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THERMODYNAMICS OF MICELLIZATION OF N-ALKYLPYRIDINIUM CHLORIDES: A POTENTIOMETRIC STUDY

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Abstract

The critical micelle concentration (CMC) and the thermodynamic functions ΔG^o_{mic}, ΔH^o_{mic} and ΔS^o_{mic} for the micellization process of the two pyridinium cationic surfactants N-dodecylpyridinium chloride (DPC) and N-cetylpyridinium chloride (CPC) in aqueous solution were studied by a potentiometric method using surfactant cation-sensitive membrane electrodes. The e.m.f. of the galvanic cell was measured as a function of surfactant concentration at temperatures of 15, 25, 35 and 45°C at different concentrations of added NaCl (0.00, 0.01, 0.05, 0.1 and 0.5 mol kg^{-1}). The properties of the DPC/CPC mixture were also investigated. The results indicate that the CMC decreases as the hydrophobic character of the surfactant increases and that the addition of NaCl favours the micellization of both studied surfactants. Increase of temperature from 25°C to 45°C did not cause a noticeable change in the CMC of DPC, but resulted in a slight increase in the CMC of CPC. Inspection of the data for thermodynamic functions of micellization shows that the micellization of the studied surfactants is governed mainly by hydrophobic interactions between the surfactant cations, and that CPC forms micelles more readily than DPC under the same conditions.

Introduction

Surfactants are widely used in different practical applications such as washing, cleaning, wetting, dispersing, emulsifying and foaming. The use of surfactants as levelling and retarding agents in textile dyeing is also of great importance. Cationic surfactants are commonly used in these processes. There are two characteristic features of surfactants, surface activity and the ability to form micelles in solution, which affect the performance of surfactants. According to the literature data [1-5], much research has been focused on the development of new methods for studying the behaviour of surfactant solutions and the influence of different factors on surfactant properties.

In this paper, a potentiometric method was used to study the thermodynamic aspects of the micellization of the two cationic surfactants N-cetylpyridinium chloride and N-dodecylpyridinium chloride in aqueous solutions in single component and mixed surfactant systems. This method, based on the use of surfactant cation-sensitive membrane electrodes, allows direct determination of the concentration at which surfactant cations tend to form micelles in solution.

Experimental

Surfactants N-dodecylpyridinium chloride (DPC), N-cetylpyridinium chloride (CPC) and sodium dodecylsulfate (SDS) were commercial products from Aldrich-Chemical Co. and were purified by four recrystallizations from acetone. All solutions were prepared in double distilled water by weight and expressed in molal concentrations.

Ion selective electrodes were prepared according to the well-known method [6] that was described previously [7]. These electrodes include the surfactant cation - surfactant anion complex incorporated within a poly(vinyl chloride) gel membrane.

Potentiometric measurements were carried out in the following electrode cell:

Ag | AgCl | reference solution; $1 \cdot 10^{-4}$ mol kg^{-1} S^+Cl^- + 0.1 mol kg^{-1} NaCl | polymer membrane + S^+DS^- | test solution of S^+Cl^-, || KCl (satd.) | Hg_2Cl_2 | Hg,

where S^+ represents the DPC or CPC surfactant cation and DS^- the SDS surfactant anion. The electrode was tested against a reference calomel electrode (Model HEK 0301, Iskra, Slovenia) via an ammonium nitrate salt bridge and the potential difference was measured with an MA 5740 mV-meter (Iskra, Slovenia).

The dependence of e.m.f. of the cell versus the surfactant concentration, m_S, in the test solution was measured in the concentration range $4 \cdot 10^{-6}$ to $4 \cdot 10^{-2}$ mol kg^{-1} for DPC and $2 \cdot 10^{-6}$ to $3 \cdot 10^{-3}$ mol kg^{-1} for CPC in aqueous solution at 15, 25, 35 and 45^{o}C (±0.1^{o}C), and also in the presence of different fixed amounts of added NaCl (0.01, 0.05, 0.10 and 0.50 mol kg^{-1}). Potentiometric measurements were also performed in mixtures of the studied surfactants DPC and CPC at 25°C, in two different ways. The first experiment included e.m.f. measurements at different concentrations of CPC in the test solution containing fixed amounts of DPC ($1\cdot10^{-4}$ and $1\cdot10^{-3}$ mol kg^{-1}). For this experiment the CPC cation-sensitive membrane electrode was used. In the second experiment a mixture of CPC and DPC (1:1) was added to the test solution in discrete steps, and the resulting potential difference was measured using the CPC- as well as the DPC-selective membrane electrode.

Results

In order to estimate the CMC of the studied surfactants a series of plots of measured e.m.f. (E) versus the logarithm of the concentration (log m_S) of DPC and CPC in aqueous solutions at different temperatures and concentrations of added NaCl salt were made. Fig. 1 and 2 show some representative plots. Plots of E versus log m_S for DPC and CPC in mixtures of the studied surfactants at 25°C are shown in Fig. 3.

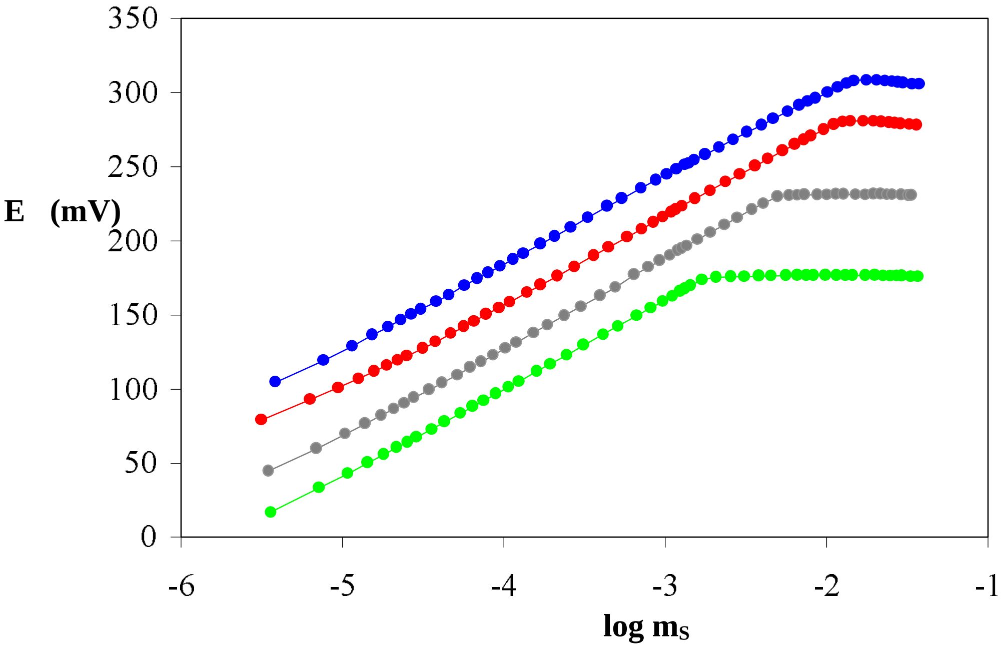

Fig. 1. Plots of e.m.f. (E) of the cell vs the log of DPC concentration (log m_S) in the presence of different concentrations of NaCl at 35°C.
-●-●-: 0 m NaCl, -●-●-: 0.01 m NaCl, -●-●-: 0.10 m NaCl, -●-●-: 0.50 m NaCl.

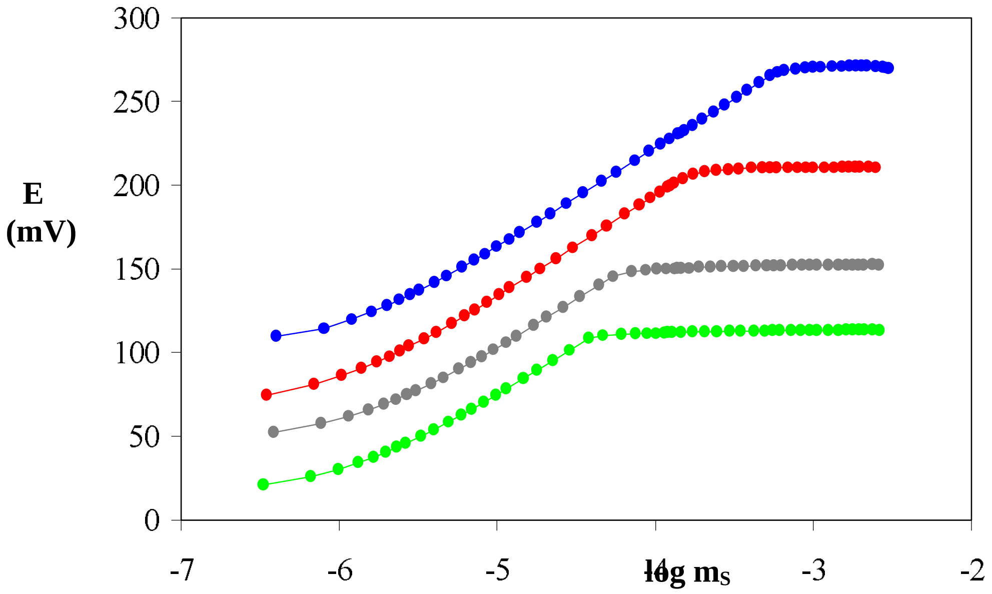

Fig. 2. Plots of e.m.f. (E) of the cell vs the log of CPC surfactant concentration (log m_S) in the presence of different concentrations of NaCl at 35^{o}C.
-●-●-: 0 m NaCl, -●-●-: 0.01 m NaCl, -●-●-: 0.05 m NaCl, -●-●-: 0.10 m NaCl.

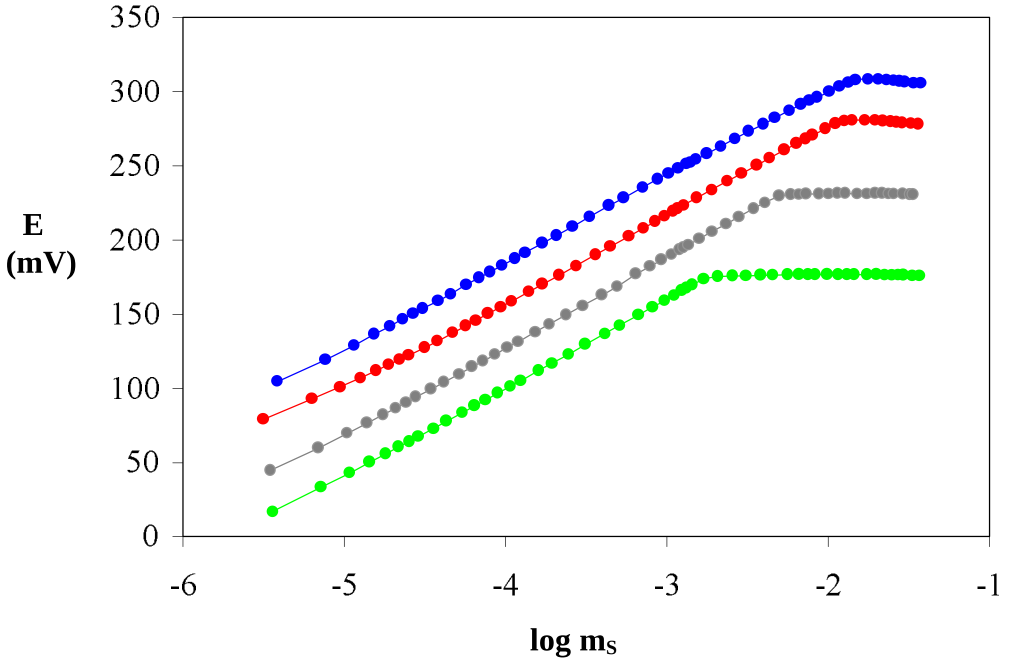

Fig. 3. Plots of e.m.f. (E) of the cell vs the log of surfactant concentration (log m_S) for DPC or CPC in mixtures of the studied surfactants at 25^{o}C.

-●-●-: E vs log m_S of CPC in $1.0 \cdot 10^{-4}$ m DPC, -●-●-: E vs log m_S of CPC in $1.0 \cdot 10^{-3}$ m DPC, -●-●-: E vs log m_S of CPC in the mixture of CPC and DPC (1:1), -●-●-: E vs log m_S of DPC in the mixture of CPC and DPC (1:1).

As evident from the figures, the e.m.f. response is linear over the concentration range $1 \cdot 10^{-6}$ mol kg^{-1} to the CMC with excellent agreement with the Nernstian response [8], and that a break of the potentiometric curve was observed above the CMC. The concentration at the point of intersection of the two linear portions of the E - log m_S plots was taken as the CMC and is presented in Table 1.

TABLE 1

Thermodynamic functions of micellization of DPC and CPC in aqueous solutions

Surfactant	T (°C)	NaCl (mol/kg)	CMC (mol/kg)	K_g	ΔG^o_{mic} (kJ/mol)	ΔH^o_{mic} (kJ/mol)	ΔS^o_{mic} (J/molK)
DPC	15	0.00	$1.56 \cdot 10^{-2}$	0.83	-18.8	-4.4	50.0
		0.01	$1.30 \cdot 10^{-2}$				
		0.10	$5.24 \cdot 10^{-3}$				
		0.50	$1.82 \cdot 10^{-3}$				
	25	0.00	$1.49 \cdot 10^{-2}$	0.80	-19.4	-4.4	50.3
		0.01	$1.18 \cdot 10^{-2}$				
		0.10	$4.99 \cdot 10^{-3}$				
		0.50	$1.79 \cdot 10^{-3}$				
	35	0.00	$1.34 \cdot 10^{-2}$	0.75	-19.9	-4.4	50.3
		0.01	$1.22 \cdot 10^{-2}$				
		0.10	$5.06 \cdot 10^{-3}$				
		0.50	$1.88 \cdot 10^{-3}$				
	45	0.00	$1.34 \cdot 10^{-2}$	0.73	-20.3	-4.4	50.6
		0.01	$1.18 \cdot 10^{-2}$				
		0.10	$5.26 \cdot 10^{-3}$				
		0.50	$1.96 \cdot 10^{-3}$				
CPC	15	0.00	$5.98 \cdot 10^{-4}$	≈0.69	-32.1	6.5	134.0
		0.01	$1.30 \cdot 10^{-4}$				
		0.10	$3.56 \cdot 10^{-5}$				
	25	0.00	$5.31 \cdot 10^{-4}$	0.75	-32.8	6.5	131.8
		0.01	$1.53 \cdot 10^{-4}$				
		0.05	$5.91 \cdot 10^{-5}$				
		0.10	$3.64 \cdot 10^{-5}$				
	35	0.00	$4.38 \cdot 10^{-4}$	0.75	-34.8	6.5	134.0
		0.01	$1.85 \cdot 10^{-4}$				
		0.05	$6.71 \cdot 10^{-5}$				
		0.10	$4.43 \cdot 10^{-5}$				
	45	0.01	$2.18 \cdot 10^{-4}$	/	/	/	/

		0.10	$4.89\cdot10^{-5}$				
DPC–CPC mixture	25	0.00	$4.27\cdot10^{-4}$ * $3.81\cdot10^{-4}$ **	/	/	/	/

* CPC cation-sensitive membrane electrode was used

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The CMC values determined for DPC are in good agreement with the literature data, where in pure water a CMC value of $1.24\cdot10^{-2}$ mol dm^{-3} at 30°C was obtained by isothermal microcalorimetry [9], a value of $1.62\cdot10^{-2}$ mol dm^{-3} at 25°C from surface tension measurements and a value of $1.78\cdot10^{-2}$ mol dm^{-3} at 25°C from conductance measurements [10]. On the other hand, the CMC value of $5.31\cdot10^{-4}$ mol kg^{-1} determined for CPC at 25°C in pure water is lower than the literature value of $9.0\cdot10^{-4}$ mol dm^{-3}, which was obtained by Hartley [11]. It is interesting that our CMC value of $8.7\cdot10^{-3}$ mol kg^{-1} determined for SDS at 25°C, using the same ion selective electrode, is in good agreement with the value of $8.0\cdot10^{-3}$ mol dm^{-3} obtained by Kale et. al. from potentiometric measurements [12]. The CMC values as a function of the temperature and the concentration of added NaCl for DPC and DPC are shown in Fig. 4.

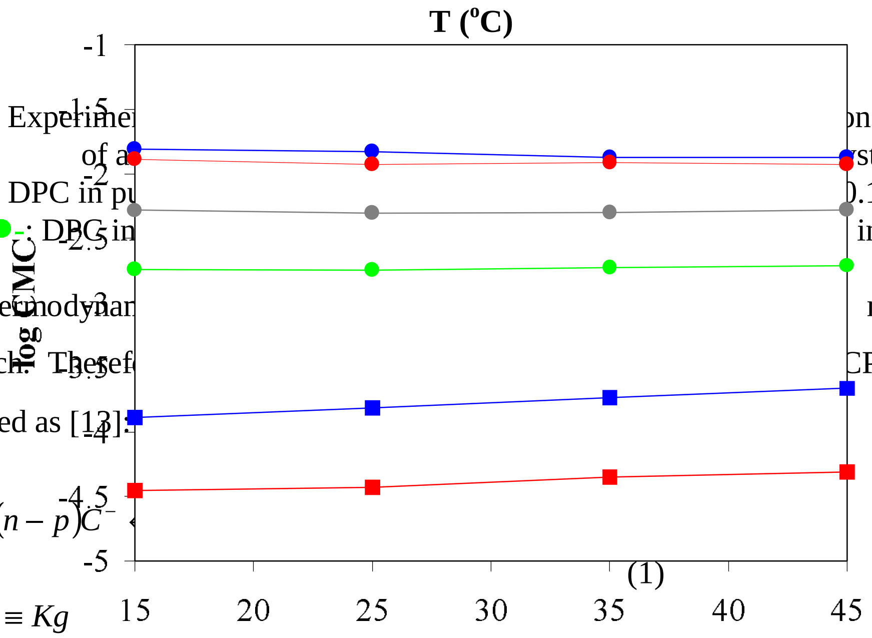


Fig. 4. Experime … ncentrations of a … stems.
-●-●-: DPC in pu … .10 m NaCl,
-●-●-: DPC in … in 0.10 m

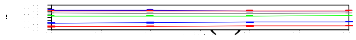
Thermodynam … mass-action approach. Theref … CPC may be described as [13]:

$$nS^{+} + (n-p)C^{-} \quad (1)$$

$$(n-p) \equiv Kg$$

where S^+ represents the surfactant cations, C^- the chloride counterions, and M^{p+} the aggregate of n surfactant monomers with an effective charge of p. K_g is the effective coefficient of electrical energy of micellization.[11].

The standard free energy, ΔG^o_{mic}, of micellization per mole of monomeric surfactant can be calculated as follows [11]:



where m_S and m_C are the molal concentrations of the surfactant cation and the chloride counterion in the solution at the CMC respectively, and γ_+ and γ_- are the activity coefficients of the surfactant and chloride ions. The activity coefficients can be calculated from the Debye-Hückel equation [11]:

(3)

where α is the mean distance of approach of the ions and is taken 0.6Å for the surfactant ion and 0.3Å for the Cl^- counterion. The total ionic strength, I, of the solution is equal to:

$$I = \frac{1}{2}\sum_i m_i z_i^2 \qquad (4)$$

Assuming that ΔG^o_{mic} does not change significantly with change in the concentration of m_C, then K_g can be evaluated from the negative slope of the linear plot of [log CMC + log γ_+] versus [log m_C + log γ_-] [11].

For determining the standard enthalpy change, ΔH^o_{mic}, and the standard entropy change, ΔS^o_{mic}, for the micellization process, the well-known equations [14]:

(5)

$$\Delta S^{o}_{mic} = \frac{\Delta H^{o}_{mic} - \Delta G^{o}_{mic}}{T} \qquad (6)$$

were used. From eqn (5) it can be seen that if $\Delta G^{o}_{mic}/T$ is plotted against 1/T, the slope of the curve at any temperature is equal to ΔH^{o}_{mic} at this temperature. The results show that the relationship between $\Delta G^{o}_{mic}/T$ and 1/T is practically linear within experimental error, indicating ΔH^{o}_{mic} is constant over the measured temperature range. It should be emphasized, that because of the small CMC changes over the measured temperature range, the inaccuracies in the log(CMC) vs T slopes are rather large, therefore the ΔH^{o}_{mic} value calculated from eqn (5) should be considered as only approximate. The thermodynamic quantities for micellization of DPC and CPC are collected in Table 1.

Discussion

The results show that the surfactant's structure, the addition of electrolyte and the temperature influence the micellar properties of the studied surfactants. As expected, the CMC depends on the hydrophobic character of the surfactants. It decreases with increasing length of the hydrocarbon chain of the surfactant. When the number of carbon atoms in the hydrophobic group rises from 12 to 16 the CMC decreases by a factor of 28 at 25°C in pure water. This factor changes only slightly with change in temperature. It is also seen that the small amount of added NaCl decreases the CMC of the studied surfactants (Fig. 4). This is due to the decrease in the electrical repulsion between the positively charged head groups in the micelle in the electrolyte solution. The effect of added NaCl on the CMC is much more pronounced for CPC than for DPC. Experimental data also indicate that an increase in the temperature appears to cause a minimal change in the CMC for DPC over the measured temperature range, and that the CMC of CPC increases slightly with increasing temperature (Fig. 5), independent of the added salt concentration. This behaviour is consistent with the fact that disruption of the structured water surrounding the hydrophobic group induced by the temperature increase, is more effective for CPC with its longer alkyl chain than for

DPC. These results are in good agreement with the results obtained for alkylpyridinium bromides [15].

The CMC of the mixture of DPC and CPC is lower than that of CPC and of DPC in single-component systems. In this case, mixed micelles of the studied surfactants occur in the mixture and the system is said to exhibit synergism in mixed micelle formation [11,16].

The results also show that the ΔH^o_{mic} value calculated for DPC is negative indicating that the micellization process of the studied surfactant is exothermic.The value of –4.4 kJ/mol for DPC is in good agreement with literature data obtained for alkylpyridinium bromide by potentiometric and calorimetric measurements [15]. On the other hand it should be mentioned that the ΔH^o_{mic} value of +6.5 kJ/mol observed for CPC is not in agreement with the explanation that exothermicity increases with increasing alkyl chain length [13,15]. It is seen that this value is positive in sign indicating the endothermic process. This result could be a consequence of a large error in calculating the temperature derivative of CMC at very low CMC values.

According to the large, positive values of ΔS^o_{mic} for both studied surfactants, the system becomes more random after micellization. The positive values of ΔS^o_{mic} clearly indicate that the micellization of the studied surfactants in aqueous solution is governed mainly by hydrophobic interactions between the surfactant cations resulting in the breakdown of the structured water surrounding the hydrophobic groups. Because more water is released during micellization of surfactacts with longer alkyl chains the ΔS^o_{mic} value of 131.8 J/molK determined for CPC at 25°C is larger than the value of 50.3 J/molK obtained for DPC under the same experimental conditions.

Inspection of the values of ΔG^o_{mic} for DPC and CPC shows, that ΔG^o_{mic} decreases with increasing temperature meaning that an increase in temperature tends to drive the equilibrium toward the hydrophobic bonding, and that CPC forms micelles more readily than DPC under the same conditions.

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Povzetek

Kritično koncentracijo micelov (CMC) in termodinamske funkcije micelizacije ΔG^o_{mic}, ΔH^o_{mic} in ΔS^o_{mic} dveh kationskih piridinijevih tenzidov N-dodecilpiridinijevega klorida (DPC) in N-cetilpiridinijevega klorida (CPC) v vodni raztopini smo določili s potenciometrično metodo, ki temelji na uporabi ionoselektivne membranske elektrode, občutljive za katione tenzida. Meritve napetosti galvanskega člena v odvisnosti od koncentracije tenzida smo opravili pri temperaturah 15, 25, 35 in 45°C pri različnih dodatkih soli NaCl (0.00, 0.01, 0.05, 0,10 in 0.50 mol kg^{-1}). Ob tem smo proučevali tudi lastnosti mešanice tenzidov DPC in CPC. Iz rezultatov meritev je razvidno, da se z večanjem hidrofobnega karakterja tenzida CMC zmanjšuje. Dodatek NaCl v raztopino proučevanih tenzidov pogojuje micelizacijo DPC kot tudi CPC. Zvišanje temperature od 25°C do 45°C bistveno ne vpliva na spremembo CMC tenzida DPC, medtem ko povzroči rahlo naraščanje CMC tenzida CPC. Na podlagi vrednosti termodinamskih funkcij lahko zaključimo, da so pri procesu micelizacije proučevanih tenzidov v vodni raztopini pomembne hidrofobne interakcije.