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Influence of the nonionic surfactant structure on surfactant-surfactant interactions

Abstract

This paper presents the influence of the structure of nonionic surfactant on interactions between a cationic surfactant and the micelle of a nonionic surfactant in aqueous solution at 25 °C. Cationic surfactant dodecyltrimethylammonium bromide (DTA) and seven nonionic surfactants of different structure--Brij 30 (BR30), Brij 35 (BR35), Brij 56 (BR56), Brij 58 (BR58), Brij 700 (BR700), Triton X-100 (TX100) and Tween 20 (TW20)--were used in this research. Interactions have been studied by means of potentiometry, based on the use of ion-selective membrane electrode sensitive to free DTA surfactant cations. The equilibrium constant, κ_1, and the standard free energy change, $\Delta G_1°$, for surfactant-surfactant complex formation, were determined. The results show that the strength of binding of DTA surfactant cations into the micelle of nonionic surfactant is dependent upon the length and shape of both hydrophilic and hydrophobic groups of the nonionic surfactant. A nonionic surfactant with shorter hy-

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Vpliv strukture neionskega tenzida na interakcije tenzid-tenzid

Izvirni znanstveni članek

Izvleček

V prispevku je predstavljen vpliv stukture neionskega tenzida na interakcije med kationskim tenzidom in micelom neionskega tenzida v vodni raztopini pri temperaturi 25 °C. V raziskavo so vključeni kationski tenzid dodeciltrimetilamonijev bromid (DTA) in sedem neionskih tenzidov različnih struktur, in sicer Brij 30 (BR30), Brij 35 (BR35), Brij 56 (BR56), Brij 58 (BR58), Brij 700 (BR700), Triton X-100 (TX100) in Tween 20 (TW20). Interakcije so proučevane po potenciometrični metodi z uporabo ionoselektivne membranske elektrode, občutljive na proste katione tenzida DTA. Določeni sta ravnotežna konstanta, κ_1, in sprememba standardne proste energije, $\Delta G_1°$, nastanka kompleksa tenzid-tenzid. Izsledki raziskave kažejo, da je jakost vezanja kationa tenzida DTA v micel neionskega tenzida odvisna od velikosti in oblike tako hidrofilne kot tudi hidrofobne skupine neionskega tenzida. Neionski tenzid s krajšo hidrofilno polioksietilensko skupino tvori šibkejše interakcije s kationom tenzida DTA kot neionski tenzid z daljšo hidrofilno skupino pri enaki dolžini hidrofobne verige. Prav tako tvori neionski tenzid z daljšo hidrofobno verigo močnejše interakcije s kationom tenzida DTA kot neionski tenzid s krajšo hidrofobno verigo pri enaki velikosti hidrofilne skupine. Razvejanje hidrofobne ali hidrofilne skupine neionskega tenzida zmanjša jakost medmolekulskih interakcij. Iz tega sledi, da so za vključitev kationa DTA v micel neionskega tenzida pomembne tako elektrostatske interakcije, ki potekajo med kvaternim dušikovim atomom tenzida DTA in polioksietilensko skupino neionskega tenzida, kot tudi hidrofobne interakcije med ogljikovodikovima verigama obeh tenzidov.

drophilic polyoxyethylene group forms weaker interactions with a DTA surfactant cation than a nonionic surfactant with a longer hydrophilic group, with the length of their hydrophobic groups being equivalent. A nonionic surfactant with a longer hydrophobic chain also forms stronger interactions with a DTA surfactant cation than a nonionic surfactant with a shorter hydrophilic chain, assuming the magnitude of their hydrophilic groups is the same. Branching of both the hydrophilic and hydrophobic group of a nonionic surfactant reduces the strength of intermolecular interactions. It can thus be concluded that the electrostatic interactions occurring between a quaternary ammonium atom of a DTA surfactant and polyoxyethylene group of a nonionic surfactant as well as the hydrophobic interactions occurring among hydrocarbonium chains of both surfactants are important for incorporation of DTA cations into the micelle of a nonionic surfactant.

Key words: cationic surfactant, nonionic surfactant, intermolecular interactions, strength of interactions, the influence of the structure, thermodynamics, potentiometry.

1 Introduction

The dyeing of both natural and synthetic fibres often leads to uniform distribution of dye along the fibre, which is the consequence of physical and chemical differences in the fibre, an inappropriate dyeing process, or inappropriate machinery [1]. One of the ways in which unlevelness of dyeing could be avoided is to use surface active agents (surfactants) as levelling agents in the dyebath. Their task is to slow down dye adsorption from the dyebath onto the fibre, which is an important condition for levelness in dyed textiles. Apart from levelling action, surfactants also perform other functions in the dyebath, i.e. increase wettability of the fibres, prevent foaming of the dyebath and increase dissolution of poorly dissoluble dye.

Surfactants used as levelling agents in the dyeing process could be divided into ionic, nonionic and zwitterionic in terms of their ionic activity [1–3]. The most frequently represented levelling agents cited in the literature are nonionic sur-

1 Uvod

Pri barvanju naravnih in sintetičnih vlaken se pogosto srečujemo z neegalnim obarvanjem, ki je posledica fizikalnih in kemijskih razlik v vlaknu, neustreznega postopka barvanja ali neustrezne strojne opreme [1]. Eden od načinov, s katerimi se lahko izognemo neegalnemu obarvanju, je uporaba površinsko aktivnih snovi (tenzidov) kot egalizirnih sredstev v barvalni kopeli. Njihova naloga je upočasniti adsorpcijo barvila iz kopeli na vlakna, kar je pomemben pogoj za enakomerno obarvanje tekstilij. Poleg egalizirnega delovanja opravljajo tenzidi še druge funkcije v barvalni kopeli, in sicer povečajo omočljivost vlaken, preprečijo penjenje barvalne kopeli ter povečajo topnost v vodi slabo topnih barvil.

Tenzide, ki se pri barvanju uporabljajo kot egalizirna sredstva, delimo glede na ionsko aktivnost na anionske, kationske, neionske in amfoterne [1–3]. Kot najpogosteje zastopana egalizirna sredstva se v literaturi navajajo neionski tenzidi [4–10], katerim sledijo ionski [4, 7, 11, 12] in amfoterni [13–15]. Izbira tenzida kot egalizirnega sredstva je odvisna od ionske narave barvila in vlaken ter postopka in pogojev barvanja.

Posebno mesto imajo med egalizirnimi sredstvi mešanice tenzidov. Le te morajo biti skrbno pripravljene s tenzidi, ki v mešanicah delujejo vzajemno. Na učinkovitost egalizirnega delovanja mešanice tenzidov neposredno vpliva njihova ionska aktivnost, HLB vrednost in koncentracija. V mešanicah lahko uporabimo tenzide enake ali različne ionske aktivnosti. Med slednjimi imajo velik tehnološki pomen mešanice kationskega in neionskega tenzida v raztopini anionskega barvila oziroma mešanice anionskega in neionskega tenzida v raztopini kationskega barvila. Pri pripravi takšnih mešanic je koncentracija ionskega tenzida nižja od kritične koncentracije nastanka micelov (c.m.c.), tako da egalizirno delujejo tenzidni ioni, koncentracija neionskega tenzida pa je večja od c.m.c., kar omogoča, da pri egalizirnem delovanju hkrati sodelujejo tudi miceli neionskega tenzida. Ker sta oba tenzida substantivna do barvila, njuno egalizirno delovanje temelji na tvorbi kompleksov barvilo-tenzid različnih jakosti. Pri tem interakcije med tenzidoma delujejo kot protiutež interakcijam med barvilom in tenzidom. Od jakosti interakcij tenzid-tenzid je odvisna jakost interakcij barvilo-tenzid in s tem učinkovitost egalizirnega delovanja. Zato je dobro poznavanje interakcij tenzid-tenzid v raztopini, predvsem pa dejavnikov, ki vplivajo nanje, pogoj za pravilno izbiro mešanice tenzidov kot egalizirnega sredstva, kot tudi za razumevanje njenega egalizirnega delovanja v barvalni kopeli ob prisotnosti barvila in vlaken.

Dosedanje raziskave interakcij tenzid-tenzid, ki obravnavajo različne mešanice anionskega in neionskega tenzida [16–18] ter kationskega in neionskega tenzida [19–24], so bile usmerjene predvsem v proučevanje sinergističnega delovanja tenzidov v mešanici

factants [4–10], followed by ionic [4, 7, 11, 12] and zwitterionic [13–15]. Selection of a surfactant as a levelling agent is dependent on the ionic character of both dye and fibre, the dyeing process and its conditions.

Mixtures of surfactants occupy a special position among levelling agents. They have to be carefully prepared with surfactants whose activity in the mixtures is mutual. The effectiveness of the levelling action of mixtures of surfactants is directly influenced by their ionic activity, HLB value and concentration. Surfactants of the same or different ionic activity can be used in the mixtures. Among the latter, mixtures of cationic and nonionic surfactants in an anionic dye solution and mixtures of an anionic and nonionic surfactant in a cationic dye solution, respectively, have a huge technological significance. In the preparation of such mixtures, the concentration of the ionic surfactant is lower than the critical micelle concentration (c.m.c.), so that ions act levelly, whilst the concentration of the nonionic surfactant is higher than c.m.c., facilitating micelles of nonionic surfactants to also participate in the levelling action. As both surfactants are substantive to dye, their levelling action is based on dye-surfactant complex formation of different strength. Interactions between two surfactants act to counterbalance against interactions between the dye and the surfactant. The strength of dye-surfactant interactions is dependent on the strength of surfactant-surfactant interactions and, accordingly, the effectiveness of levelling action. That is why familiarity with surfactant-surfactant interactions in the solution and in particular with the factors influencing them is a precondition for the right selection of a mixture of surfactants as a levelling agent and to understand its levelling action in the dyebath, while both dye and fibre are present in it.

Research into surfactant-surfactant interactions dealing with different mixtures of anionic and nonionic surfactant [16–18] and cationic and nonionic surfactant [19–24], conducted so far, was mainly focused on the study of the synergistic action of surfactants in the mixtures and the impact of the structure of ionic surfactant on the strength of intermolecular interactions. It is evident from that research that

in vpliva strukture ionskega tenzida na jakost medmolekulskih interakcij. Iz njih je razvidno, da se tako tenzidni anioni kot kationi vključujejo v strukturo micela neionskega tenzida. Pri tem se tvorijo kompleksi, ki se pri večjih koncentracijah ionskega tenzida lahko obravnavajo kot mešani miceli. Kompleksi, ki nastanejo med ionskim in neionskim tenzidom, imajo površinski naboj. Ker med enako nabitimi ioni v kompleksu delujejo elektrostatske odbojne sile, se pri višji koncentraciji ionskega tenzida v micelu zmanjša njegova kompaktnost v primerjavi z enokomponentnimi neionskimi miceli [16]. To so potrdili tudi rezultati meritev površinske napetosti mešanic anionskih tenzidov različnih struktur z neionskim tenzidom TX100 [17], iz katerih je razvidno, da se stopnja sinergističnega delovanja tenzidov v mešanici zmanjšuje z naraščanjem molskega deleža anionskega tenzida. Medtem ko je c.m.c mešanice tenzidov z majhnim molskim deležem anionskega tenzida nižja kot c.m.c. neionskega tenzida TX100, pa le-ta močno naraste pri molskih deležih anionskega tenzida večjih, od 0,5. Vzrok za to so pripisali odboju v mešanih micelih kar nasprotuje kompleksiranju. Pomembnost delovanja odbojnih elektrostatskih sil med anioni tenzida v micelih potrjuje tudi dejstvo, da že najmanjši dodatek neionskega tenzida TX100 močno zniža c.m.c mešanice v primerjavi s c.m.c. anionskega tenzida. Iz tega sledi, da dodatek neionskega tenzida v raztopino anionskega tenzida deluje sinergistično.

Iz raziskav je tudi razvidno [17, 24], da so interakcije med kationskim in neionskim tenzidom na splošno šibkejše od interakcij med anionskim in neionskim tenzidom. Ta ugotovitev kaže na to, da je učinkovitost polioksietilenske skupine neionskega tenzida večja pri manjših anionskih polarnih skupinah anionskega tenzida kot v primeru voluminoznejših polarnih skupin kationskega tenzida. Tudi delno protoniranje kisika polioksietilenske skupine neionskega tenzida pri določenih pogojih poveča privlačne interakcije z anionsko in ne s kationsko skupino tenzida. Kationski tenzid z daljšo alkilno verigo se lažje vključi v micel neionskega tenzida kot kationski tenzid s krajšo alkilno verigo [24]. Stabilnost kompleksa je odvisna od dolžine alkilne verige kationskega tenzida. Kationski tenzid z daljšo alkilno verigo tvori stabilnejše mešane micele kot kationski tenzid s krajšo alkilno verigo. Tako je točka motnišča neionskega tenzida, večja v prisotnosti oktadeciltrimetilamonijevega bromida kot v prisotnosti heksadeciltrimetilamonijevega bromida [24].

Podrobnih podatkov o vplivu strukture neionskega tenzida na jakost interakcij z ionskim tenzidom v literaturi nismo zasledili. Zato je bil namen naše raziskave proučiti vpliv strukture hidrofilne in hidrofobne skupine neionskega tenzida na medmolekulske interakcije v mešanici kationskega in neionskega tenzida. Pri tem smo predpostavili, da HLB vrednost neionskega tenzida pomembno vpliva na jakost kompleksiranja.

both surfactant anions and cations are incorporated into the structure of the nonionic micelle. In that process, complexes are formed which, at a higher concentration of ionic surfactant, can be considered as mixed micelles. Complexes formed between ionic and nonionic surfactant have surface charges. In the complex where there are ions of the same charge the electrostatic repulsion forces act among them. At higher concentration of ionic surfactant in the micelle, the compactness of the micelle structure goes down in comparison with one-component nonionic micelles [16]. This was confirmed by the results of the surface tension of mixtures of anionic surfactants of different structure with nonionic surfactant TX100 [17]. From those results it can be seen that the degree of synergistical action of surfactants in the mixture decreases by increasing the mole fraction of an anionic surfactant. Whilst the c.m.c of mixture of surfactants with low mole fraction of an anionic surfactant is lower than the c.m.c. of the nonionic surfactant TX100, it strongly increases if the mole fractions of an anionic surfactant is higher than 0.5. The cause for this increase can be ascribed to the repulsion in mixed micelles, which oppose the complex formation. The importance of the activity of repulsive electrostatic forces among surfactant anions in the micelles is also confirmed by the fact that the lowest addition of the nonionic surfactant TX100 strongly decreases the c.m.c. of the mixture in comparison to the c.m.c. of an anionic surfactant. Hence, it follows that the addition of a nonionic surfactant into the solution of an anionic surfactant acts synergistically.

From the studies, it can be seen [17, 24] that interactions between a cationic and a nonionic surfactant are, in general, weaker than those between an anionic and a nonionic surfactant. This finding shows the effectiveness of the polyoxyethylene group of a nonionic surfactant, which is higher in the presence of smaller anionic polar groups of an anionic surfactant than in the case of the bulkiest polar groups of a cationic surfactant. Partial protonation of an oxygen of the polyoxyethylene group increases, under specific conditions, attractive interaction with an anionic and not with the cationic group of surfactant. A cationic surfactant with a longer alkyl

2 Eksperimentalni del

2.1 Tenzidi

Pri eksperimentalnem delu smo uporabili kationski tenzid N-dodeciltrimetilamonijev bromid (DTA) in sedem različnih neionskih tenzidov Brij 30 (BR30), Brij 35 (BR35), Brij 56 (BR56), Brij 58 (BR58), Brij 700 (BR700), Triton X-100 (TX100) in Tween 20 (TW20). Stukturne formule tenzidov so prikazane na sliki 1. Anionski tenzid natrijevdodecil sulfat (SDS) smo uporabili pri pripravi polimerne membrane. Vsi tenzidi so proizvodi Aldrich – Chemical Co. Tenzida DTA in SDS smo očistili s trikratno prekristalizacijo iz acetona. Neionskih tenzidov, ki so bili v obliki visoko koncentrirane tekočine, paste ali granul, naknadno nismo čistili. Vse raztopine smo pripravili v bidestilirani vodi. Koncentracija raztopin neionskih tenzidov je bila višja od c.m.c. in je znašala $5{,}0 \cdot 10^{-3}$ mol/kg. Ker smo raztopine pripravili s tehtanjem, so koncentracije izražene v mol/kg.
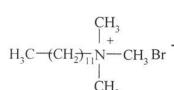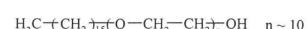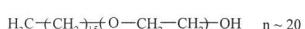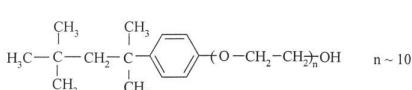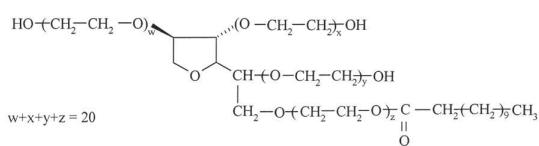

Figure 1: Structural formulae of used surfactants.

2.2 Potenciometrija

Potenciometrične titracije smo izvedli z galvanskim členom in uporabo ionoselektivne membranske elektrode (ISE). Sestava galvanskega člena je naslednja:

chain incorporates into the micelle of a nonionic surfactant more willingly than a cationic surfactant with a shorter alkyl chain [24]. The stability of the complex is dependent on the length of the alkyl chain of the cationic surfactant. A cationic surfactant with a longer alkyl chain forms more stable mixed micelles than a cationic surfactant with a shorter alkyl chain. Thus, the cloud point of the nonionic surfactant is higher in the presence of octadecyltrimethylammonium bromide than in the presence of hexadecyltrimethylammonium bromide [24].

Detailed data about the influence of the structure of a nonionic surfactant on the strength of interactions with an ionic surfactant has not been found in the literature. Therefore the purpose of our research was to study the influence of the structure of both the hydrophilic and hydrophobic group of the nonionic surfactant on intermolecular interactions between a cationic and a nonionic surfactant in the mixture. Thereby, we suppose that the HLB value of the nonionic surfactant significantly affects the strength of complex formation.

2 Experimental

2.1 Surfactants

Cationic surfactant N-dodecyltrimethylammonium bromide (DTA) and seven different nonionic surfactants Brij 30 (BR30), Brij 35 (BR35), Brij 56 (BR56), Brij 58 (BR58), Brij 700 (BR700), Triton X-100 (TX100) and Tween 20 (TW20) were used for the experimental work reported in this paper. Structural formulae of the surfactants are given in Figure 1. Anionic surfactant sodium dodecyl sulphate (SDS) was used during the preparation of the polymer membrane. All surfactants are Aldrich – Chemical Co. products. Surfactants DTA and SDS were purified by means of three recrystallizations from acetone. Nonionic surfactants which were in the form of highly concentrated liquid, paste or granule were not purified further. All solutions were prepared in double distilled water. The concentration of the nonionic surfactants was higher than c.m.c. and amounted to $5.0 \cdot 10^{-3}$ mol/kg. Since solutions were prepared by weighing, the concentrations were expressed in mol/kg.

Hg | Hg$_2$Cl$_2$ | KCl$_{(nas.)}$ || merjena raztopina | polimerna membrana | $1,0 \cdot 10^{-4}$ mol/kg DTA v 0,1m NaCl (notranja referenčna raztopina) | AgCl | Ag.

ISE je vključevala nosilni kompleks DTA-SDS, ki membrani zagotavlja, da je občutljiva za katione tenzida DTA in anione tenzida SDS. ISE smo izdelali sami na podlagi že objavljenih postopkov [25]. Podroben opis priprave ISE in galvanskega člena je predstavljen v literaturnem viru [26].

Meritve napetosti galvanskega člena, E, v odvisnosti od koncentracije tenzida DTA, m_S, so potekale v treh zaporednih korakih: izdelava prve umeritvene krivulje, izdelava titracijske krivulje in izdelava druge umeritvene krivulje.

Meritve za izdelavo umeritvene krivulje smo izvedli tako, da smo v celico nalili 25 ml raztopine NaBr koncentracije $5,0 \cdot 10^{-3}$ mol/kg ter vanjo potopili ISE. Z batno bireto smo nato dodajali osnovno raztopino tenzida DTA, tako da je koncentracija tenzida v merjeni raztopini postopoma naraščala. Pri vsakem dodatku tenzida smo izračunali m_s ter v ravnotežju odčitali E. Meritve odvisnosti E od m_s smo opravili v koncentracijskem območju od $1,0 \cdot 10^{-6}$ do $2,0 \cdot 10^{-2}$ mol/kg tenzida DTA pri temperaturi 25 °C.

Meritve za izdelavo titracijske krivulje smo izvedli na enak način kot za umeritveno krivuljo, le s to razliko, da smo v titracijsko celico nalili 25 ml $5,0 \cdot 10^{-3}$ m raztopine neionskega tenzida BR30, BR35, BR56, BR58, BR700, TX100 ali TW20. Raztopine neionskih tenzidov smo pripravili v $5,0 \cdot 10^{-3}$ m raztopini NaBr.

Po potenciometrični titraciji smo izdelali drugo umeritveno krivuljo, ki je služila za kontrolo prve umeritvene krivulje in za čiščenje membrane.

3 Rezultati meritev in razprava

Na sliki 2 so prikazane krivulje E v odvisnosti od log m_s tenzida DTA v $5,0 \cdot 10^{-3}$ m raztopini neionskega tenzida BR30, BR35, BR56, BR58, BR700, TX100 in TW20 pri temperaturi 25 °C. Iz slike 2 je razvidno, da so umeritvene krivulje linearne v koncentracijskem območju od $6,0 \cdot 10^{-5}$ do $6,0 \cdot 10^{-3}$ mol/kg tenzida DTA z naklonom 58,5 mV/dekado, kar je v skladu z Nernstovo odvisnostjo [27]:

$$E = E^o + 2.303 \cdot \frac{R \cdot T}{z_i \cdot F} log \ m_{S,F} \qquad (1)$$

kjer je E^o standardni potencial, R plinska konstanta, T absolutna temperatura, z_i naboj iona, ki vključuje predznak, F Faradayeva konstanta in $m_{S,F}$ koncentracija prostih ionov tenzida. Premosorazmerna odvisnost E od log m_S pomeni, da je pri vsaki meritvi E stehiometrična koncentracija, m_S, tenzida DTA enaka koncentraciji prostih ionov, $m_{S,F}$, tenzida DTA, ki jih zazna ISE. Na sliki lahko opazimo, da umeritvene krivulje odstopajo od linearno-

2.2 Potentiometry

Potentiometric titrations were carried out by an electrode cell and the use of an ion-selective membrane electrode (ISE) of the following composition:

Hg | Hg₂Cl₂ | KCl(satd.) ‖ test solution | polymer membrane | 1.0 · 10⁻⁴ mol/kg DTA in 0.1m NaCl (inner reference solution) | AgCl | Ag

sti pri zelo nizkih koncentracijah tenzida DTA v raztopini zaradi limitne vrednosti odziva elektrode in pri koncentracijah tenzida, višjih od c.m.c., kar je posledica micelizacije tenzida. S slike 2 je tudi razvidno, da titracijske krivulje, ki smo jih dobili v raztopinah neionskih tenzidov BR30, BR35, BR56, BR58, BR700, TX100 in TW20 po obliki in legi odstopajo od umeritvenih krivulj in ležijo pod umeritvenimi krivuljami. Lega titracijskih krivulj pod umeritveno krivuljo pove, da elektroda, ki je občutljiva le na proste
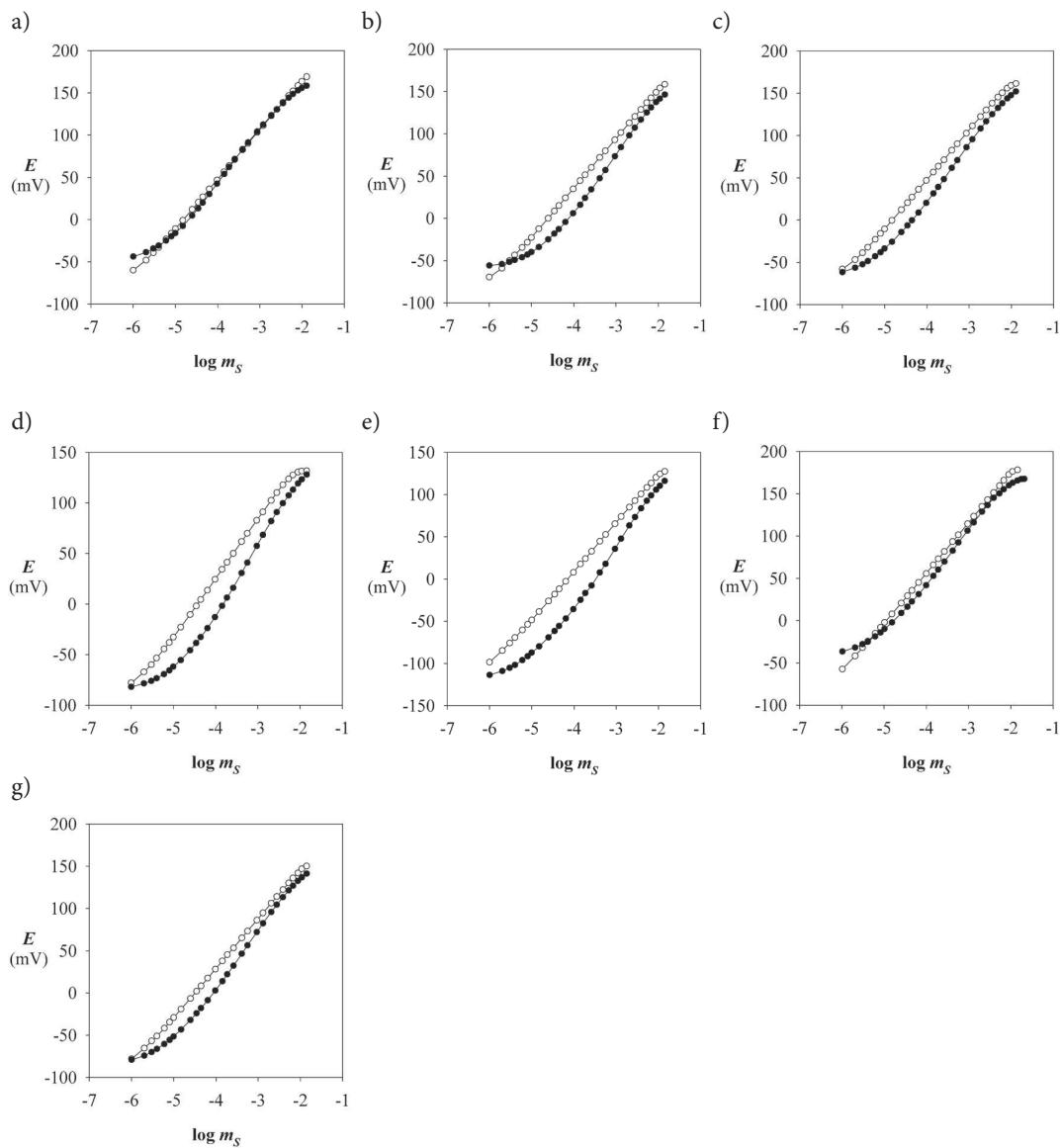

Figure 2: Plot of e.m.f., E, of the cell versus the logarithm of the molal concentration, log m_S of surfactant DTA in 5.0 · 10⁻³ m solution of nonionic surfactant at 25 °C. — ○ — ○ —calibration curve, — • — • — titration curve. a) BR30, b) BR35, c) BR56, d) BR58, e) BR700, f) TX100, g) TW20.

ISE includes carried complex DTA-SDS that assure a membrane to be sensitive for both DTA cations and SDS anions. ISE was constructed by us on the basis of already published procedures [25]. The detailed description of the preparation of both ISE and electrode cell is presented in the literature [26].

Measurements of e.m.f., E, versus total concentration, m_S, of DTA, were carried out by three consecutive steps: first calibration curve, titration curve and second calibration curve.

Measurements of the calibration curve were carried out by filling the cell with a 25 ml solution of NaBr, concentration 5.0 · 10^{-3} mol/kg and dipping the ISE into it. The stock solution of DTA was added into the test solution by means of a bat burette, so that the concentration of surfactant was increasing gradually. With each addition of the surfactant, the m_S was calculated and the E was read from the mV-meter at equilibrium. Measurements of E versus m_S were done over a concentration range from 1.0 · 10^{-6} to 2.0 · 10^{-2} mol/kg of the surfactant DTA at 25 °C.

Measurements for generating the titration curve were done in the same manner as the calibration curve, with the only difference that the titration cell was filled up with 25 ml of 5.0 · 10^{-3} m solution of the nonionic surfactant BR30, BR35, BR56, BR58, BR700, TX100 or TW20. All solutions of nonionic surfactants were prepared in a 5.0 · 10^{-3} m solution of NaBr.

After potentiometric titration, the second calibration curve was done, which served for checking the first calibration curve and for cleaning the membrane.

3 Results and discusion

Figure 2 shows curves of e.m.f. of the cell, E, versus the logarithm of the molal concentration, log m_S, surfactant DTA in 5.0 · 10^{-3} m solution of nonionic surfactant BR30, BR35, BR56, BR58, BR700, TX100 in TW20 at 25 °C. It can be seen from Figure 2 that the calibration curves are linear over the concentration range of 6.0 · 10^{-5} – 6.0 · 10^{-3} mol/kg with a slope of 58,5 mV per decade, which is in compliance with Nernstian behaviour [27]: (Equation 1), where E^o is standard potential, R is gas constant, T is absolute temperature, z_i is charge of

ione tenzida DTA v raztopini, ne zazna celotne koncentracije tenzida. Koncentracija prostih ionov tenzida DTA je v tem primeru nižja od stehiometrične koncentracije tenzida DTA. Vzrok za znižanje koncentracije prostih ionov tenzida DTA v raztopini je njegovo vezanje v kompleks z neionskim tenzidom, ki ga elektroda ne zazna. Pri zelo nizkih koncentracijah tenzida DTA v raztopini lahko točke titracijske krivulje ležijo tudi nad umeritveno krivuljo, kar je posledica slabše odzivnosti elektrode v raztopini neionskega tenzida.

Iz grafov odvisnosti E od log m_S tenzida DTA smo pri vsaki izmerjeni vrednosti E, iz titracijske krivulje odčitali stehiometrično koncentracijo DTA, m_S, iz umeritvene krivulje pa pripadajočo koncentracijo prostih ionov tenzida, $m_{S,F}$. Iz razlike koncentracij m_S in $m_{S,F}$ smo izračunali koncentracijo vezanih ionov tenzida DTA, $m_{S,B}$, v micel neionskega tenzida.

V skladu z izbranim teoretičnim modelom Rossotti in Rossotti [28], ki predpostavlja, da se v razredčenih raztopinah tvorijo le mononuklearni kompleksi s splošno formulo $M_q S_p$, kjer je $q = 1$ in $p = n$ (n je število ligandov vezanih na centralno skupino), smo nastanek kompleksov med kationom tenzida (S^+) in micelom neionskega tenzida (M) opisali z naslednjimi ravnotežnimi enačbami, ki opisujejo postopno vezanje liganda (S^+) na centralno skupino (M):

$$S^+ + M \xrightleftharpoons{\kappa_1} MS^+ \qquad \kappa_1 = \frac{m_{MS}}{m_{S,F} \cdot m_{M,F}} \qquad (2)$$

$$S^+ + MS^+ \xrightleftharpoons{\kappa_2} MS_2^{+2} \qquad \kappa_2 = \frac{m_{MS_2}}{m_{S,F} \cdot m_{MS}} \qquad (3)$$

$$S^+ + MS_{n-1}^{+(n-1)} \xrightleftharpoons{\kappa_n} MS_n^{+n} \qquad \kappa_n = \frac{m_{MS_n}}{m_{S,F} \cdot m_{MS_{n-1}}} \qquad (4)$$
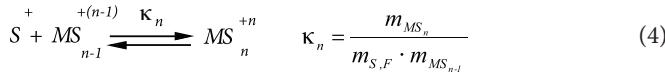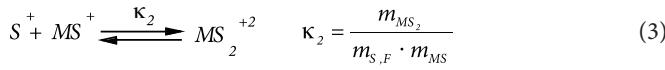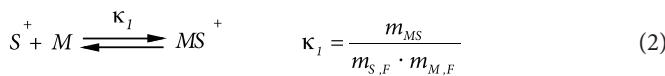
V ravnotežnih reakcijah od (2) do (4) predstavlja ligand kation tenzida, S^+, centralna skupina pa je micel neionskega tenzida, M. MS^+, MS_2^{+2} in MS_n^{+n} so kompleksi z različnim številom, n, vezanih ionov kationskega tenzida, κ_1, κ_2, κ_n, so pripadajoče ravnotežne konstante za nastanek kompleksa MS^+, $m_{S,F}$ in $m_{M,F}$, sta koncentraciji prostih ionov kationskega tenzida in micelov neionskega tenzida, m_{MS}, m_{MS_2} in $m_{MS_{n-1}}$ pa so koncentracije nastalih kompleksov.

Stehiometrična koncentracija kationov tenzida, m_S, v raztopini je v skladu s teoretičnim modelom podana kot vsota koncentracij prostih kationov in kompleksov MS^+ različnih velikosti, prisotnih v raztopini. Zapišemo jo lahko takole:

$$m_S = m_{S,F} + m_{MS} + 2m_{MS_2} + 3m_{MS_3} + ... + nm_{MS_n} \qquad (5)$$

kjer je upoštevano, da vsak mol kompleksa vključuje n molov vezanega tenzida. V skladu s tem se stehiometrična koncentracija micelov neionskega tenzida izrazi takole:

an ion, including sign, F is the Faraday constant and $m_{S,F}$ is the concentration of the free ions of surfactant. The straight line dependence of E versus log m_S means that at each measurement of E, the stoichiometric concentration of the surfactant DTA is equal to the concentration of the free ions, $m_{S,F}$, of surfactant DTA, perceived by ISE. From Figure 2 it can be noticed that the calibration curves deviate from linearity at a very low concentration of the surfactant DTA in the solution. This is because of the limit of detection of the ISE. Deviation appears also at surfactant concentration higher than c.m.c., as the consequence of surfactant micellization. Figure 2 also demonstrates that the titration curves, obtained in solutions of nonionic surfactant BR30, BR35, BR56, BR58, BR700, TX100 and TW20, deviate in both the shape and the position from calibration curves and that they lie below calibration curves. The position of the titration curves below the calibration curve implies that the electrode, which is sensitive only to free ions of surfactant DTA in the solution, does not perceive the total concentration of the surfactant. The concentration of free DTA ions in this case is lower than the stoichiometric concentration of DTA. The reason for the decreased concentration of free DTA ions in the solution is in its binding into the complex with the nonionic surfactant, which can not be detected by the electrode. At a very low concentration of DTA in the solution, some points of the titration curve could lie above the calibration curve as a consequence of a poor response of the electrode in the nonionic surfactant solution.

In plots of E versus log m_S of the surfactant DTA, the stoichiometric concentration, m_S, of the DTA was read from the titration curve and the corresponding concentration of free ions of the surfactant, $m_{S,F}$, was read from the calibration curve at each measured value of E. From the difference between m_S and $m_{S,F}$, the concentration of bound ions, $m_{S,B}$, of DTA into the micelle of nonionic surfactant, were calculated.

In compliance with the theoretical model of Rossotti and Rossotti [28], which presumes that only monomolecular complexes can be formed in diluted solutions with a general formula $M_q S_p$, where q =1 and p = n, (n is the number of ligands bound on the central group) the com-

$$m_M = m_{M,F} + m_{MS} + m_{MS_2} + m_{MS_3} + ... + m_{MS_n} \tag{6}$$

Koncentracija micelov, m_M, v enačbi (6) je enaka:

$$m_M = \frac{m_N - c.m.c.}{\upsilon} \tag{7}$$

kjer je m_N stehiometrična koncentracija neionskega tenzida, c.m.c kritična koncentracija za tvorbo micelov in υ micelarno agregacijsko število. V primeru, ko smo predpostavili, da je centralna skupina molekula neionskega tenzida, N, vezana v micel, smo koncentracijo micelov v enačbi (6) izrazili:

$$m_M = m_N - c.m.c. \tag{8}$$

V enačbah (5) in (6) smo koncentracije kompleksov MS^+ različnih oblik izrazili kot produkt med ravnotežno konstanto za nastanek kompleksa MS^+ in koncentracijo prostih kationov tenzida ter enačbi zapisali takole:

$$m_S = m_{S,F} + \kappa_1 m_{M,F} m_{S,F} + 2\kappa_1 \kappa_2 m_{M,F} m_{S,F}^2 + 3\kappa_1 \kappa_2 \kappa_3 m_{M,F} m_{S,F}^3 + ... \tag{9}$$

$$... + (\kappa_1 \kappa_2 \kappa_3 ... \kappa_n) m_{M,F} m_{S,F}^n = m_{S,F} + m_{M,F} \sum_1^N n\kappa_n m_{S,F}^n$$

$$m_M = m_{M,F} + \kappa_1 m_{M,F} m_{S,F} + \kappa_1 \kappa_2 m_{M,F} m_{S,F}^2 + \kappa_1 \kappa_2 \kappa_3 m_{M,F} m_{S,F}^3 + ... \tag{10}$$

$$... + (\kappa_1 \kappa_2 \kappa_3 ... \kappa_n) m_{M,F} m_{S,F}^n = m_{M,F} + m_{M,F} \sum_1^N \kappa_n m_{S,F}^n$$

Stopnjo nastanka kompleksa MS^+ smo opisali z ligandovim številom, β, ki izraža povprečno število kationov tenzida, S^+, ki so vezani v micel neionskega tenzida, M, oziroma na molekulo neionskega tenzida, N, vezano v micel:

$$\beta = \frac{m_{S,B}}{m_M} = \frac{m_S - m_{S,F}}{m_M} \tag{11}$$

ter jo za proučevane mešanice tenzidov predstavili tudi grafično kot izoterme vezanja (sliki 3 in 4).

Z upoštevanjem enačb (9) in (10) smo enačbo (11) zapisali v naslednji obliki:

$$\beta = \frac{\kappa_1 m_{S,F} + 2\kappa_1 \kappa_2 m_{S,F}^2 + 3\kappa_1 \kappa_2 \kappa_3 m_{S,F}^3 + ... + n\kappa_n m_{S,F}^n}{1 + \kappa_1 m_{S,F} + \kappa_1 \kappa_2 m_{S,F}^2 + \kappa_1 \kappa_2 \kappa_3 m_{S,F}^3 + ... + \kappa_n m_{S,F}^n} \tag{12}$$

Iz enačbe (12) smo ravnotežno konstanto κ_1 za nastanek kompleksa MS^+ (ravnotežna reakcija 1) izračunali takole:

$$\lim_{m_{S,F} \to 0} \frac{\beta}{m_{S,F}} = \kappa_1 \tag{13}$$

Vrednost κ_1 v enačbi (13) smo določili grafično, in sicer tako, da smo krivuljo v grafu odvisnosti $\beta/m_{S,F}$ od $m_{S,F}$ ekstrapolirali na koncentracijo $m_{S,F} = 0$ (slika 5).

plex formation between the surfactant cation (S^+) and the micelle of a nonionic surfactant (M) can be represented by means of the following equilibrium equations, describing the gradual binding of ligand S^+ onto central group M: (Equations 2, 3 and 4).

In equilibrium equations from (2) to (4), the ligand represents a surfactant cation, S^+, and the central group is the micelle of nonionic surfactant, M. MS^+, MS_2^{+2} and MS_n^{+n} are complexes with different number, n, of bound ions of the cationic surfactant. κ_1, κ_2, κ_n, are the corresponding equilibrium constants for MS^+ complex formation. $m_{S,F}$ and $m_{M,F}$, are concentrations of free ions of the cationic surfactant and micelles of the nonionic surfactant. m_{MS}, m_{MS_2} and $m_{MS\,n-1}$ are concentrations of formed complexes.

The stoichiometric concentration of cationic surfactant, S^+, in the solution, is in accordance with the theoretical model, given as the sum of concentration of free cations and complexes MS^+ of different sizes, presented in the solution. It can be written as follows: (Equation 5), where it is considered that each mol of the complex incorporates n moles of bound surfactant. Therefore the stoichiometric concentration of the micelles of nonionic surfactant can be written as: (Equation 6).

The concentration of micelles, m_M, in Equation (6) is equal: (Equation 7), where m_N is the stoichiometric concentration of nonionic surfactant, c.m.c is its critical micelle concentration and υ is its micellar aggregation number. In cases where it is presumed that the central group represents the molecule of nonionic surfactant bound into the micelle, the concentration of micelles in Equation (6), can be expressed as: (Equation 8).

If the concentration of complexes MS^+ of different shapes in Equations (5) and (6) are expressed as the product between equilibrium constant for complex formation and concentration of free surfactant cations, equations (5) and (6) could be written in the following way: (Equations 9 and 10).

The degree of binding or ligand number, β, expresses an average number of surfactant cations, S^+, bound on the micelle of nonionic sur-
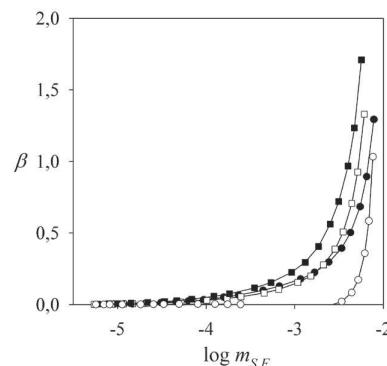

Figure 3: Plot of β vs log $m_{S,F}$ of surfactant DTA in $5.0 \cdot 10^{-3}$ m solution of nonionic surfactant at 25 °C. — ○ — BR30, — • — BR35, — □ — BR56, —■— BR58
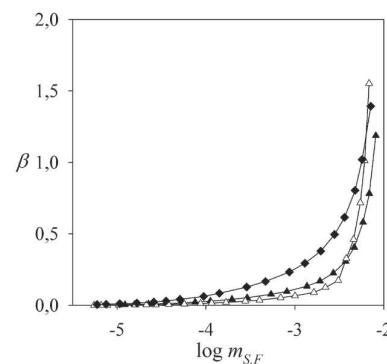

Figure 4: Plot of β vs log $m_{S,F}$ of surfactant DTA in $5.0 \cdot 10^{-3}$ m solution of nonionic surfactant at 25 °C. —△— TX100, — ▲ — TW20, —◆— BR700
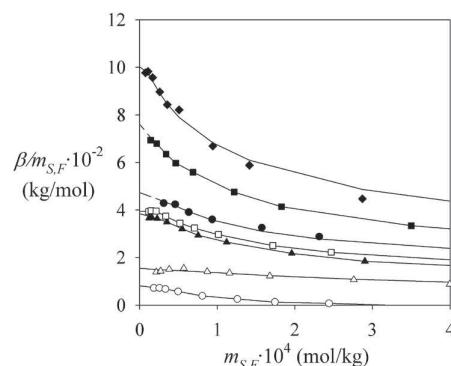


Figure 5: Plot of $β/m_{S,F}$ versus molal concentration of free surfactant DTA cations, $m_{S,F}$, in $5.0 \cdot 10^{-3}$ m solution of nonionic surfactant at 25 °C. — ○ — BR30, — • — BR35, — □ — BR56, —■— BR58, —◆— BR700, —△— TX100, — ▲ — TW20

factant, M, and on the molecule of nonionic surfactant, N, bound in the micelle, respectively: (Equation 11),

and is graphically presented as a binding isotherm for mixtures of the surfactants under consideration (Figure 3 and 4).

Taking into account Equations (9) and (10), equation (11) can be written as: (Equation 12). The equilibrium constant κ_1 for MS⁺ complex formation (equilibrium equation 1) was calculated in the following manner: (Equation 13).

In equation (13), the value of κ_1 was determined graphically by extrapolation of the curve of the plot $\beta/m_{S,F}$ versus $m_{S,F}$ to the concentration, where $m_{S,F} = 0$ (Figure 5).

On the basis of κ_1, the standard free energy change of the MS⁺ complex formation was calculated on the basis of the following equation: (Equation 14).

Values of κ_1 and $\Delta G_1°$ are gathered in Table 1.

Adsorption isotherms of binding DTA to nonionic surfactants of different structures, presented in Figure 3 and 4, show no difference between each other in the shape. The degree of binding of the surfactant DTA to the micelle of the nonionic surfactant increases gradually

Na podlagi vrednosti κ_1 smo izračunali spremembo standardne proste energije, $\Delta G_1°$, nastanka kompleksa *MS⁺* iz naslednje enačbe:

$$\Delta G_1^o = -RT \ln \kappa_1 \tag{14}$$

Vrednosti κ_1 in $\Delta G_1°$ smo zbrali v preglednici 1.

Iz slik 3 in 4 je razvidno, da se adsorpcijske izoterme vezanja tenzida DTA na neionske tenzide različnih struktur po obliki med seboj bistveno ne razlikujejo. Stopnja vezanja tenzida DTA na micel neionskega tenzida postopoma narašča z naraščajočo koncentracijo kationskega tenzida v raztopini.

Iz preglednice 1 je razvidno, da vrednosti κ_1 in $\Delta G_1°$, ki odražata jakost vezanja kationa DTA na micel neionskega tenzida, nista odvisni le od strukture neionskega tenzida, temveč tudi od načina njune določitve. Vrednosti κ_1 in $\Delta G_1°$ sta podani tako na monomolekulski kot tudi na micelarni osnovi. Pri tem je vrednost κ_1, izračunana na monomolekulski osnovi, za v-krat nižja od vrednosti, izračunane na micelarni osnovi. V prvem primeru se namreč kot vezno mesto oziroma centralna skupina upošteva molekula neionskega tenzida, *N*, vezana v micel (enačba 8), v drugem pa celoten micel, *M* (enačba 7). Analiza rezultatov je pokazala, da je vpliv strukture hidrofilne in hidrofobne skupine neionskega tenzida na jakost interakcij velik, če sta vrednosti κ_1 in $\Delta G_1°$ določeni na monomolekulski osnovi. Tako je vezanje DTA na BR35, ki vključuje 23 oksietilenskih skupin, močnejše kot na BR30 s 4 oksietilenskimi skupinami, vezanje DTA na BR58 z 20 oksietilenskimi skupinami pa močnejše kot na BR56 z 10 oksietilenskimi skupi-

Table 1: Critical micelle concentration (c.m.c.), micellar aggregation number, v, and HLB value of nonionic surfactant, equilibrium constant, κ_1, and thermodynamic function, $\Delta G_1°$, of MS⁺ complex formation for different surfactant-surfactant studied systems.

System *surfactant-surfactant*	c.m.c.[a] *(mol/kg)*	v[b]	HLB[c]	$\kappa_1 \cdot 10^{-2}$ *(kg/mol)*		$\Delta G_1°$ *(kJ/mol)*	
				N[d]	M[e]	N	M
BR30-DTA	$6.4 \cdot 10^{-5}$	/[f]	9	0.72	–	−10.6	–
BR35-DTA	$9.0 \cdot 10^{-5}$	40	16.9	4.25	170	−15.0	−24.1
BR56-DTA	$1.05 \cdot 10^{-6}$	141	12	3.95	560	−14.8	−27.1
BR58-DTA	$1.07 \cdot 10^{-6}$	92	16	6.95	640	−16.2	−27.4
BR700-DTA	$2.0 \cdot 10^{-5}$	/	18	10.0	–	−17.1	–
TX100-DTA	$2.8 \cdot 10^{-4}$	136	13.5	1.69	230	−12.7	−24.9
TW20-DTA	$6.0 \cdot 10^{-5}$	86	16.7	3.9	320	−14.8	−25.7

[a] *Values from references [29–33];* [b] *Values from references [30], [31] in [34];* [c] *Values from reference [35];* [d] *monomolecular basis,* [e] *micellar basis;* [f] *No reference data.*

with an increase in the concentration of cationic surfactant in the solution.

From Table 1 it can be seen that the values of κ_1 and $\Delta G_1°$, which reflect the strength of binding of DTA cations onto the micelle of a nonionic surfactant, are not only dependent on the structure of the nonionic surfactant but also on the way of their determination. Values of κ_1 and $\Delta G_1°$ are given on both monomolecular and micellar basis. The value of κ_1, calculated on a monomolecular basis is v-times lower than the value calculated on a micellar basis. In the first case the binding place or the central group is accounted for by the molecule of the nonionic surfactant, N, bound into the micelle (Equation 8), while in the second case, it is accounted for by the whole micelle, M (Equation 7). If the values of κ_1 and $\Delta G_1°$ are determined on a monomolecular basis, the huge influence of the structure of both hydrophilic and hydrophobic structure of the nonionic surfactant on the strength of interactions has been seen from the analysis of the results. Binding of DTA onto BR35, which includes 23 oxyethylene groups, is stronger than binding onto BR30, which includes 4 oxyethylene groups, while binding of DTA onto BR58, which includes 20 oxyethylene groups, is stronger than binding of DTA onto BR56, which includes 10 oxyethylene groups. The strongest binding is present when binding DTA onto BR700, which has the highest level of ethoxylation among the studied nonionic surfactants. From these results it can be seen that the strength of binding S^+ onto N at a given length of the hydrophobic group increases along with an increasing number of oxyethylene hydrophilic groups of nonionic surfactant. The structure of the hydrophobic group of the nonionic surfactant influences the surfactant-surfactant interactions too, where an increase in the length of linear hydrocarbonium chain causes the growth in the strength of MS^+ complex formation. Surfactant DTA forms stronger interactions with surfactant BR58, containing hexadecyl alkyl group, than with surfactant BR35, containing dodecyl alkyl group, in spite of the fact that the hydrophilic group of surfactant BR35 is larger by 3 oxyethylene groups. These results are shown in Figure 6 and 7. It can be seen that the strength of intermolecular inter-
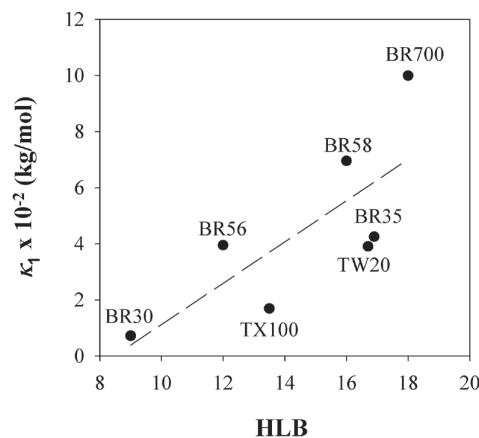

Figure 6: Equilibrium constant, κ_1, of MS^+ complex formation determined on monomolecular basis in dependence of the HLB value of the nonionic surfactant.
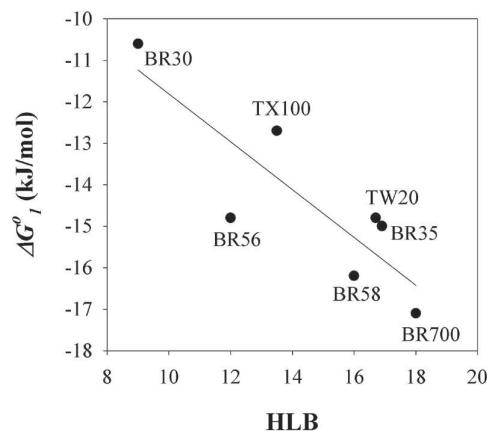

Figure 7: Standard free energy change, $\Delta G_1°$, of MS^+ complex formation, determined on monomolecular basis, in dependence of the HLB value of nonionic surfactant.

nami. Najmočnejše je vezanje DTA na BR700, ki ima med neionskimi tenzidi največjo stopnjo etoksiliranja. Iz teh rezultatov je razvidno, da jakost vezanja S^+ na N narašča z naraščanjem števila oksietilenskih hidrofilnih skupin v strukturi neionskega tenzida pri enako veliki hidrofobni skupini. Na interakcije tenzid-tenzid pa vpliva tudi struktura hidrofobne skupine neionskega tenzida, kjer povečanje dolžine linearne ogljikovodikove verige vpliva na povečanje jakosti nastanka kompleksov MS^+. Tako tvori BR58 s heksadecilno alkilno skupino močnejše interakcije z DTA kot BR35 z dodecilno alkilno skupino, in to kljub temu, da ima BR35 za tri oksietilenske skupine večjo hidrofilno skupino. Ti rezultati so prikazani tudi na slikah 6 in 7, iz katerih je razvidno, da jakost medmolekulskih interakcij narašča z naraščajočo stopnjo etoksi-

actions increases with an increase in the degree of ethoxylation and the length of hydrocarbonium chain in the structure of the nonionic surfactant. The strength of interactions between a cationic and a nonionic surfactant in general increases with increasing the HLB value of the nonionic surfactant.

Lower values of κ_1 and $\Delta G_1°$ for binding DTA to TX100 in comparison with values of κ_1 and $\Delta G_1°$ for binding DTA to BR56 showed that the branching of the hydrophobic group of the nonionic surfactant might affect the lower strength of interactions. Surfactant BR56 includes a linear alkyl chain with 16 carbonium atoms in comparison with surfactant TX100, which includes a shorter and branched hydrophobic group. Their hydrophilic groups are the same. Decreasing the strength of complex formation is the consequence of both branching of the hydrophobic group and growth of the bulkiness of the polyoxyethylene group of the nonionic surfactant, which can be confirmed by weaker binding of DTA to TW20 than to BR35. While both surfactants TW20 and BR35 have otherwise comparable hydrophobic groups, the hydrophilic group of surfactant TW20 is strongly branched and has 20 oxyethylene groups in comparison with the hydrophilic group of surfactant BR35, which includes 23 oxyethylene groups in its linear chain.

Table 1 also shows that the values of κ_1 and $\Delta G_1°$, determined on micellar basis, reflect the influence of the structure of a nonionic surfactant on intermolecular interactions to a smaller extent. This is understandable, as the micelle represents a similar environment for binding a surfactant cation in spite of the structure of the hydrophilic and hydrophobic group and micellar aggregation number of the nonionic surfactant. In other words, a micelle is formed so that maximum covering of hydrophobic groups of molecules are achieved and oriented towards the interior of the complex, while their hydrophilic groups are oriented towards the aqueous phase.

It can be concluded from those results that the strength of interactions between the surfactant cation and the micelle of a nonionic surfactant is affected by attractive forces of hydrophilic and hydrophobic groups of both cationic and

liranja, kot tudi z dolžino linearne ogljikovodikove verige v strukturi neionskega tenzida. Iz slik je tudi razvidno, da jakost interakcij med kationskim in neionskim tenzidom na splošno narašča z naraščanjem HLB vrednosti neionskega tenzida.

Nižji vrednosti κ_1 in $\Delta G_1°$ za vezanje DTA na TX100 v primerjavi z BR56 sta pokazali, da razvejenje hidrofobne skupine neionskega tenzida vpliva na zmanjšanje jakosti interakcij. Medtem ko imata tenzida enako veliko polioksietilensko skupino, vključuje BR56 linearno alkilno verigo s 16 ogljikovimi atomi, TX100 pa krajšo in razvejano hidrofobno skupino. Prav tako kot razvejanje hidrofobne skupine pa na zmanjšanje jakosti nastanka kompleksov MS^+ vpliva tudi povečanje voluminoznosti polioksietilenske skupine neionskega tenzida. To potrjuje šibkejše vezanje DTA na TW20 v primerjavi z BR35. Oba tenzida imata sicer primerljivo hidrofobno skupino, hidrofilna skupina TW20 pa je v nasprotju z BR35, ki vključuje 23 oksietilenskih skupin v linearni verigi, močno razvejana s skupaj 20 oksietilenskimi skupinami.

Iz preglednice 1 je tudi razvidno, da vrednosti κ_1 in $\Delta G_1°$, ki so izračunane na micelarni osnovi, v veliko manjši meri odražajo vpliv strukture neionskega tenzida na medmolekulske interakcije. To je tudi razumljivo, saj micel kot centralna skupina predstavlja podobno okolje za vezanje kationa tenzida ne glede na strukturo njegove hidrofilne in hidrofobne skupine ter agregacijsko število. Micel se namreč oblikuje tako, da se molekule tenzida s hidrofobnimi skupinami maksimalno prekrivajo in so usmerjene proti notranjosti skupka, s hidrofilnimi skupinami pa so usmerjene proti vodni fazi.

Iz teh rezultatov lahko sklepamo, da na jakost interakcij med kationom tenzida in micelom neionskega tenzida vplivajo tako privlačne sile med hidrofilnimi kot tudi hidrofobnimi skupinami kationskega in neionskega tenzida. Med temi so pomembne elektrostatske in hidrofobne interakcije. Prve delujejo med kvaternim dušikovim atomom kationskega tenzida in polioksietilensko skupino neionskega tenzida, druge pa med hidrofobnima ogljikovodikovima verigama obeh tenzidov. Močnejše ko so te interakcije, večja je jakost vezanja kationskega tenzida na molekulo neionskega tenzida, vezano v micel.

4 Sklepi

V raziskavi smo proučevali termodinamiko interakcij med kationskim in neionskim tenzidom pri koncentracijah neionskega tenzida, višjih od c.m.c. Na podlagi rezultatov smo ugotovili, da so vrednost ravnotežne konstante, κ_1, vezanja tenzida DTA v micel neionskega tenzida neposredno odvisne od tega, ali kot vezalno mesto v micelu upoštevamo molekulo tenzida ali celoten micel. Medtem ko je micel podobno okolje, ne glede na velikost in obliko hidrofilne ter hidrofobne skupine neionskega tenzida, pa je vpliv strukture neionskega tenzida na jakost vezanja kationa ten-

nonionic surfactants. Among these interactions, electrostatic and hydrophobic interactions are important. While the first one acts between a quaternary ammonium atom of a cationic surfactant and a polyoxyethylene group of a nonionic surfactant, the second one acts between the hydrophobic hydrocarbonium chains of both surfactants. The stronger these interactions are, the greater is the strength of binding of the cationic surfactant to the molecule of a nonionic surfactant, bound in the micelle.

4 Conclusion

We have studied the thermodynamics of interactions between a cationic and a nonionic surfactant with the concentration of the nonionic surfactant higher than c.m.c. The results demonstrate that the values of the equilibrium constant, κ_1, of binding surfactant DTA to the micelle of a nonionic surfactant are directly dependant on the binding group in the micelle, which can be considered as a molecule or the whole micelle. Whereas the micelle as the binding group represents the similar environment for binding DTA cations, regardless of the magnitude and the shape of hydrophilic and hydrophobic group of nonionic surfactant, the influence of the structure of nonionic surfactant on the strength of DTA binding is strongly expressed, when an individual molecule of the nonionic surfactant bound in the micelle, is taken as a binding group. The strength of intermolecular interactions governed by surfactant-surfactant complex formation increase as the length of the linear hydrophobic hydrocarbonium chain and the degree of ethoxylation of nonionic surfactant increases. Differences in the structure of the nonionic surfactants, like shortening and branching of both the alkyl and the polyoxethylene group, can cause weaker attractive forces which can affect the decreasing strength of complex formation.

zida močno izražen, ko se kation veže na posamezno molekulo tenzida v micelu. Jakost medmolekulskih interakcij, ki pogojujejo nastanek kompleksa tenzid-tenzid, narašča z naraščanjem linearne hidrofobne ogljikovodikove verige in stopnje etoksiliranja neionskega tenzida. Spremembe v strukturi neionskega tenzida, kot so skrajšanje in razvejanje alkilne in polioksietilenske skupine, povzročijo šibkejše privlačne medmolekulske sile, kar vpliva na zmanjšanje jakosti nastanka kompleksa MS^+.

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