

## Importance of dye-surfactant interactions in dyeing

Rewiew

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### Abstract

*The importance of dye-surfactant intermolecular interactions for understanding the mechanism of how surfactants act as levelling agents in dyebaths is presented in this paper. The mechanisms of various dye surfactant interactions are presented. The influence of different factors, such as dye or surfactant structure, surfactant concentration, temperature, pH, presence of electrolytes and the presence of cosolvents, on the strength and the stability of the dye-surfactant complex are exposed. The dye absorption onto fibres is directly influenced by the strength and the stability of the dye-surfactant complex.*

*Keywords: dye-surfactant interactions, ionic activity, binary mixtures, ternary mixtures, influence of factors, strength of interactions.*

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## Pomen interakcij barvilo-tenzid v barvarstvu

**Pregledni znanstveni članek**

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### Izvleček

V prispevku je predstavljen pomen medmolekulskih interakcij barvilo-tenzid pri razumevanju mehanizma delovanja tenzidov kot egalizirnih sredstev v barvalni kopeli. Prikazani so mehanizmi interakcij med ionskim barvilom in ionskim oziroma neionskim tenzidom, neionskim barvilom in ionskim oziroma neionskim tenzidom ter ionskim barvilom in ionskim tenzidom v prisotnosti neionskega tenzida. Izpostavljen je vpliv različnih dejavnikov, kot so struktura barvila in tenzida, koncentracija tenzida, temperatura, pH, prisotnost elektrolita in prisotnost sotpila, na jakost in stabilnost kompleksov barvilo-tenzid. Slednji namreč neposredno vplivajo na stopnjo adsorpcije barvila na vlakna.

**Ključne besede:** interakcije barvilo-tenzid, ionska aktivnost, dvo-komponentne mešanice, trikomponentne mešanice, vpliv dejavnikov, jakost interakcij.

### 1 Uvod

Pri barvanju tekstilnih vlaken imajo interakcije barvilo-tenzid in tenzid-tenzid velik praktični pomen. Tenzidi lahko opravljajo v barvalni kopeli več funkcij, in sicer zvečajo omakanje vlaken, preprečujejo penjenje barvalne kopeli, zvečajo topnost slabo topnih barvil in ne nazadnje upočasnijo adsorpcijo barvila iz barvalne kopeli na vlakna. Slednje je še zlasti pomembno za enakomerno obarvanje tekstilnega substrata. V zadnjem času se kot egalizirna sredstva pogosto uporabljajo mešanice tenzidov, ki so zmesi ionskega in neionskega tenzida, pri čemer je koncentracija ionskega tenzida nižja od kritične koncentracije micelov

## 1 Introduction

*Dye-surfactant and surfactant-surfactant interactions have huge practical significance in the dyeing of textile fibres. Surfactants perform different functions in the dyebath. They can operate as wetting and antifoaming agents, enhance the solubility of less soluble dyes, as well as slow down adsorption of the dye. The latter is particularly important when an evenly dyed textile substrate is desired. In recent years, surfactant mixtures have been used as levelling agents. Mixtures are compounds of ionic and nonionic surfactants, where the concentration of the ionic surfactant is lower than the critical micelle concentration (c.m.c.) and the concentration of the nonionic surfactant is higher than the c.m.c.*

*Ionic surfactants can be dye- or fibre-substantive [1]. A surfactant is dye-substantive when it carries a charge opposite to that of the dye, and thus dye-surfactant complexes can be formed. At low temperatures, dyeing complexes reduce dye adsorption onto textile fibres and therefore, enable an evenly dyed textile substrate. However, the strength of complexes should not be strong enough to allow the complexes to break down as the temperature rises; otherwise, insufficient bath exhaustion could occur. The addition of an ionic surfactant to the solution of an ionic dye of an opposite charge often leads to the formation of insoluble complexes, which manifest as precipitates. Precipitation can be prevented by adding either an amount of the ionic surfactant that exceeds the stoichiometric amount or a nonionic surfactant at a concentration higher than the c.m.c. of the solution. The latter causes solubilisation of the formed complexes by micelles of a nonionic surfactant [1]. Fibre-substantive ionic surfactants are usually of the same ionic type as the dye. In such systems, both surfactant and dye ions compete for the adsorption sites in the fibre. If dye ions have a greater affinity for fibres than surfactant ions, the dye ions will displace surfactant ions during dyeing and bind to the functional groups of fibres [1].*

*The dye-surfactant interactions in an aqueous solution are the main topic of several studies*

(c. m. c.), koncentracija neionskega tenzida pa višja od c. m. c. Ionski tenzidi so lahko substantivni do barvila ali do tekstilnih vlaken [1]. Tenzid je substantiven do barvila, ko je naboj tenzida nasproten naboju barvila in tvori z barvilom komplekse. Nastali kompleksi zmanjšajo adsorpcijo barvila na tekstilna vlakna pri nižji temperaturi barvanja in s tem omogočijo enakomernejše obarvanje tekstilnega substrata. Jakost kompleksov pa ne sme biti previsoka, tako da ti lahko pri višji temperaturi razpadejo. V nasprotnem primeru bi prišlo do nezadostnega izčrpanja barvila. Dodatek ionskega tenzida v raztopino ionskega barvila nasprotnega naboja pogosto povzroči nastanek netopnega kompleksa, ki se kaže v obliki oborine. Temu se lahko izognemo tako, da povečamo koncentracijo ionskega tenzida ali pa v raztopino dodamo neionski tenzid koncentracije, višje od c. m. c. Slednji povzroči, da se nastali kompleksi lahko solubilizirajo v micelle neionskega tenzida [1]. Ionski tenzidi, substantivni do vlaken, imajo enak naboj kot barvilo, zato z ioni barvila tekmujejo za prosta mesta na vlaknih. Če ima barvilo večjo afiniteto do vlaken kot tenzid, med barvanjem zamenja tenzidne ione in se samo veže na funkcionalne skupine vlaken [1].

Interakcije barvilo-tenzid v vodni raztopini so zaradi svojega velikega tehnološkega pomena predmet številnih raziskav. Razumevanje teh interakcij lahko pomembno prispeva k racionalnejši uporabi tenzidov kot egalizirnih sredstev v barvalni kopeli in s tem k tehnološko, ekološko in ekonomsko sprejemljivejšim postopkom barvanja. V okviru raziskave medmolekulskih interakcij, ki delujejo med barvilom in tenzidom v barvalni kopeli, želimo podrobneje predstaviti vpliv različnih dejavnikov na jakost in stabilnost kompleksov barvilo-tenzid.

## 2 Interakcije med ionskim barvilom in ionskim tenzidom

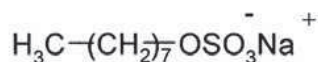
### 2.1 Interakcije pri koncentracijah tenzida, nižjih od c. m. c.

V vodnih raztopinah, ki vključujejo ione barvila in tenzida, lahko delujejo medmolekulske interakcije, katerih posledica je združevanje ionov v komplekse različnih oblik. Te so neposredno odvisne od ionske aktivnosti ter koncentracije barvila in tenzida. V razredčenih raztopinah barvila in tenzida nasprotnega naboja lahko med prostimi ioni sočasno delujejo privlačne elektrostatske, van der Waalsove in hidrofobne interakcije, ki vodijo do nastanka kompleksa, v katerem je razmerje med barvilom in tenzidom 1 : 1. Nastanek takega ionskega para lahko zapišemo z naslednjima ravnotežnima reakcijama:

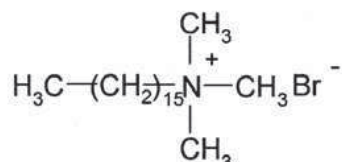


*Anionic surfactants:*

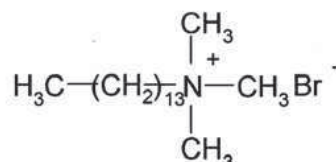
sodium dodecyl sulphate



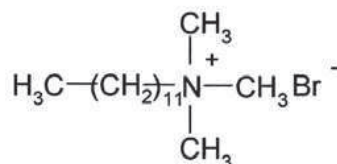
sodium octyl sulphate

*Cationic surfactants:*

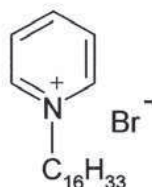
hexadecyltrimethylammonium bromide



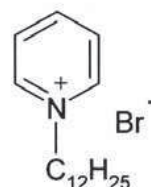
tetradecyltrimethylammonium bromide



dodecyltrimethylammonium bromide



hexadecylpyridinium bromide



dodecylpyridinium bromide

Figure 1: Structural formulae of ionic surfactants.

due to their great technological value. Understanding their working mechanism can significantly contribute to more rational uses of surfactants as levelling agents in dye baths and therefore, to technologically, ecologically and economically more acceptable dyeing processes. Within the frame of our research of the intermolecular interactions acting between dyes and surfactants in dye baths, the influences of different factions on the strength and stability of the dye-surfactant complexes are presented.

kjer je  $B^-$  anion barvila,  $B^+$  kation barvila,  $T^-$  anion tenzida,  $T^+$  kation tenzida,  $BT$  kompleks barvilo-tenzid in  $K_{BT}$  konstanta nastanka kompleksa barvilo-tenzid.

Iz dosedanjih raziskav [2–18] je razvidno, da je jakost interakcij med ioni barvila in tenzida nasprotnega naboja odvisna od različnih dejavnikov, in sicer od strukture barvila in tenzida, prisotnosti elektrolita, temperature in vrste topila.

Pri vplivu strukture tenzida in barvila na medmolekulske interakcije je obravnavan tako vpliv hidrofobne kot hidrofilne skupine. Ugotovljeno je, da struktura hidrofobne skupine pomembno vpliva na tvorbo kompleksov barvilo-tenzid, saj težnja po tvorbi kompleksov močno narašča z večanjem hidrofobnosti tenzida

## 2 Interactions between ionic dyes and ionic surfactants

### 2.1 Interactions at surfactant concentrations lower than the c.m.c.

*In aqueous solutions that include ions of dyes and surfactants, association of ions into complexes of different forms can occur as a consequence of intermolecular forces acting between ions. The form of the complexes is directly influenced by the ionic activity and the concentrations of both the dye and the surfactant. In dilute solutions, attractive electrostatic forces, van der Waals forces and hydrophobic interactions simultaneously act among the free ions of dye and surfactant of opposite charges, leading to complex formation, where the ratio between the dye and surfactant is 1:1. Formation of such an ionic couple can be written by the following equilibrium reactions: (Equations 1 and 2),*

*where  $B^-$  is a dye anion,  $B^+$  is a dye cation,  $T^-$  is a surfactant anion,  $T^+$  is a surfactant cation,  $BT$  is a dye-surfactant complex and  $K_{BT}$  is a constant of dye-surfactant complex formation.*

*From studies conducted so far [2–18], it can be seen that the strength of interactions between dye ions and surfactant ions of opposite charges is influenced by different factors, such as dye and surfactant structure, the presence of an electrolyte, temperature and the type of solvent.*

*The influence of both hydrophobic and hydrophilic groups of dyes and surfactants on intermolecular interactions has been discussed.*

*It was established that the structure of the hydrophobic group significantly influences the dye-surfactant complex formation. Thus the tendency for complex formation is strongly enhanced by increasing the hydrophobicity of the dye or surfactant. The strength of the dye-surfactant interaction increases with the length of the surfactant alkyl chain [2–10, 15, 18]. The anionic surfactant sodium dodecyl sulphate, with twelve carbonium atoms in its alkyl chain, forms stronger interactions with cationic dyes than sodium octyl sulphate, which has eight carbonium atoms in its alkyl chain [5]. Among the studied cationic surfactants, hexadecylammonium bromide forms the strongest, tetradecyltrimethylammonium bromide forms weaker and dodecyltrimethylammonium bromide*

ali barvila. Jakost interakcij barvilo-tenzid narašča z dolžino alkilne verige tenzida [2–10, 15, 18]. Anionski tenzid natrijev dodecilsulfat z dvanajstimi ogljikovimi atomi v alkilni verigi tvori veliko močnejše interakcije s kationskim barvilom kot natrijev oktilsulfat z osmimi ogljikovimi atomi [5]. V skupini kationskih tenzidov tvori heksadeciltrimetilamonijev bromid najmočnejše interakcije z anionskim barvilom, sledita mu tetradeciltrimetilamonijev bromid s šibkejšimi interakcijami in dodeciltrimetilamonijev bromid z najšibkejšimi interakcijami [2, 6]. Prav tako je konstanta nastanka kompleksa med heksadecilpiridinijevim kloridom in anionskim barvilom večja v primerjavi z dodecilpiridinijevim kloridom pri enakih pogojih [3, 8, 15]. Heksadecilpiridinijev bromid tvori močnejše interakcije z anionskim barvilom kot heksadeciltrimetilamonijev bromid [6, 7]. Vzrok za to so pripisali večji hidrofobnosti piridinijeve skupine v primerjavi s trimetilamonijevo skupino. Hkrati s tem planarna zgradba piridinijeve skupine ne otežuje zblížanja med kationom tenzida in anionom barvila v primerjavi s kvarterno amonijevo spojino, v kateri tri metilne skupine, vezane na kvarterni dušikov atom, zaradi svoje voluminoznosti prostorsko ovirajo dostop anionski sulfonski skupini barvila. V primeru alkilpiridinijevih kationskih tenzidov lahko med aromatskim obročem tenzida in aromatskim obročem barvila delujejo še privlačne  $\pi$ - $\pi$  elektronske interakcije in van der Waalsove sile [2, 4, 7, 9], ki še dodatno povečajo konstanto nastanka kompleksa. Strukturne formule proučevanih anionskih in kationskih tenzidov so prikazane na sliki 1.

Simončič in sodelavci [15, 18] so potrdili, da na jakost interakcij barvilo-tenzid vpliva tudi hidrofobnost barvila. Povečanje števila aromatskih obročev v strukturi barvila vpliva na povečanje privlačnih interakcij v kompleksu s kationskim tenzidom. Dutta in Bhat [5] sta ugotovila, da vključitev metilne skupine, ki inducira protonacijo barvila, v strukturo kationskega barvila fenosafranina poveča konstanto nastanka kompleksa barvilo-tenzid. Iz raziskav je tudi razvidno, da pri tvorbi ionskega para sodelujejo tako dolgosežne privlačne elektrostatske interakcije kot kratkosežne privlačne polarne in nepolarne van der Waalsove sile ter hidrofobne interakcije. Dutta in Bhat [6] sta ugotovila, da na jakost interakcij barvilo-tenzid vpliva tudi protiion, vezan na pozitivni center kationskega tenzida. Pri enaki strukturi tenzidnega kationa tvori alkiltrimetilamonijev klorid močnejše interakcije z anionskim barvilom kot alkiltrimetilamonijev bromid. Vzrok za to je v različni hidrataciji kloridnega in bromidnega iona ter njunem vplivu na strukturo vode. Tako ima kloridni protiion večji izsoljevalni učinek kot bromidni protiion.

Z rezultati spektrofotometričnih meritev sta Forte in Špan [7] dokazala, da dodatek elektrolita v raztopino ionskega barvila in ionskega tenzida nasprotnega naboja povzroči zasenčenje naboja barvila in tenzida, kar zmanjša elektrostatski privlak med ioni v kompleksu. Zmanjšanje elektrostatskih privlačnih sil se v širšem smislu nadomesti s hidrofobnimi interakcijami.

forms the weakest interactions with anionic dyes [2, 6]. Likewise, the constant of complex formation between hexadecylpyridinium chloride and an anionic dye is higher compared to dodecylpyridinium chloride at the same conditions [3, 8, 15]. Hexadecylpyridinium bromide forms stronger interactions with an anionic dye than hexadecyltrimethylammonium bromide [6, 7]. The cause for this was ascribed to higher hydrophobicity of the pyridinium than the trimethylammonium group. At the same time, the planar structure of pyridinium does not prevent the surfactant cation and the dye anion from closing together if compared to a quaternary ammonium compound, where three methylene groups are bound to a quaternary nitrogen atom and their bulkiness hinders the closing together of the anionic sulphonic group of a dye. In the case of an alkylpyridinium cationic surfactant, attractive  $\pi$ - $\pi$  interactions and van der Waals forces can act among aromatic rings of the dye and surfactant [2, 4, 7, 9]. These interactions additionally contribute to an enhancement of the constant of complex formation. Structural formulae of both anionic and cationic studied surfactants are presented in Figure 1. Simončič and coworkers confirmed that the strength of dye-surfactant interactions is also influenced by dye hydrophobicity. As the number of aromatic rings in the dye structure increases, attractive forces will be enhanced in the complexes with a cationic surfactant [15, 18]. Dutta and Bhat [5] found that the incorporation of a methyl group into the structure of the cationic dye fenosafranine, which induces protonation of the dye, increases the constant of dye-surfactant complex formation. From the results obtained, it can be seen that both long-range electrostatic and short-range polar attractive, nonpolar van der Waals and hydrophobic forces as well cooperate during ion pair formation.

Dutta and Bhat [6] established that the counterion that is bound to the positive centre of a cationic surfactant also influences the strength of dye-surfactant interactions. Alkyltrimethylammonium chloride forms stronger interactions with anionic dyes than alkyltrimethylammonium bromide with the same surfactant structure. This is due to the differences in hydration

Konstanta nastanka kompleksa barvilo-tenzid se zmanjšuje z naraščajočo temperaturo [2–8, 11, 16, 17]. Zaradi večje kinetične energije, ki jo imajo ioni pri višji temperaturi, se težnja po združevanju med njimi zmanjšuje. Pri določeni temperaturi se kompleksi med barvilom in tenzidom celo ne tvorijo več [2]. Iz raziskav je tudi razvidno, da se pri višji temperaturi začnejo tvoriti kompleksi anionsko barvilo-kationski tenzid pri višji koncentraciji tenzida kot pri nižji temperaturi [3, 12].

Bračko in Špan [4] sta s proučevanjem vpliva topila na interakcije anionsko barvilo-kationski tenzid ugotovila, da dodatek etanola v vodno raztopino zmanjša težnjo po tvorbi ionskega para. Pri tem je vpliv etanola dvojen. Zvečanje deleža etanola v mešanici etanol-voda povzroči znižanje dielektrične konstante topila, kar vpliva na zvečanje privlačnih elektrostatskih interakcij. Hkrati s tem pa etanol negativno vpliva na hidrofobne interakcije, saj povzroči porušitev urejene strukture molekul vode okrog hidrofobnih delov barvila in tenzida. Znižanje konstante nastanka kompleksa barvilo-tenzid v mešanem topilu etanol-voda kaže na to, da so elektrostatske privlačne sile bistvenega pomena za tvorbo ionskega para. Omogočijo namreč, da se ioni barvila in tenzida približajo na tako majhne razdalje, da lahko med njimi začnejo delovati kratkosežne, a močne privlačne necoulombske sile, kot so van der Waalove in hidrofobne. Te ugotovitve sta potrdila tudi Neumann in Gehlen z določitvijo proste energije, ki spremlja tvorbo ionskega para [13]. V razredčenih vodnih raztopinah barvila in tenzida enakega naboja delujejo močne elektrostatske odbojne sile, ki preprečujejo tvorbo kompleksov, kar je dokazala Simončič s sodelavci [15, 19]. Ker je jakost kratkosežnih privlačnih interakcij premajhna, da bi presegla močan elektrostatski odboj med enako nabitimi ioni barvila in tenzida, v takih raztopinah ni kompleksov barvilo-tenzid.

## 2.2 Interakcije pri koncentracijah tenzida, višjih od c. m. c.

V raztopinah tenzida koncentracij, višjih od c. m. c., se zaradi delovanja privlačnih medmolekulskih sil ioni tenzida združujejo v večje skupke, imenovane miceli. V takih raztopinah so poleg prostih ionov tenzida prisotni tudi miceli. Zaradi svoje ionske aktivnosti lahko miceli tvorijo privlačne elektrostatske interakcije z ioni barvila nasprotnega naboja. Posledica tega je vezanje iona barvila v micel tenzida. Proces raztapljanja barvila v micelu tenzida imenujemo solubilizacija. Reakcijo micelizacije tenzida in solubilizacije barvila v micel lahko ponazorimo z naslednjimi ravnotežnimi reakcijami:



oziroma:





and their effects on water structure. The chloride counterion has a greater salting-out effect and water structuring ability compared to the bromide counterion.

Forte and Špan discovered by spectrophotometric measurements that the addition of an electrolyte to the solution of an ionic dye and an ionic surfactant of opposite charges causes screening of the charge on the dye and surfactant, which diminishes the electrostatic attraction among ions in a complex. However, the reduction is compensated to a greater extent by hydrophobic interactions [7].

The constant of dye-surfactant complex formation decreases with increasing temperature [2–8, 11, 16, 17]. When ions possess higher kinetic energy due to a rise in temperature, the tendency for complex formation between the ions is reduced. At a certain temperature, ion pair formation does not appear [2]. From studies, it can also be seen that at higher temperature, a higher surfactant concentration is needed for anionic dye-cationic surfactant complex formation than at lower temperatures [3, 12].

The influence of a solvent on anionic dye-cationic surfactant interactions was studied by Bračko and Špan [4]. They found that the addition of ethanol to an aqueous solution of an anionic dye and a cationic surfactant reduces the tendency for dye-surfactant ion pair formation. The influence of ethanol is two-fold: firstly, the increase in ethanol content in the water-ethanol mixture causes a reduction of the dielectric constant of the solvent, which causes an increase in the attractive electrostatic interactions among ions in the solution; secondly, ethanol has a negative influence on hydrophobic interactions, because it can cause the breakdown of the structured water molecules around the hydrophobic parts of the dye and surfactant. With the reduction of the association constant of dye-surfactant complex formation in the water-ethanol mixture, it was pointed out that the electrostatic attractive forces are essential for ion pair formation. The function of electrostatic attractive forces is to bring the dye and surfactant ions so close that short-range, but strong, attractive non-Coulombic forces, like van der Waals and hydrophobic forces, can act among them. This was also stated by Neuman and Gehlen, who

kjer je  $n$  agregacijsko število tenzida,  $M^{+n}$  micel kationskega tenzida,  $M^{-n}$  micel anionskega tenzida,  $BM^{+(n-1)}$  kompleks med anionom barvila in micelom kationskega tenzida,  $BM^{-(n+1)}$  kompleks med kationom barvila in micelom anionskega tenzida,  $\kappa$  konstanta nastanka micela tenzida in  $K_{BM}$  konstanta nastanka kompleksa ionsko barvilo-ionski micel.

Pogoj za solubilizacijo ionskega barvila v micel ionskega tenzida nasprotnega naboja so elektrostatske in hidrofobne interakcije [9, 12, 20–38]. Pomembnost hidrofobnih interakcij pri vezanju barvila v micel potrjujejo rezultati, po katerih konstanta nastanka kompleksa barvilo-micel narašča z naraščajočo hidrofobnostjo tenzida [9, 20] ali barvila [30, 35, 38]. V obeh primerih se v raztopini barvila zaradi povečanja hidrofobnosti kompleksa barvilo-micel zniža c. m. c. tenzida v primerjavi z raztopino tenzida brez barvila. Göktürk [9] je ionski micel opisal s tremi različnimi področji: prvo je nepolarno jedro, ki ga tvorijo dolge alkilne verige tenzida, drugo je gosta Sternova plast, ki vsebuje hidrofilne skupine, tretje področje pa je relativno široka Gouy-Chapmanova plast, ki jo obdajajo protiioni. Predpostavil je, da lahko ioni barvila prodirajo globoko v nepolarno hidrofobno jedro micela ali ostajajo adsorbirani na njegovi relativno polarni površini, kar je odvisno od razmerja med elektrostatskimi in hidrofobnimi interakcijami med barvilom in micelom. Medtem ko elektrostatske privlačne sile med nasprotno nabitimi ioni barvila in tenzida v kompleksu povzročajo vezanje barvila v polarno z vodo bogato Sternovo plast, pa so hidrofobne interakcije pogoj za vezanje barvila v nepolarno jedro micela [9, 20, 38]. Večja ko je hidrofobnost tenzida, globlje prodira barvilo v micel. Anionsko antrakinonsko barvilo se zaradi močnih hidrofobnih interakcij močneje veže v nepolarno jedro micela heksadecilpiridinijevega klorida ali bromida v primerjavi z manj hidrofobnimi heksadecil-, tetradecil- ali dodeciltrimetilamonijevimi bromidi [9].

Iz raziskave interakcij med amfoternim hemicianinskim barvilom z različnimi hidrofobnimi skupinami in micelom kationskega tenzida heksadeciltrimetilamonijevega bromida, ki jo je izvedel Shah s sodelavci [38], je razvidno, da ima dolžina hidrofobne alkilne verige, ki je vezana na barvilo, pomembno vlogo pri solubilizaciji barvila v micel. S povečanjem hidrofobnosti barvila se namreč povečuje razmerje med hidrofobnimi in elektrostatskimi interakcijami v kompleksu. Barvilo s krajšo alkilno verigo je bolj polarno in se zato veže na površino micela, ki je polaren medij. Pri tem premik barvila iz polarnega mikrookolja v nepolarno jedro micela ni favoriziran. Ion barvila prodre globlje v jedro micela le, če je njegova hidrofobnost tako velika, da hidrofobne interakcije prevladajo nad elektrostatskimi [38]. Te ugotovitve so v skladu z izsledki raziskav Behere in Mishre s sodelavci [20, 30] ter njihovim proučevanjem interakcij med kationskimi stirilpiridinijevimi barvili in miceli anionskih tenzidov natrijevega alkilbenzensulfonata in natrijevega dodecilsulfata, kjer so pri vezanju manj hidrofobnih barvil v micel pomembne elektrostatske in hi-

determined the free energy that accompanies the ion pair formation [13].

Simončič and coworkers [15, 19] proved that strong electrostatic repulsive forces, which prevent complex formation, act between dye and surfactant ions of the same ionic charge in dilute water solutions. Since the strength of short-range attractive interactions is too weak to overcome the strong electrostatic repulsion between the same charged ions of the dye and surfactant, no dye-surfactant complex formation is observed in such solutions.

## 2.2 Interactions at surfactant concentrations higher than the c.m.c.

In solutions where the surfactant concentration is higher than the c.m.c., surfactant ions join into bigger aggregates called micelles, due to attractive intermolecular forces that act between the ions. In such solutions, micelles are also present in addition to free ions of the surfactant. Because of their ionic activity, micelles might form attractive electrostatic interactions with dye ions of the opposite charge, which results in the binding of dye ions to surfactant micelles. Solubilisation is defined as the spontaneous dissolution of a nonionic dye in the surfactant micelle. Micellisation and solubilisation of a dye in the micelle can be illustrated by the equilibrium equations as follows:

(Equations 3 and 4) and (Equations 5 and 6), where  $n$  is the aggregation number of the surfactant,  $M^{+n}$  is the cationic micelle,  $M^{-n}$  is the anionic micelle,  $BM^{+(n-1)}$  is the complex between the dye anion and cationic micelle,  $BM^{-(n+1)}$  is the complex between the dye cation and anionic micelle,  $\kappa$  is the constant for micelle formation and  $K_{BM}$  is the constant for ionic dye-ionic micelle complex formation.

Solubilisation of an ionic dye by an ionic micelle of the opposite charge is governed by electrostatic and hydrophobic interactions [9, 12, 20–38]. The importance of hydrophobic interactions for binding of a dye to a micelle is confirmed by the results indicating that the constant for dye-micelle complex formation increases with increasing hydrophobicity of both the surfactant [9, 20] and the dye [30, 35, 38]. The c.m.c. of the surfactant is reduced in dye solutions due to enhancement of the hydrophobicity of the dye-

drofobne interakcije, pri zelo hidrofobnih barvilih pa prevladujejo hidrofobne interakcije.

Na način vezanja anionskega barvila v micel kationskega tenzida pomembno vplivata tudi struktura in število anionskih skupin v barvilu, kar sta potrdili Nemcová in Čermaková [32]. Vključitev anionske sulfonske skupine na kromogen barvila preprečuje prodiranje barvila v hidrofobno jedro kationskega micela. Barvilo ostaja na hidrofilni površini micela. Hkrati s tem pa je tudi kvarтерна amonijeva skupina tenzida močno asociirana z aromatskim obročem barvila, kar prav tako preprečuje, da bi barvilo prodrlo globoko v notranjost micela. Barvilo je s hidrofilnimi sulfonskimi ali karboksilnimi skupinami vključeno v Sternovo plast micela, bogato z vodo, v obliki sendviča [9, 29, 36, 37]. Poleg hidratacije hidrofilnih skupin barvila poteče tudi solvatacija aromatskega obroča barvila, zato delujejo med sosednjimi verigami tenzida, kjer so prisotne hidrofobne interakcije, in barvilom še van der Waalove sile, ki povzročijo spremembo v mikrokolju kromogena. Ta se kaže v batokromnem premiku valovne dolžine absorpcijskega maksimuma kompleksa v primerjavi z valovno dolžino absorpcijskega maksimuma barvila [9, 25, 26].

Göktürk in Tunçay [28] sta ugotovila, da je vezanje kationskega barvila Safranin O na natrijev dodecilsulfat večje kot na natrijev dodecilsulfonat. Vzrok za to je v različnih polarnih skupinah tenzida, saj je žveplo sulfonske skupine neposredno vezano na ogljik hidrofobne verige, žveplo sulfatne skupine pa prek kisikovega mostu. Ta strukturna razlika bistveno vpliva na težnjo tenzida po tvorbi kompleksov.

Raziskave interakcij barvilo-micel v mešanih topilih, ki sta jih prav tako izvedla Göktürk in Tunçay [28], so pokazale, da dodatek metanola, dimetilformamida in 1,4-dioksana v vodo poveča c. m. c. ionskega tenzida. Posledica tega je znižanje stopnje vezanja barvila v micel z zvečanjem volumenskega razmerja sotopila v mešanici.

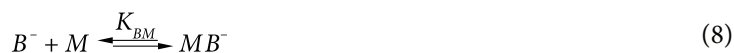
Pri interakcijah med ioni barvila in miceli tenzida enakega naboja močni elektrostatski odboj med enako nabitimi ioni prepreči tvorbo kompleksa, tako da solubilizacija barvila v micel ni mogoča [21, 22, 26, 27, 29, 31, 35–37]. Izjema so le zelo hidrofobna barvila, pri katerih privlačne hidrofobne interakcije med barvilom in micelom, ki so močnejše od elektrostatskega odboja, omogočajo vezanje barvila v micel [27].

## 3 Interakcije med ionskim barvilom in neionskim tenzidom

Interakcije med ionskim barvilom in neionskim tenzidom potečejo pri koncentracijah tenzida, višjih od c. m. c., posledica teh interakcij je nastanek kompleksa barvilo-micel. Interakcije med ioni barvila in prostimi molekulami neionskega tenzida so zanemarljive [39]. Micelizacijo neionskega tenzida in vezanje iona barvila v micel lahko ponazorimo z naslednjimi ravnotežnimi reakcijami:

micelle complex compared to surfactant solutions where the dye is not present. Göktürk [9] characterised ionic micelles by three distinct regions: the non-polar core formed by long alkyl chains of the surfactant; a compact Stern Layer, including hydrophilic groups, and a relatively wider Gouy-Chapman Layer that encompasses the majority of counterions. He assumes that dye ions can penetrate deep into the non-polar hydrophobic core of the micelle or adsorb to its relative polar surface, which depends on the ratio between electrostatic and hydrophobic interactions between the dye and micelle. While electrostatic interactions between ions of dyes and surfactants of opposite charge in the complex govern binding of the dye to the polar, water-rich Stern Layer, the hydrophobic interactions govern binding of the dye to the non-polar core of the micelle [9, 20, 38]. Dye molecules penetrate deeper towards the hydrocarbon core with increasing hydrophobicity of the surfactant. The anionic antraquinone dye binds stronger to the non-polar core of micelles of hexadecylpyridinium chloride or bromide in comparison with less hydrophobic hexadecyl-, tetradecyl- or dodecyltrimethylammonium bromides [9].

From the study of interactions between amphiphilic hemicyanine dyes with different hydrophobic groups and cationic micelles of hexadecyltrimethylammonium bromide carried out by Shah and coworkers [38], it can be seen that the length of the hydrophobic alkyl chain bound to the dye molecule has an important role in solubilisation of the dye by the micelle. By increasing the dye hydrophobicity, the ratio between hydrophobic and electrostatic interactions in the complex increases. Dyes with shorter alkyl chains are more polar and bind to the micelle surface, which is a polar medium. The shift of the dye from a polar microenvironment to a nonpolar micellar core is not favourable. Dye ions penetrate deeper into the micellar core only if the hydrophobicity is so great that hydrophobic interactions can overcome the electrostatic interactions [38]. These findings are in accordance with the results obtained by Behera, Mishra and co-workers [20, 30]. They studied interactions between cationic styryl pyridinium dyes and anionic surfactant micelles of sodium alkylbenzenesulphonate and sodium dodecyl



kjer sta  $N$  in  $M$  molekula in micel neionskega tenzida,  $MB^-$  in  $MB^+$  kompleksa med ionom barvila in micelom neionskega tenzida in  $K_{MB}$  konstanta nastanka kompleksa ionsko barvilo-neionski micel.

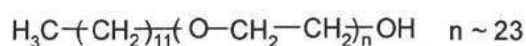
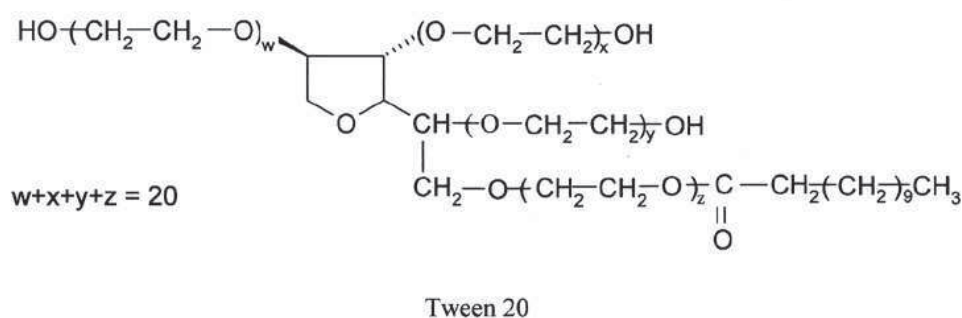
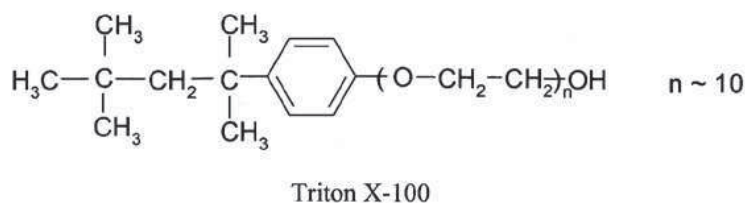
Iz raziskav, ki so bile opravljene z uporabo različnih metod, kot so NMR, UV-VIS-spektrofotometrija, potenciometrija, merjenje viskoznosti, gostote ter površinske napetosti raztopin, je ugotovljeno, da so za tvorbo kompleksa med anionom barvila in micelom neionskega tenzida v večji meri odgovorne hidrofobne interakcije, za tvorbo kompleksa med kationom barvila in micelom neionskega tenzida pa poleg hidrofobnih interakcij tudi charge-transfer oziroma elektron donor-akceptor interakcije [21–29, 31, 32, 35–37, 39–51]. Pri tem deluje kationska skupina barvila kot elektron akceptor, polioksietilenska skupina neionskega tenzida pa kot elektron donor. Če anionsko barvilo vključuje substituentne, ki omogočijo nastanek pozitivnega centra v vzbujenem stanju barvila, lahko tudi med anionskim barvilom in micelom delujejo charge-transfer interakcije [22, 23]. Barvilo v vzbujenem stanju deluje kot elektron akceptor, neionski tenzid pa kot elektron donor.

Na splošno je jakost interakcij med anionom oziroma kationom barvila in micelom neionskega tenzida večja v primerjavi z micelom ionskega tenzida nasprotnega naboja [21, 28, 37]. To pomeni, da je neionski micel prijaznejše mikrookolje za ionsko barvilo kot ionski micel nasprotnega naboja.

Jakost interakcij narašča z naraščajočo hidrofilnostjo tenzida in hidrofobnostjo barvila [27, 44, 45, 49]. Ugotovljeno je, da se konstanta vezanja anionskega barvila na micel neionskega tenzida povečuje z naraščajočo polioksietilensko skupino tenzida [44, 49]. To lahko razložimo tako, da je mikrookolje micela, ki vključuje daljšo polioksietilensko skupino, ugodnejše za vezanje polarne barvila, kot če vključuje krajšo polioksietilensko skupino. V seriji kationskih N-alkilstirilpiridinijevih barvil se konstanta vezanja barvila v micelo neionskega tenzida Triton X-100 (TX-100) povečuje z naraščajočo dolžino alkilne verige, vezane na kationski dušik barvila [45], pri anionskih azobarvilih pa z večanjem alkilne skupine, vezane na benzenski obroč kromogena [49]. Z naraščanjem hidrofilnosti anionskega barvila, ki je posledica povečanja števila sulfonskih skupin v strukturi barvila, se stopnja nastanka kompleksa zmanjšuje [38, 44, 46].

Stevenson in sodelavci [49] so dokazali, da struktura anionskega barvila ne vpliva le na jakost interakcij, temveč tudi na način vezanja barvila v neionski micel. Jocić, Oakes in Gratton [42, 46] so ugotovili, da se barvilo zaradi prisotnosti anionske polar-





Brij 35

Figure 2: Structural formulae of nonionic surfactants.

sulphate. It was established that for the binding of less hydrophobic dyes to micelles, both electrostatic and hydrophobic interactions are important, while for more hydrophobic dyes, only hydrophobic interactions prevail.

Nemcová and Čermaková [32] confirmed that the dye structure and the number of anionic groups of the dye influence the mode of binding of an anionic dye to a cationic surfactant micelle. Incorporation of an anionic sulphone group to the dye chromogene prevents the dye from penetrating the hydrophobic core of a cationic micelle. The dye resides in the hydrophilic surface of the surfactant micelle. At the same time, the quaternary ammonium group of the surfactant is strongly associated with the aromatic ring of the dye, which prevents the dye from penetrating deeper into the micelle core. The dye, with its hydrophilic sulphonic or carboxylic groups, is incorporated into the water-rich Stern Layer of the micelle in a sandwich arrangement [9, 29, 36, 37]. Besides hydration of the hydrophilic group of the dye, solvation of

ne sulfonske skupine ne solubilizira v nepolarno jedro micela, ampak ostaja tik ob polioksietilenskih verigah in le delno prodira v hidrofobno področje micela. Na globino prodiranja vplivajo substituenti, vezane na kromogen barvila. Stopnja nastanka kompleksa anionsko barvilo-micel neionskega tenzida narašča z naraščanjem hidrofobnosti p-substituent barvila v vrstnem redu  $-\text{CH}(\text{CH}_3)_2 > -\text{CH}_3 > -\text{Cl} > -\text{H} > -\text{OCH}_3$  oziroma pade, če so na p-mestu vezane hidrofilne substituenti, kot sta  $-\text{SO}_3^-$  in  $-\text{COO}^-$  [46].

Iz rezultatov spektrofotometričnih meritev, ki sta jih izvedla Dakiky in Dutta s sodelavci [25, 27], je tudi razvidno, da se v kompleksu, ki nastane med anionskim barvilom in micelom neionskega tenzida, barvilo veže globlje v nepolarno jedro micela v primerjavi s kationskim micelom, pri katerem ostane vezano le na njegovi površini. To je tudi vzrok, da neionski micel bolj vpliva na obliko spektra anionskega barvila kot kationski micel.

Kationska barvila tvorijo z miceli neionskega tenzida v vodnem mediju komplekse [21, 27, 29, 35, 36, 39, 41], v katerih med kationom barvila in polioksietilensko skupino tenzida delujejo elektrostatske privlačne sile. V primeru neionskega tenzida TX-100, ki vsebuje fenilno skupino, bogato z elektroni, ta dodatno sodeluje pri tvorbi privlačnih interakcij z elektronsko deficitarnim barvilom [35, 39]. Prav tako sta Bhattacharya in Sarkar s sodelavci

*the aromatic ring of the dye also appeared. Van der Waals forces also participate between adjacent surfactant chains, where hydrophobic interactions are present, and the dye, which causes a change in the microenvironment of the dye chromophore. This can be seen in the bathochromic shift of the wavelength of the absorption maximum of the complex in comparison with the wavelength of the absorption maximum of the pure dye [9, 25, 26].*

*Göktürk and Tunçay [28] established that the cationic dye Safranin O binds stronger to sodium dodecyl sulphate compared to sodium dodecyl sulphonate. The reason for this is in the difference between the surfactant polar groups. The sulphur atom of the sulphonic group directly joins to the carbon atom of the hydrophobic chain, while the sulphur atom of the sulphate group joins to the carbon atom of hydrophobic chain via an oxygen atom. This structural difference has an essential influence on the surfactant tendency for complex formation.*

*Studies of dye-micelle interactions in solvent mixtures, achieved by Göktürk and Tunçay [28], showed that addition of methanol, dimethylformamide and 1,4-dioxane to water increases the c.m.c. of an ionic surfactant. This is reflected in the reduction of the binding degree of the dye to the micelle, due to an increase in the volumetric ratio of a cosolvent in the mixture.*

*Electrostatic repulsion acts strongly between dye ions and surfactant micelles of the same ionic charge, which prevents complex formation and thus, the solubilisation of the dye by the micelle is not possible [21, 22, 26, 27, 29, 31, 35–37]; however, very hydrophobic dyes are an exception. Attractive hydrophobic interactions, which act between the dye and the micelle, are stronger than electrostatic repulsion, and therefore, govern binding of the dye to micelles [27].*

### 3 Interactions between ionic dyes and nonionic surfactants

*Interactions between an ionic dye and a nonionic surfactant take place at a surfactant concentration higher than the c.m.c., which causes dye-micelle complex formation. However, interactions between dye ions and free molecules of a nonionic surfactant can be neglected [39].*

[21, 37] ugotovila, da se med kationskim barvilom in neionskim micelom tvorijo kompleksi v razmerju 1 : 1 glede na strukturo tenzida.

Jakost interakcij, ki je neposredno odvisna od strukture tenzida in barvila, narašča z naraščanjem hidrofobnosti tenzida [21, 28, 37]. Zvečanje ogljikovodikove verige v strukturi tenzida namreč poveča elektron donorsko kapaciteto tenzida zaradi induktivnega efekta, kar pogojuje nastanek kompleksa. Iz raziskave neionskih tenzidov Tween s kationskim barvilom je razvidno, da konstanta nastanka kompleksa barvilo-micel premo sorazmerno narašča z naraščajočo hidrofobno alkilno verigo tenzida in je obratno sorazmerna s c. m. c. Pomembnost hidrofobnih interakcij potrjuje tudi ugotovitev, da je konstanta vezanja kationskega barvila na neionski tenzid Tween 20, ki vključuje 20 oksietilenskih skupin, večja v primerjavi z neionskim tenzidom Brij 35, ki vključuje 23 oksietilenskih skupin. To je namreč v skladu z njuno hidrofobnostjo, ki je za Tween 20 večja kot za Brij 35 [28]. Čeprav lahko oba tenzida s končno hidroksilno skupino tvorita vodikove vezi s proučevanim barvilom Safranin O, pa iz rezultatov sledi, da so vodikove vezi pri tvorbi kompleksov manj pomembne [28]. Konstanta vezanja kationa barvila na micel neionskega tenzida narašča tudi z naraščanjem hidrofobnosti barvila [35]. Hkrati s tem bolj hidrofobno barvilo prodira globlje v jedro tenzida kot manj hidrofobno. Na sliki 2 so prikazane strukturne formule proučevanih neionskih tenzidov.

Göktürk in Tunçay [28] sta pri proučevanju vpliva dodatka sotopila v vodno raztopino kationskega barvila in micelov neionskega tenzida ugotovila, da dodatek sotopila vpliva na jakost interakcij kationsko barvilo-neionski micel. Prisotnost sotopila, kot so metanol, dimetilformamid in 1,4-dioksan, zmanjša stopnjo vezanja barvila v micel, ki se zmanjšuje z naraščajočo koncentracijo sotopila v mešanici z vodo. V mešanici vode in sotopila se namreč zmanjša polarnost topila v primerjavi z vodo, kar bistveno vpliva na zmanjšanje hidrofobnih interakcij pri tvorbi kompleksa.

Težnja po interakcijah med ionskim barvilom in micelom neionskega tenzida in s tem povezana stabilnost kompleksa padata z naraščanjem temperature raztopine [27, 37, 47].

## 4 Interakcije med neionskim barvilom in ionskim/neionskim tenzidom

Neionsko barvilo je v vodi slabo topno. Za povečanje njegove topnosti v vodi dodajamo v barvalno kopel tenzid. Tenzid pri koncentracijah, višjih od c. m. c., povzroči spontano raztapljanje neionskega barvila v micel tenzida. Pri tem se tvori termodinamsko stabilen sistem. Solubilizacijo neionskega barvila v micel omogočajo hidrofobne, charge-transfer in elektrostatske interakcije. Reakcijo solubilizacije neionskega barvila v micel ionskega ali neionskega tenzida lahko zapišemo z naslednjimi ravnotežnimi enačbami:

Micellisation of a nonionic surfactant as well as binding of a dye ion to a nonionic micelle can be illustrated by the following equilibrium reactions: (Equations 7, 8 and 9),

where  $N$  and  $M$  are a molecule and a micelle of a nonionic surfactant,  $MB^-$  and  $MB^+$  are complexes between an ionic dye and a nonionic micelle and  $K_{MB}$  is the constant for ionic dye–nonionic micelle complex formation.

From the use of different methods, like NMR, UV-VIS spectrophotometry, potentiometry, viscosimetry, density and surface tension, it can be seen that complex formation between a dye anion and a nonionic micelle is mainly governed by hydrophobic interactions, compared to complex formation between a dye cation and a nonionic micelle, which is governed by hydrophobic and charge-transfer or donor-acceptor interactions [21–29, 31, 32, 35–37, 39–51]. In these complexes, the cationic dye group acts as an electron acceptor, whereas the polyoxyethylene group of a nonionic surfactant acts as an electron donor. If the anionic dye contains substituents, which might form positive charges in the excited state, then charge-transfer interactions will also appear [22, 23]. The dye in its excited state acts as an electron acceptor and the nonionic surfactant as an electron donor.

In general, the strength of interactions between dye anions or dye cations and the micelle of a nonionic surfactant is stronger in comparison with an ionic micelle of the opposite charge [21, 28, 37]. This means that the nonionic surfactant is a more favourable microenvironment for the ionic dye than the ionic micelle of the opposite charge.

The strength of interactions increases with increasing surfactant hydrophilicity and dye hydrophobicity [27, 44, 45, 49]. It has been stated that the binding constant of an anionic dye to a surfactant micelle increases with increasing polyoxyethylene group length of the surfactant [44, 49]. This can be explained with the microenvironment of the micelle. If a nonionic surfactant includes a longer polyoxyethylene chain, then the microenvironment of the micelle will be more favourable for binding the polar dye than the microenvironment of the nonionic micelle with a shorter polyoxyethylene chain. In the series of cationic *N*-alkyl styryl pyridin-



kjer je  $B$  molekula neionskega barvila,  $BM^{+n}$ ,  $BM^{-n}$  in  $BM$  so kompleksi med neionskim barvilom in ionskim oziroma neionskim micelom.

Raziskave s področja interakcij neionsko barvilo-ionski tenzid oziroma neionsko barvilo-neionski tenzid so opravljene pretežno na modelnih barvilih, kot so naftalen, piren in fenantren. Izsledki raziskav solubilizacije neionskih barvil v micel tenzida kažejo, da se neionsko barvilo lahko vključi v hidrofobno področje micela, tj. v njegovo notranjost, ali pa ostaja adsorbirano na medfazi micela, tj. v njegovi hidrofilni plasti [52–60]. Mesto v micelu, na katero se veže neionsko barvilo, je odvisno od strukture barvila in tenzida [52]. Polarna spojina se solubilizira v hidrofilni del micela, nepolarna spojina pa v hidrofobni del micela [53, 54]. Torej, manjša ko je polarnost spojine in večja ko je njena hidrofobna skupina, lažje spojina prehaja iz vodne v micelarno fazo [53]. Stopnja solubilizacije je odvisna od strukture barvila in tenzida, ionske narave micelov in koncentracije tenzida [52, 56]. Manjše molekule barvila se lažje solubilizirajo kot večje molekule [52]. Z zvišanjem koncentracije tenzida se povečuje količina solubilizirane snovi. To je tudi razumljivo, saj je s povečanjem koncentracije tenzida v raztopini prisotnih več micelov, ki so sposobni solubilizirati netopne snovi [54]. V splošnem kažejo kationski tenzidi s kvarterno amonijevo skupino manjšo sposobnost solubilizacije v primerjavi z neionskimi tenzidi z enako dolžino hidrofobne verige. Povečanje hidrofobnosti ionske skupine kationskega tenzida, tj. vključitev etilne ali benzilne skupine, povzroči povečanje solubilizacijske sposobnosti kationskega tenzida [55]. V primeru, da neionsko barvilo v svoji strukturi vključuje substituent, ki zaradi prehoda v vzbujeno stanje omogočijo nastanek ionskega centra na barvilu, pa ostaja barvilo adsorbirano le na medfazi neionskega micela [23]. Količina snovi, ki se solubilizira, je odvisna od koncentracije tenzida.

Schwuger in von Rybinski [54] sta v raziskavi vpliva dodatka polietilenglikola ali polivinilpirolidona v vodno raztopino anionskega tenzida natrijevega dodecilsulfata (SDS) in v vodi slabo topnega barvila Orange OT ugotovila, da se solubilizacija barvila v micel tenzida SDS povečuje z dodatkom polimera. Polimer povzroči, da poteče solubilizacija barvila Orange OT že pri koncentracijah tenzida SDS, nižjih od c. m. c. Ugotovljeno je, da imajo kompleksi polimer-SDS podobne lastnosti kot miceli SDS in zato kažejo podoben učinek solubilizacije kot raztopine čistega tenzida SDS. Mejna koncentracija mešanice polimer/SDS, pri kateri poteče solubilizacija barvila Orange OT, je veliko nižja od c. m. c. tenzida SDS. Na mejno koncentracijo vplivata tako struktura ionskega tenzida kot dodatek elektrolita, saj se s povečanjem dolžine hidrofobne verige

ium dyes, the binding constant of a dye to the nonionic micelle of Triton X-100 (TX100) increases with increasing alkyl chain length, when bound to the cationic dye nitrogen [45]. With anionic azo dyes, the binding constant increases with increasing alkyl group length, when bound to the benzene ring of the chromogene [49]. The binding constant of complex formation decreases with increasing hydrophobicity of an anionic dye due to the increasing number of sulphonic groups in the dye structure [38, 44, 46].

Stevenson and co-workers [49] proved that the structure of an anionic dye influenced not only the strength of interactions, but also the way the dye bound to the nonionic micelle. Jocić, Oakes and Gratton [42, 46] stated that a dye anion, due to the presence of an anionic polar sulphonic group, does not solubilise in the nonpolar micellar core, but resides close to the polyoxyethylene chains and partially penetrates into the hydrophobic region of the micelle. Substituents, bound to the dye chromogene, dictate the depth of the dye penetration. The anionic dye–nonionic micelle complex formation increases with increasing hydrophobicity of the *p*-substituents of dye, in the following order:  $-\text{CH}(\text{CH}_3)_2 > -\text{CH}_3 > -\text{Cl} > -\text{H} > -\text{OCH}_3$ . However, complex formation decreases if the *p*-substituents include  $-\text{SO}_3^-$  and  $-\text{COO}^-$  [46].

From the results of spectrophotometric measurements obtained by Dakiky, Dutta and co-workers [25, 27], it can be seen that the dye penetrates into the micelle further from the surface of the micelle and resides in the nonpolar micellar core in anionic dye–nonionic micelle complexes compared to cationic micelles, where the dye resides at the surface of the micelle. This may be the reason why the effect of a nonionic surfactant micelle on the dye spectra is greater than that obtained for a cationic micelle.

Cationic dyes form complexes with nonionic micelles in aqueous media [21, 27, 29, 35, 36, 39, 41] due to attractive electrostatic interactions, which act between dye cations and the polyoxyethylene groups of a nonionic surfactant. If the nonionic surfactant contains an electron-rich phenyl group, like TX100, the phenyl group of the nonionic surfactant can additionally contribute to the formation of attractive forces with an electron-poor dye [35, 39]. Likewise, Bhat-

anionskega tenzida za eno  $-\text{CH}_2$  skupino in z dodatkom elektroлита v raztopino polimer-anionski tenzid solubilizacija barvila Orange OT poveča.

Paria in Yuet [56] sta z raziskavo solubilizacije naftalena v kationski in kationsko-neionski micel ugotovila, da hidrofobne interakcije omogočajo solubilizacijo naftalena v notranjost kationskega micela, elektrostatske interakcije, ki potečejo med  $\pi$ -elektroni naftalena in pozitivnim nabojem tenzida, pa tudi na medfazo kationskega micela [55]. Solubilizacija naftalena je odvisna od dolžine alkilne verige kationskega tenzida. Kationski tenzid z daljšo alkilno verigo ima večje micelarno agregacijsko število in s tem večje področje znotraj micela, na katerem lahko poteče solubilizacija naftalena. Do enakih sklepov so prišli tudi pri proučevanju solubilizacije drugih organskih spojin v micel kationskega tenzida [53]. Na solubilizacijo naftalena vpliva tudi ionska aktivnost tenzida. Dokazano je, da poteče solubilizacija naftalena le v jedro anionskega micela, medtem ko solubilizacija v neionski micel ni odvisna od dolžine polioksietilenskih enot neionskega tenzida [56].

V vodnih raztopinah ionskega in neionskega tenzida, v katerih je koncentracija ionskega tenzida višja od c. m. c., koncentracija neionskega pa nižja od c. m. c. ali obratno, prihaja do tvorbe mešanih micelov. Delež posameznega tenzida v mešanem micelu je odvisen od koncentracije tenzida. Solubilizacija neionskega barvila v mešani micel, sestavljen iz ionskega in neionskega tenzida, je odvisna od strukture barvila, ionske narave tenzida in od molskega deleža posameznega tenzida v mešanem micelu. Pri mešanih micelih, ki vključujejo kationski in neionski tenzid ali anionski in neionski tenzid, poteče solubilizacija naftalena pri nižji koncentraciji tenzida v primerjavi z enokomponentnim tenzidom [56]. V mešanem micelu, sestavljenem iz ionskega in neionskega tenzida, neionski tenzid delno zasenči naboj in s tem zniža adsorpcijo. V mešanem kationsko-neionskem micelu so molekule bolj tesno zložene zaradi zmanjšane elektrostatske odboja med kationskimi skupinami tenzida, kar pripomore k zmanjšanju solubilizacijske sposobnosti [60].

Zhou, Zhao in sodelavci [57, 58] so z raziskavo solubilizacije pirena in fenantrena v mešani anionsko-neionski micel ugotovili, da solubilizacija pirena in fenantrena v mešani anionsko-neionski micel narašča z dolžino polioksietilenske verige neionskega tenzida oziroma z naraščanjem njegove HLB-vrednosti. Dokazali so, da količina solubiliziranega fenantrena v mešani anionsko-neionski micel narašča z naraščanjem molskega deleža neionskega tenzida oziroma pada, ko je molski delež neionskega tenzida višji od 0,9 [58].

Dar in Zhou sta skupaj s sodelavci [55, 59] proučevala solubilizacijo policikličnih aromatskih ogljikovodikov (PAHs) v mešane micelne. Ugotovila sta, da ima ekvimolarna dvokomponentna mešanica kationskega in neionskega tenzida večjo solubilizacijsko sposobnost kot kationski tenzid, neionski tenzid ali mešanica dveh kationskih tenzidov, saj solubilizacija narašča z naraščanjem



tacharya and Sarkar [21, 37] found out that 1 : 1 complexes between cationic dyes and nonionic micelles are formed irrespective of the dye structure.

The strength of interactions, which is directly affected by the dye and surfactant structures, increases with increasing surfactant hydrophobicity [21, 28, 37]. By elongation of the hydrocarbonium chain of the surfactant, the electron donor capacity of the surfactant increases due to an inductive effect, which governs complex formation. From the studies between the nonionic surfactant Tween and a cationic dye, it can be seen that the equilibrium constants for the dye-micelle complex are directly proportional to the carbon number of the Tween and inversely proportional to the c.m.c of the surfactant. From the binding constants, the significance of hydrophobic interactions is stated. The binding constant of the cationic dye-Tween 20 nonionic micelle, which includes 20 polyoxyethylene units, is bigger compared to the binding constant of the cationic dye-Brij 35 nonionic micelle, which includes 23 polyoxyethylene units. Values of the binding constants are in compliance with surfactant hydrophobicity, which is bigger for Tween 20 than for Brij 35 [28]. The results showed that hydrogen bonding is not significant for complex formation, even though both surfactants form H-bonds with the studied dye Safranin-O [28]. The binding constant of the cationic dye-nonionic micelle increases with increasing dye hydrophobicity [35]. A more hydrophobic dye penetrates deeper into the micellar core than a less hydrophobic one. The structural formulae of the nonionic surfactants studied are shown in Figure 2.

Göktürk and Tunçay [28] ascertained that the addition of a cosolvent to an aqueous solution of a cationic dye and micelles of a nonionic surfactant showed a significant influence on the strength of cationic dye-nonionic micelle interactions. The presence of a cosolvent, such as methanol, dimethylformamide and 1,4-dioxane, reduces the binding degree of the dye to the micelle, which diminished with increasing cosolvent concentration in the water mixture. The solvent polarity is reduced in water-cosolvent mixtures compared to water, which may cause

hidrofobnega značaja PAHs. Trikomponentne mešanice tenzidov, sestavljene iz dveh kationskih tenzidov in enega neionskega tenzida, imajo manjšo solubilizacijsko sposobnost od dvokomponentne mešanice, sestavljene iz kationskega in neionskega tenzida, vendar višjo od dvokomponentne mešanice, sestavljene iz dveh kationskih tenzidov. [55]. Pri proučevanju solubilizacije PAHs v mešani anionsko-neionski micel je ugotovljeno, da dodatek neionskega tenzida Triton X-405 (TX-405) poveča sposobnost solubilizacije anionskega tenzida SDS za PAHs ne glede na sestavo raztopine, medtem ko dodatek SDS v raztopino TX-405 poveča solubilizacijo PAHs v raztopino TX-405 le pri določeni sestavi raztopine. [59]

## 5 Interakcije med ionskim barvilom in ionskim tenzidom v prisotnosti neionskega tenzida

Raziskave, ki vključujejo študij medmolekulskih interakcij v vodni raztopini barvila in dveh tenzidov, so kljub svoji veliki tehnološki pomembnosti redke. Vzrok za to je prav gotovo v kompleksnosti trikomponentnega sistema, v katerem lahko delujejo tako interakcije med barvilom in tenzidom kot tudi med dvema tenzidoma. Ravnotežne reakcije, s katerimi opišemo te interakcije ne glede na njihovo jakost, so:



kjer je  $\kappa_{MT}$  konstanta nastanka kompleksa ionski tenzid-micel neionskega tenzida,  $MBT$  kompleks, ki se tvori pri vezanju kompleksa  $BT$  v micel neionskega tenzida, in  $K_{MBT}$  konstanta nastanka kompleksa  $MBT$ .

Le malo je eksperimentalnih metod, ki bi bile primerne za proučevanje interakcij barvilo-tenzid v trikomponentnih sistemih. Med njimi naj poudarimo UV-VIS-spektroskopijo [61–67] in potenciometrijo [17, 18, 67]. Pri spektrofotometričnih meritvah se zaradi interakcij med barvilom in tenzidom v spektru barvila spremeni vrednost absorbance in tudi valovna dolžina absorpcijskega maksimuma. Vzrok za to je nastanek obarvanega kompleksa barvilo-tenzid, ki ima drugačne lastnosti kot prosti ioni barvila v raztopini. Pri potenciometričnih meritvah lahko nastanek kompleksa med barvilom in tenzidom določimo na podlagi rezultatov meritev napetosti galvanskega člana, pri čemer uporabimo ionoselektivno membransko elektrodo.

*a reduction in hydrophobic interactions when complexes are formed.*

*The tendency of ionic dye–nonionic micelle interactions and the stability of the complex as well decrease with increasing temperature of the solution [27, 37, 47].*

#### 4 Interactions between nonionic dyes and ionic/nonionic surfactants

*Since nonionic dyes are poorly soluble in water, the addition of surfactant in the dye bath is needed to improve solubility. Surfactants, at concentrations higher than the c.m.c., are able to spontaneously dissolve nonionic dyes by reversible interaction with the micelle of the surfactant in a solvent to form a thermodynamically stable system. Solubilisation of a nonionic dye by micelles is governed by hydrophobic, charge-transfer and electrostatic interactions. Solubilisation of a nonionic dye by an ionic or nonionic micelle can be described with the following equilibria equations: (Equations 10, 11 and 12),*

*where B is a molecule of a nonionic dye and  $BM^{+n}$ ,  $BM^{-n}$  and  $BM$  are the complexes between a nonionic dye and an ionic or nonionic micelle.*

*Studies of nonionic dye–ionic surfactants and nonionic dye–nonionic surfactants are predominantly done with model dyes, such as naphthalene, pyrene and phenanthrene. Studies of the solubilisation of nonionic dyes by surfactant micelles showed that a nonionic dye can incorporate into the hydrophobic region of the micelle, i.e. its inner core, or adsorb in the micelle-water interface, i.e. its hydrophilic layer [52–60]. The location in the micelle where a nonionic dye will be placed is dependent upon the structure of both the dye and the surfactant [52]. Polar compounds solubilise into the hydrophilic region, but non-polar compounds solubilise into the hydrophobic region of the micelle [53, 54]. The weaker the compound polarity and the longer the hydrophobic chain of solubilised molecule, the easier the transfer of the compound from the aqueous phase to the micelle phase will be [53]. Solubilisation power is dependent upon the surfactant and dye structures, the ion-*

Simončič in Kert [17, 67] sta s potenciometričnimi titracijami, ki so bile izvedene v mešanici anionskega barvila C.I. Acid Red 88 (AR88) in kationskega tenzida dodeciltrimetilamonijevega bromida (DTA) brez neionskega tenzida TX-100 in v njegovi prisotnosti, dokazali, da dodatek tenzida TX-100 pri koncentracijah, večjih od c. m. c., povzroči znižanje konstante nastanka kompleksa AR88-DTA. To pomeni, da se stabilnost kompleksa med barvilom AR88 in tenzidom DTA zmanjša v prisotnosti micelov tenzida TX-100 v primerjavi z dvokomponentnim sistemom, v katerem tenzid TX-100 ni prisoten. Znižanje vrednosti konstante nastanka kompleksa AR88-DTA je neposredno povezano z interakcijami AR88 in DTA z neionskimi miceli tenzida TX-100, ki istočasno potekajo v raztopini in so protiutež interakcijam med AR88 in DTA. Iz rezultatov je tudi razvidno, da tenzid TX-100 neposredno vpliva na hidrofилno-hidrofobno ravnotežje kompleksov in da se kompleksi AR88-DTA lahko solubilizirajo v micelle tenzida TX-100.

Izsledke potenciometričnih raziskav sta potrdili Akbaş in Kartal, ki sta interakcije med barvili in tenzidi v trikomponentnih sistemih proučevali spektrofotometrično [61–63]. Iz spektrov barvila C.I. Reactive Orange 16 (RO16) sta razbrali, da se z naraščajočo koncentracijo neionskega tenzida alkil poli(oksietilen) etra v raztopini barvila RO16 in kationskega tenzida dodecilpiridinijevega klorida (DPC) zvišuje absorbanca barvila. Vzrok za zvišanje absorbanca sta pripisali znižanju stabilnosti kompleksov med RO16 in DPC v prisotnosti neionskih micelov. Podobne rezultate sta dobili tudi, ko sta v raztopino RO16 dodali mešanico anionskega tenzida natrijevega dodecilsulfata in neionskega tenzida alkil poli(oksietilen) etra. Rezultati spektrofotometričnih meritev so tudi pokazali, da zvišanje temperature ne vpliva na absorbanco barvila v trikomponentni mešanici. Vzrok za to je zmanjšanje polarnosti polioksietilenske verige pri višji temperaturi. Znižanje polarnosti polioksietilenske verige neionskega tenzida vpliva na zmanjšanje hidrofилnih interakcij, ki so v ravnotežju s hidrofobnimi interakcijami, tj. interakcijami med alkilnimi verigami barvila in anionskega tenzida.

Pojav solubilizacije anionskega barvila v micel neionskega tenzida je s spektrofotometrično metodo potrdil tudi Oakes [65]. Ugotovil je, da dodatek neionskega tenzida v raztopino, v kateri sta prisotna azobarvilo in kationski tenzid, vpliva na zvišanje intenzitete celotnega spektra za 30–40 %. Iz tega je sklepal, da v raztopini nastanejo mešani miceli, v katere se vključi barvilo. Zvišanje absorbanca je pripisal solubilizaciji barvila, ki poteče v mešanem micelu.

Simončič in Kert [18] sta s proučevanjem vpliva strukture barvila in tenzida na jakost interakcij anionsko barvilo-kationski tenzid v prisotnosti micelov neionskega tenzida s potenciometrično metodo ugotovili, da povečanje hidrofobnosti barvila ali kationskega tenzida vpliva na zvečanje jakosti interakcij kationski tenzid-micel neionskega tenzida v dvokomponentnem sistemu oziroma zvečanje jakosti interakcij anionsko barvilo-kationski tenzid v trikomponentnem sistemu. Na jakost interakcij anionsko barvilo-kationski tenzid vpliva tudi struktura neionskega tenzida. Z zvečanjem

ic activity of the micelle and the surfactant concentration [52, 56]. Smaller molecules solubilise more readily in micellar solution than bigger ones [52]. The amount of solubilised compound in the surfactant micelle increases with increasing surfactant concentration. This is understandable, since at higher surfactant concentrations, more micelles are present, which are able to solubilise the insoluble substances [54]. In general, cationic surfactants with quaternary ammonium head groups, exhibited lower solubilisation capacity than nonionic surfactants of the same hydrophobic chain length. An increase in the hydrophobicity of the head groups by incorporation of ethyl or benzyl groups enhanced the solubilisation capacity of cationic surfactants [55]. When the nonionic surfactant includes substituents in its structure that enable the formation of an ionic centre on the dye due to its transfer into the excited state, the dye resides in the nonionic micelle interface [23]. The amount of solubilised substance is dependent on the surfactant concentration.

In the study of the influence of the addition of polyethylene glycol and polyvinylpyrrolidone to aqueous solution of the anionic surfactant sodium dodecyl sulphate and the poorly soluble dye Orange OT by Schwuger and von Rybinski [54], it was found that the solubilisation of the dye by the SDS micelle increases with the addition of a polymer. The latter causes solubilisation of Orange OT by SDS at concentrations lower than the c.m.c. of SDS. It has been stated that the polymer-SDS complexes have similar characteristics as SDS micelles. However, polymer-SDS complexes showed the same solubilisation effect as the pure SDS surfactant solution. The concentration limit of the polymer-SDS mixture at which solubilisation of Orange OT occurs is much lower than the c.m.c. of SDS. It is affected by the ionic surfactant structure and the addition of an electrolyte. Solubilisation of Orange OT dye increases with the increasing length of the surfactant hydrophobic group for one  $-CH_2$  group as well as by the addition of an electrolyte to the polymer-anionic surfactant solution. Paria and Yuet [56] established, with the study of solubilisation of naphthalene by cationic and cationic-nonionic micelles, that naphthalene molecules solubilise into the interior of a cationic

HLB-vrednosti neionskega tenzida narašča težnja po tvorbi kompleksov kationski tenzid-micel neionskega tenzida, posledica tega pa je znižanje težnje po tvorbi kompleksov anionsko barvilo-kationski tenzid v trikomponentnem sistemu.

## 6 Zaključki

Na podlagi pregleda raziskav lahko ugotovimo naslednje:

- jakost interakcij barvilo-tenzid se povečuje z naraščanjem hidrofobnosti tenzida in barvila,
- razvejanost strukture tenzida otežuje tesno zблиžanje ionov barvila in tenzida, kar vpliva na znižanje jakosti interakcij barvilo-tenzid,
- interakcije med barvilom in micelom tenzida omogočajo solubilizacijo barvila v micel,
- mesto vključitve barvila v micel je odvisno od strukture barvila in tenzida,
- ionsko barvilo se veže v hidrofilno področje micela, neionsko barvilo pa v hidrofobno področje micela,
- dodatek neionskega tenzida v raztopino barvila in tenzida nasprotnega naboja zniža jakost interakcij barvilo-tenzid,
- z naraščanjem HLB-vrednosti neionskega tenzida narašča težnja po tvorbi kompleksov tenzid-tenzid, posledica tega pa je znižanje težnje po tvorbi kompleksov barvilo-tenzid,
- miceli neionskega tenzida so sposobni solubilizirati komplekse barvilo-tenzid,
- dodatek elektrolita zmanjša jakost interakcij med ionskim barvilom in tenzidom nasprotnega naboja,
- povišanje temperature vpliva na zmanjšanje jakosti interakcij barvilo-tenzid in
- dodatek sotopila v raztopino barvila in tenzida zniža jakost njihovih interakcij.

Iz tega lahko zaključimo, da je pri izbiri tenzida kot egalizirnega sredstva treba upoštevati vse dejavnike, ki lahko vplivajo na jakost interakcij barvilo-tenzid, saj bo le v tem primeru doseženo enakomerno obarvanje tekstilnih vlaken.

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onic micelle by hydrophobic interactions, but they can also adsorb at the interface of the cationic micelle due to electrostatic interactions between the  $\pi$ -electrons of naphthalene and the positive charge of the surfactant [55]. Solubilisation of naphthalene depends upon the length of the alkyl chain of a cationic surfactant. Cationic surfactants with longer alkyl chains have larger micellar aggregation numbers, which provide a larger micellar core region for solubilising naphthalene molecules. The same was confirmed by studies of the solubilisation of other organic compounds by cationic micelles [53]. Solubilisation of naphthalene is also affected by the ionic activity of the surfactant. It was proven that the solubilisation of naphthalene by an anionic micelle occurs only in its core, but solubilisation of naphthalene by a nonionic micelle is not governed by the length of the polyoxyethylene units of a nonionic surfactant [56].

In aqueous solutions of an ionic and a nonionic surfactant, where the concentration of ionic surfactant is higher than the c.m.c. and the nonionic surfactant lower than the c.m.c. or the inverse, mixed micelles can be formed. The proportion of an individual surfactant in a mixed micelle depends on the surfactant concentration. Solubilisation of a nonionic dye by an ionic-nonionic mixed micelle depends upon the dye structure, the ionic activity of the surfactant and the molar fraction of the individual surfactants in the mixed micelle. Naphthalene solubilises in cationic-nonionic or anionic-nonionic mixed surfactants at lower surfactant concentrations than in the pure surfactants [56]. In the mixture of cationic and nonionic surfactants, the nonionic surfactant partly shields the charges of the micelle, hence reducing the adsorption. The surfactant molecules are more closely packed in a mixed cationic-nonionic micelle due to a reduction in electrostatic repulsion among surfactant heads, which may also help to reduce micellar solubilisation [60].

Zhou, Zhao and co-workers [57, 58] established, with the study of the solubilisation of pyrene and phenantrene by anionic-nonionic mixed micelles, that solubilisation increases with the length of the polyoxyethylene chain of a nonionic surfactant and its HLB value, respectively. They proved that the amount of solu-

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bilised phenantrene by an anionic-nonionic micelle increases with increasing molar fraction of a nonionic surfactant, but decreases at a molar fraction larger than 0.9 [58].

Dar and Zhou together with co-workers [55, 59] studied the solubilisation of polycyclic aromatic hydrocarbons (PAHs) by mixed micelles. They established that an equimolar binary mixture of a cationic and a nonionic surfactant better facilitates solubilisation than pure cationic, nonionic, or cationic-cationic mixtures, which increased with increasing hydrophobic character of PAHs. However, cationic-cationic-nonionic ternary mixtures showed lower solubilising efficiency than their binary cationic-nonionic counterparts, but higher than the cationic-cationic combinations [55]. Studies on the solubilisation of PAHs by mixed anionic-nonionic micelles showed that the addition of the nonionic surfactant Triton X-405 (TX405) increases the solubilisation capability of SDS for PAHs in any solution composition, while addition of SDS to TX405 in a certain solution composition range can also increase PAH solubilisation in a TX405 solution [59].

### 5 Interactions between ionic dyes and ionic surfactants in the presence of nonionic surfactants

Investigations, including studies of intermolecular interactions in aqueous solutions, of a dye and two surfactants, are still rare despite their huge technological meaning. The cause for this lies in the complexity of the three component system, where interactions between the dye and surfactant as well as interactions between two surfactants can act. Equilibrium reactions that describe the strength of these are as follows: (Equations 1, 7, 8, 13 and 14),

where  $\kappa_{MT}$  is the constant for ionic surfactant-nonionic micelle,  $M_{BT}$  is the complex formed by binding of the BT complex to the nonionic micelle and  $K_{MBT}$  is the constant for MBT complex formation.

Only a few experimental methods are suitable for studying dye-surfactant interactions in ternary systems. Among them, UV-VIS spectroscopy [61–67] and potentiometry [17, 18, 67] should be emphasized. With spectrophotomet-

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ric measurements, the change in both the value of the absorbance and the wavelength of the absorption maximum in the absorption spectra of the dye can be detected due to interactions between the dye and surfactant. This is because the dye-surfactant complex formation has different characteristics than free dye ions in the solution. With potentiometric measurements, complex formation between the dye and the surfactant can be determined from electromotive force measurements, carried out by the use of an ion-selective membrane electrode.

Potentiometric titrations, carried out on the mixture of the anionic dye C.I. Acid Red 88 (AR88) and the cationic surfactant dodecyltrimethylammonium bromide (DTA) in the presence or absence of the nonionic surfactant TX100 by Simončič and Kert [17, 67], showed that addition of TX100 at concentrations higher than the c.m.c. causes a decrease in the constant for AR88-DTA complex formation. The stability of the complex between the AR88 dye and DTA surfactant is reduced in the presence of TX100 micelles, compared to the binary system, where TX100 is not present. The decrease in the value of the constant of AR88-DTA complex formation is directly connected to interactions between AR88 and DTA with TX100 nonionic micelles, which simultaneously act in the solution and present a counter-balance to interactions between AR88 and DTA. From the results, it can be concluded that the TX100 surfactant directly influences the hydrophilic-hydrophobic balance of the complex, and that AR88-DTA complexes are solubilised into TX100 micelles.

The results of potentiometric studies were also confirmed by Akbaş and Kartal [61–63]. They studied interactions between dyes and surfactants in ternary systems by the use of spectrophotometry. From the absorption spectra of the dye C.I. Reactive Orange 16 (RO16), they showed that the absorbance of the dye increases with increasing concentration of the nonionic surfactant alkyl polyoxyethylene ether in the solution of the RO16 dye and the cationic surfactant dodecylpyridinium chloride (DPC). The cause for increased absorbency was ascribed to the reduction of the stability of the complex between RO16 and DPC in the presence of noni-

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onic micelles. Very similar results were obtained with the addition of the anionic surfactant sodium dodecyl sulphate and the nonionic surfactant alkyl polyoxyethylene ether to the RO16 solution. The results of spectrophotometric measurements showed that the increased temperature does not affect dye absorption in the ternary mixture. The cause for that lies in the reduction of the polarity of the polyoxyethylene chain at increased temperature. The decrease in polarity of the nonionic surfactant polyoxyethylene chain influences the decrease in hydrophilic interactions, which are in balance with hydrophobic interactions, i.e. interactions between alkyl chains of the dye and anionic surfactant.

Solubilisation of an anionic dye by nonionic micelles was spectrophotometrically confirmed by Oakes [65]. He found out that the addition of a nonionic surfactant to the solution of an azo dye and a cationic surfactant causes an increase in the intensity of the dye spectra by 30–40%. From that he concluded that mixed micelles are formed in the solution and the dye incorporates into them. The enhancement of the absorbency was ascribed to dye solubilisation, which occurs in mixed micelles.

Simončič and Kert [18] studied the influence of both dye and surfactant structure on the strength of anionic dye-cationic surfactant interactions in the presence of nonionic micelles by the use of potentiometry. They established that the increase in the hydrophobicity of the dye and surfactant causes an enhancement of both the cationic surfactant-nonionic micelle interaction in the binary system and anionic dye-cationic surfactant in the ternary system. The structure of the nonionic surfactant also influences the anionic dye-cationic surfactant interactions. Increasing the HLB value of the nonionic surfactant increases the tendency for cationic surfactant-nonionic micelle formation, but decreases the tendency for anionic dye-cationic surfactant formation in the ternary system.

## 6 Conclusion

In compliance with the results obtained in several studies, the following can be concluded:

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- the strength of dye-surfactant interactions increases with increasing hydrophobicity of the surfactant and dye;
- branched surfactant structure prevents close junctions between the dye and surfactant ions, which might influence the reduction of the strength of dye-surfactant interactions;
- solubilisation of the dye by surfactant micelles is governed by interactions between the species;
- the structure of the dye and surfactant dictate the location in the micelle where the dye will be placed;
- an ionic dye is incorporated in the hydrophilic region of the micelle, but a nonionic dye is incorporated in the hydrophobic region of the micelle;
- the addition of a nonionic surfactant to the solution of a dye and surfactant of opposite charges decreases the strength of the dye-surfactant interactions;
- by increasing the HLB value of a nonionic surfactant, the tendency for surfactant-surfactant complex formation is increased, which causes a reduction in the tendency for dye-surfactant complex formation;
- dye-surfactant complexes are solubilised by micelles of a nonionic surfactant;
- the strength of interactions between dye ions and surfactant ions of opposite charges is reduced by the addition of an electrolyte to the solution;
- increased temperature causes a decrease in the strength of the dye-surfactant interactions;
- the strength of dye-surfactant interactions decreases with the addition of a cosolvent to the dye-surfactant solution.

According to the facts obtained, it can be concluded that all of the factors that can influence the strength of dye-surfactant interactions should be considered when a surfactant is selected as a levelling agent. It is only in this way that evenly dyed textile fibres will be achieved.

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