of works. At a tenside concentration of $c_t < cmc$, the change in pK_a can be explained through the formation of dye–tenside ion pairs[12], which are solubilized in the micelles above the *cmc*, above which further changes do not occur. For $c_t >$ *cmc*, the changes in pK_a are most often explained on the basis of the theory of the pseudo-phase ion-exchange model[13]. Although the relationships derived in this theory often fail[14] at tenside concentrations close to the *cmc*, in this case, where a simple dissociation equilibrium is present, the shift directions obtained even for small tenside concentrations (of the order of 10^{-4} mol l^{-1}) are in agreement with this theory. It is apparent that it must be borne in mind that the *cmc* value of the tenside is greatly decreased in the presence of the dye and salt (here, by almost one order of magnitude) and, in addition, premicellar aggregates are formed in solution at even lower tenside concentrations. These aggregates can be considered as a premicellar pseudophase whose properties would be decisive for the dye behaviour. It can then be assumed that the dye molecules are bonded through electrostatic and hydrophobic interactions to the sodium lauryl sulfate pseudophase, which bonds a limited number of OH^- ions from solution[15] as a consequence of electrostatic repulsion; the dye dissociation is then suppressed and the pK_a value increases. The slight decrease in pK_a at high tenside concentrations is a consequence of the slight decrease in the micelle surface potential[16]. For the same reason, the curves of the dependence of pK_a on the tenside concentration sometimes pass through a minimum in the study of the interactions of dye anions with cationogenic tensides[16 - 18].

The Effect of the Cationogenic Tenside Septonex

It has been shown[1] that cationogenic tensides do not affect the polymerization of azure B. However, it has been found in a study of the effect of the pH on the absorption spectra of the dye at various tenside concentrations that Septonex affects the dye dissociation and that thus, similar to other cases, e.g. refs[4,19], the dye interacts with the tenside irregardless of its charge, which can exclude the formation of ion associates. Hydrophobic interactions play a decisive role here[20].

In the absence of $NaNO_3$, in the strongly alkaline region and at Septonex concentrations up to its *cmc* ($7.74 \cdot 10^{-4}$ mol l^{-1} in solutions in the absence of salts and dyes[21]), azure B is decomposed similarly as in solutions in the absence of tensides. At c_{Sept} > *cmc*, Septonex binds the dye in micelles and prevents its decomposition. After the dissociation of the dye, the curves pass through the isosbestic point at λ = 580 nm.

At higher ionic strengths of the solution (0.01 – 0.5 mol l^{-1}), the isosbestic point is sharp at lower tenside concentrations, once again corresponding to a decrease in the *cmc* and binding of the dye in the tenside micelle.

On the basis of the measured absorption curves, a plot was again made of the dependence of the absorbance at the wavelength of the dye monomer on the pH for solution ionic strengths of 0.01, 0.1 and 0.5 mol l^{-1}. For illustration, Fig. 7 depicts these curves at I = 0.01 mol l^{-1}. In the absence of $NaNO_3$ and at all the ionic strength values employed, the pK_a values decrease with increasing Septonex concentration. This decrease in pK_a (increased dissociation) can once again be explained using the pseudophase model: the dye is bonded in the tenside micelle; OH^- ions from solution are bonded and concentrated on the positive surface of these micelles and favour dye dissociation. At higher ionic strength values, the decrease in pK_a is smaller because the

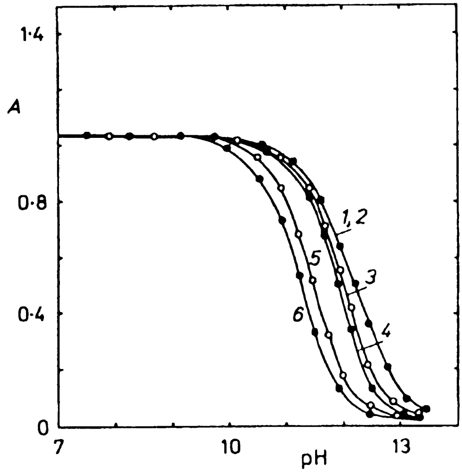


FIG. 7
The dependence of the absorbance of the azure B monomer on the pH in the presence of Septonex and $NaNO_3$ (I = 0.01 mol l^{-1}). $c_{AB} = 1 \cdot 10^{-4}$ mol l^{-1}; λ_m = 640 – 644 nm; c_{Sept} (mol l^{-1}): *1* 0; *2* $1 \cdot 10^{-4}$; *3* $5 \cdot 10^{-4}$; *4* $1 \cdot 10^{-3}$; *5* $5 \cdot 10^{-3}$; *6* $1 \cdot 10^{-2}$

salt anions are preferentially bonded to the surface of the tenside micelle[13], preventing approach of OH^- ions.

It can thus be concluded that anionogenic and cationogenic tensides produce a change in the pK_a of azure B, whose direction (increase or decrease) depends on the type of tenside (charge). Changes occur at tenside concentrations lower than the *cmc* value in pure solutions, especially at elevated ionic strength values of the solutions. This could be a consequence of the decrease in the *cmc* value and formation of premicellar aggregates.

REFERENCES

1. Němcová I., Dušková M.: Collect. Czech. Chem. Commun. *57*, 296 (1992).
2. Hinze W. L. in: *Solution Chemistry of Surfactants* (K. L. Mittal, Ed.), Vol. 1, p. 79. Plenum Press, New York 1979.
3. Pelizetti E., Pramauro E.: Anal. Chim. Acta *169*, 1 (1985).
4. Rychlovský P., Němcová I.: Talanta *35*, 211 (1988).
5. Rychlovský P., Němcová I.: Česk. Farm. *40*, 108 (1991).
6. Abbott D. C.: Analyst *87*, 286 (1962).
7. Corrin M. J., Harkins W. D.: J. Am. Chem. Soc. *69*, 683 (1974).
8. Neumann M. G., Gehlen M. H.: J. Colloid Interface Sci. *135*, 209 (1990).
9. Diaz Garzia M. A., Sanz-Medel A.: Talanta *33*, 255 (1986).
10. Holzwarth J., Knoche W., Robinson B. H.: Ber. Bunsenges. Phys. Chem. *82*, 1001 (1978).
11. Cavel R. G., Byers W., Day E. D.: Inorg. Chim. *10*, 2710 (1971).
12. Havel J., Burešová-Jančářová I., Kubáň V.: Collect. Czech. Chem. Commun. *48*, 1290 (1983).
13. Bunton A., Romsted L. S., Sepúlveda L.: J. Phys. Chem. *84*, 2611 (1980).
14. Romsted L. S. in: *Surfactants in Solution* (K. L. Mittal and B. Lindman, Eds),Vol. 2, p. 1015. Plenum Press, New York 1984.
15. Quina F. H., Politi M., Cucciova I. M., Martins-Franchetti S. M., Chaimovich H. in: *Solution Behaviour of Surfactants* (K. L. Mittal and E. J. Fendler, Eds), Vol. 2, p. 1125. Plenum Press, New York 1982.
16. Funasaki N.: J. Phys. Chem. *83*, 237 (1974).
17. Berthold A., Georges J.: Nouv. J. Chim. *9*, 101 (1985).
18. Němcová I., Skleničková H., Valel O., Makovička J.: Tensides – Surfactants – Detergents, in press.
19. Esteve Romero J. S., Ramis Ramos G., Garciá Alvarez-Coque M. C.: J. Colloid Interface Sci. *141*, 44 (1991).
20. Hirose C., Sepúlveda L.: J. Phys. Chem. *85*, 3689 (1981).
21. Čermáková L., Rosendorfová J., Malát M.: Collect. Czech. Chem. Commun. *45*, 210 (1980).

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