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COMPOSITION OF THE SODIUM DODECYLSULFATE – 1-PENTANOL MIXED MICELLES AS DETERMINED USING ACID-BASE INDICATORS**A.Yu. Kharchenko**

The composition of mixed surfactant–alcohol micelles is governed by the parameters of alcohol partition between the aqueous and micellar phases. In this paper, the indicator method of determination of 1-pentanol molar fraction in the mixed sodium *n*-dodecylsulfate – 1-pentanol micelles and the partition constant of the alcohol is reported. This method relies on the determination of the apparent ionization constants, K_a^{app} , of acid-base indicators. The electrical surface potential Ψ is equal to -58 mV and -39 mV for entire and mixed micelles, respectively, as evaluated using $\text{p}K_a^{\text{app}}$ values of the indicator *N,N'*-di-*n*-octadecylrhodamine. In terms of the slope of the dependence of $\text{p}K_a^{\text{app}}$ vs. $\log[\text{Na}_w^+]$ for the indicator neutral red, the degree of counter-ion binding in entire surfactant micelles, β , equals 0.71 ± 0.02 , whereas the corresponding value at 0.20 M 1-pentanol is substantially lower, $\beta' = 0.52 \pm 0.03$. The β , β' , and Ψ values allow estimating the molar fraction of 1-pentanol in the mixed micelles using the Ohshima–Healy–White equation. Finally, the partition constant of the 1-pentanol between the aqueous phase and micelles is determined as $K = 10.3 \text{ M}^{-1}$ and 15.4 M^{-1} in terms of the spherical and cylindrical model of mixed micelles, respectively. These values are accorded with the corresponding data obtained by other methods.

Keywords: acid-base indicators, sodium *n*-dodecylsulfate micelles, 1-pentanol, electrical surface potential, degree of counter-ion binding, alcohol molar fraction, partition constant.

Introduction

The mixed sodium *n*-dodecylsulfate (SDS) – alcohol micelles were an object of numerous studies for a long time. In particular, the properties of SDS–1-pentanol micelles have been examined since 1-pentanol is a typical co-surfactant used for preparation of the microemulsion systems [1-3]. Namely it is important to know the aggregation number of SDS in mixed micelles, the molar fraction of alcohol, the micelles size [4,5], and the *cmc* values [6]. Also, the distribution of 1-pentanol as well as other aliphatic alcohols between aqueous and micellar phase has been studied by different methods, particularly via the vapor pressure of the alcohols in aqueous solutions as determined using the gas chromatographic technique [7-9], by determination of alcohols solubility using measurements of the density or turbidity [10], by estimation of the self-diffusion coefficients [11], and by the calorimetric data [12]. Recently, we have proposed a method of calculation of the partition constant [13,14]. This method is based on the experimental values of the electrical surface potential Ψ of micelles and the degree of counter-ion binding by micelle surface, β . The method was tested using the system of cetyltrimethylammonium bromide–1-butanol [13] and SDS–1-butanol [14]. The aim of present study is to apply the same approach to the determination of the composition of mixed SDS–1-pentanol micelles. In addition, a brief review of the literature data on the SDS–1-pentanol mixed micelles is presented.

The experimental values of Ψ and β are obtained by the indicator method. This method consists in the inclusion of small acid-base indicator molecules in individual surfactant micelles and mixed micelles by solubilization and the determination of acid strength of indicator in micellar microenvironment. In the case of colloidal solution, the acid strength may be expressed as the apparent ionization constant, K_a^{app} . The dependences $\text{p}K_a^{\text{app}}$ values on different parameters of micellar solution allow determining the electrical surface potential and the degree of counter-ion binding.

The characterization of the mixed SDS–1-pentanol micelles: State of art

For a start, let us consider the properties of entire SDS micelles in water. The value of the degree of counter-ions binding, β , is 0.63–0.79 [6,15,16], the aggregation number is 60–69 [15-19], the critical micelle concentration value, *cmc*, is $8 \times 10^{-3} \text{ M}$ [15,18-20]. The solubilities of 1-pentanol and 1-butanol in water at 25 °C are 0.30 and 1.05 M, respectively [21]. 1-Pentanol is more hydrophobic

alcohol than 1-butanol and is solubilized in both palisade layer and hydrocarbon core of ionic micelles, especially near the solubility limit [22]. Nevertheless, according to the ^1H NMR studies of solutions containing mixed SDS–1-pentanol micelles, the alcohol molecules are solubilized close to the head groups of the micelle [23]. The *cmc* value of SDS monotonously decreases on addition of 1-pentanol. The *cmc* values of SDS in the presence of $\text{C}_5\text{H}_{11}\text{OH}$ are gathered in Table 1. For instance, *cmc* = 1.6×10^{-3} at 0.20 M 1-pentanol [24]. The size (radius) of mixed SDS–1-pentanol micelles at 0.02 M SDS and 0.20 M 1-pentanol is 1.7 nm [4,5,25] as determined using the fluorescence quenching technique. For individual SDS micelles radius is 1.8 nm [4,5,25]. Førlund et al. [22] measured the minor and major radius of mixed micelles as 1.46 nm and 55.4, respectively, by small-angle neutron scattering (SANS) method ($c(\text{SDS}) = 0.04 \text{ mol kg}^{-1}$, $c(1\text{-pentanol}) = 0.16 \text{ mol kg}^{-1}$, $I = 0.40 \text{ mol kg}^{-1}$). It follows that SDS–1-pentanol micelles are ellipsoids or rods. Moreover, the major to minor ratio is constant (~ 10) from 0.06 to 0.13 mol kg^{-1} and begins to grow at 0.16 mol kg^{-1} , i.e. around the solubility limit of 1-pentanol in water. The β value of the mixed micelles, designated as β' , decreases as compared with the β value in pure SDS, down to 0.53 at 0.139 M 1-pentanol [6] or 0.47 at 0.1 M 1-pentanol [26]. In 0.02–0.03 M SDS solutions and 1-pentanol concentration $c(\text{ROH}) = 0.20 \text{ M}$, the aggregation number of SDS molecules and the number of 1-pentanol molecules in the SDS–1-pentanol micelles are upon average 30 and 63, respectively [4,5,25]. The surface concentration of the surfactant head groups equals 0.810 per nm^2 (0.02 M SDS; 0.1895 M 1-pentanol), according to Varela et al.[5]. Hence, the surface area per head group in mixed micelles, a , is 1.235 nm^2 . For pure SDS micelles, the surface area per head group was found to be equal to 0.591 nm^2 [4] or 0.628 nm^2 [27].

Experimental section

Materials. SDS was used as received from Vekton (Russia). The stock solution of the dye neutral red was prepared from the commercial solid sample without further purification. N,N' -di-*n*-octadecylrhodamine was put to our disposal by Dr. V. I. Alekseeva (Research Institute of Organic Intermediates and Dyes, Moscow, Russia). Hydrochloric, acetic, and phosphoric acids, borax, sodium carbonate and bicarbonate, and sodium chloride used for preparation of working solutions were of analytical grade. The NaOH aqueous solution was prepared by diluting the saturated stock solution with CO_2 -free water and kept protected from the atmosphere. The pH values of the solutions were adjusted using HCl for $\text{pH} < 4$, or buffer solutions: acetate ($\text{pH} 3.7\text{--}5.4$), phosphate ($\text{pH} 5.8\text{--}8.0$), borate ($\text{pH} 8.0\text{--}10.0$), and carbonate (sodium carbonate and bicarbonate, $\text{pH} 8.8\text{--}10.0$). The pH values around 11–12 were adjusted by diluted sodium hydroxide. The total ionic strength of the bulk (aqueous) phase was maintained by appropriate NaCl additions. 1-Pentanol was purified by the standard procedure via rectification.

Methods. The dyes N,N' -di-*n*-octadecylrhodamine and neutral red were dissolved directly in SDS solutions, which were filtrated and then diluted before spectroscopic studies. The initial SDS concentration was 0.20 or 0.40 M. In all spectroscopic experiments, the concentrations of SDS and 1-pentanol were 0.02 and 0.20 M, respectively; the dye concentrations were of about $1 \times 10^{-5} \text{ M}$. Absorption spectra were measured at 25°C with Hitachi U-2000 spectrophotometer against pure water as solvent blank. The pH determinations were performed by using R 37-01 potentiometer and pH-121 pH-meter (Russia) with an ESL-43-07 glass electrode (Gomel, Belarus) in a cell with liquid junction (3.0 M KCl). An Ag|AgCl electrode was used as a reference electrode. The cell was calibrated with standard buffer solutions: pH 9.18, 6.86, 4.01, and 1.68 at 25°C .

The apparent ionization constant of an indicator was calculated as [25,30,31]:

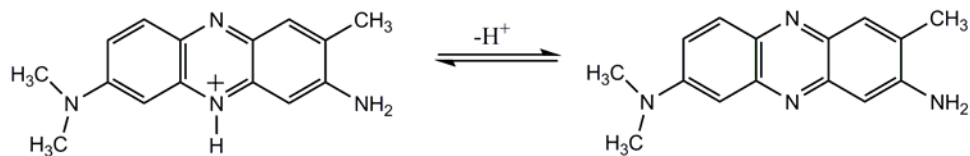
$$\text{p}K_a^{\text{app}} = \text{pH}_w + \log \frac{[\text{H}_i\text{B}^z]_t}{[\text{H}_{i-1}\text{B}^{z-1}]_t} = \text{pH}_w + \log \frac{A_B - A}{A - A_{\text{HB}}} \quad (1)$$

The acid-base couple $\text{H}_i\text{B}^z/\text{H}_{i-1}\text{B}^{z-1}$ is expected to be located within the micellar microenvironment whereas the pH_w value is the pH value of continuous (aqueous) phase. The suffix t (total) denotes that the concentration is expressed in moles per dm^3 of the whole solution. The ratio of the equilibrium concentrations, $[\text{H}_i\text{B}^z]_t/[\text{H}_{i-1}\text{B}^{z-1}]_t$, was determined by using the spec-

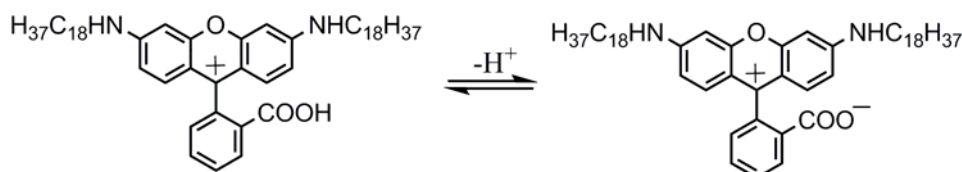
Table 1. The micellization parameters and structure of mixed SDS–1-pentanol micelles reported in the literature.

Ref.	Conditions	Methods	β'	N_{aggr}	$N_{1\text{-butanol}}$ (x_{ROH})	r , nm	cmc , mM	a , nm ²
[4]	$c(\text{SDS})=0.0336 \text{ M}$, $c(\text{ROH}) = 0.1846 \text{ M}$; $c(\text{SDS})=0.0332 \text{ M}$, $c(\text{ROH}) = 0.227 \text{ M}$.	steady-state fluorescence quenching	—	33.3; 26.9	62.3 (0.65); 63.1 (0.70)	1.73; 1.67	—	1.129; 1.303
[25]	$c(\text{SDS})=0.02 \text{ M}$, $c(\text{ROH}) = 0.2 \text{ M}$; $c(\text{SDS})=0.05 \text{ M}$, $c(\text{ROH}) = 0.22 \text{ M}$, $I = 0.1 \text{ M}$.	fluorescence quenching	—	27; 49	52 (0.66); 66 (0.57)	1.63; 1.89	—	—
[16]	$c(\text{SDS}) = 0 \div 0.1 \text{ M}$ the SDS/1-pentanol mole ratio of 1	conductivity	0.55 (0.72 – pure SDS)	—	—	—	—	—
[5]	$c(\text{SDS})=0.02 \text{ M}$ $c(\text{ROH}) = 0.1895 \text{ M}$; 0.2714 M.	fluorescence quenching	—	31; 30	73 (0.70); 100 (0.77)	1.76; 1.86	—	1.235; 1.429
[28]	$c(\text{SDS})=0.2 \text{ M}$ $\eta(\text{ROH}) = 1.92 \text{ \% v/v}$ (0.178 M)	SANS	—	62.1	37.1 (0.37)	—	—	—
[22]	$c(\text{SDS}) = 0.04 \text{ mol kg}^{-1}$ $c(\text{ROH}) = 0.16 \text{ mol kg}^{-1}$, $I = 0.40 \text{ mol kg}^{-1}$	SANS	—	—	—	1.46 (minor), 55.4 (major)	—	—
[6]	$c(\text{SDS}) = 0.03 - 0.1 \text{ M}$ $c(\text{ROH}) = 0.046 \text{ M}$; 0.139 M (1.5 % v/v).	potentiometry	0.69 ; 0.53	—	—	—	6.5 ; 2.1	—
[24]	$c(\text{ROH}) = 0.20 \text{ M}$	calculated	—	—	—	—	1.6	—
[26]	$c(\text{SDS}) = 0.02 \text{ M}$ (β) $c(\text{ROH}) = 0.1 \text{ M}$	membrane potential measurement	0.47 (0.68 – pure SDS)	—	—	—	3.0	—
[29]	$c(\text{SDS}) = 0.2 \text{ M}$ $c(\text{ROH}) = 0.2 \text{ M}$.	positron annihilation lifetime spectroscopy	—	40	—	1.46	—	—

trophotometric method. The pH_w values were maintained by buffer solutions and determined using a glass electrode in the aforementioned cell with liquid junction. It should be noted, that the complete binding of dyes to micelles is ensured by the hydrophobicity of indicator molecules and by the positive charge of their protonated forms [14]. It is important for the calculation of electrical surface potential and the degree of counter-ion binding. The protolytic equilibria of these dyes are represented in Scheme 1-2.



Scheme 1. The protolytic equilibrium of neutral red.



Scheme 2. The ionization of N,N' -di- n -octadecylrhodamine.

Determination of the Ψ value. The Ψ value for mixed 1-pentanol-containing micelles was determined by the indicator method using N,N' -di- n -octadecylrhodamine as the most suitable probe, as noted earlier [13,32,33]. Using this indicator is reasonable because it contains two n -octadecyl tails, which fixed the carboxyl group of indicator in the surface layer of micelles regardless of its charge character. Consequently, in this case one can compare the obtained values of Ψ for different systems due to the absence of error at the expense of various locations of indicators in different micelle types. To calculate the $\text{p}K_a^{\text{app}}$ s the linear combinations of absorbances at different wavelengths were used as described earlier [32]. The absorption spectra and the dependence of the linear combination of absorbances vs. pH at 0.02 M SDS and 0.20 M 1-pentanol are represented in Figure 1. The $\text{p}K_a^{\text{app}}$ values of N,N' -di- n -octadecylrhodamine in pure SDS micelles and mixed SDS–1-pentanol-1 micelles are 5.21 ± 0.09 [32] and 4.89 ± 0.03 , respectively.

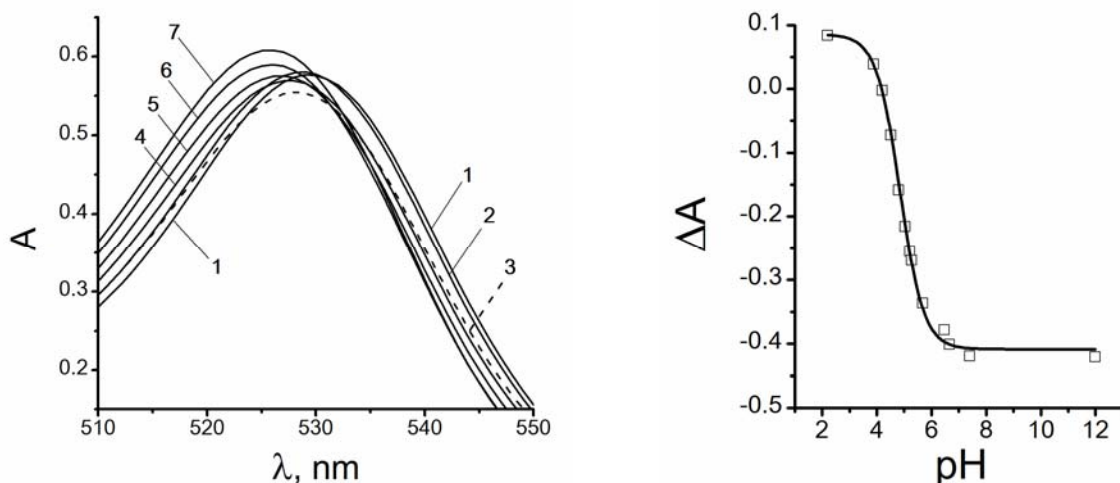


Figure 1. The absorption spectra of N,N' -di- n -octadecylrhodamine at 0.02 M SDS and 0.20 M 1-pentanol; $I_{\text{salt}}=0.05$ M; pH = 2.2 (1), 4.21 (2), 4.52 (3), 4.80 (4), 5.27 (5), 6.48 (6), 7.4 (7); HB^+ species: $\lambda_{\text{max}} = 529$ nm, pH = 2.2 (1); B^{\pm} species: $\lambda_{\text{max}} = 526$ nm, pH = 7.4 (7). (left)

The dependences of the linear combination of absorbances (1.00 cm optical path cell) vs. pH for N,N' -di- n -octadecylrhodamine at 0.02 M SDS and $I_{\text{salt}} = 0.05$ M (NaCl); $\Delta A = A(535 \text{ nm}) + A(540 \text{ nm}) + A(545 \text{ nm}) - A(510 \text{ nm}) - A(515 \text{ nm}) - A(520 \text{ nm})$; 0.20 M 1-pentanol. (right)

The pK_a^{app} value of the acid-base couple, which is completely bound to micelles, may be represented by the Hartley – Mukerjee – Funasaki – Fromherz (HMFF) equation [30]:

$$pK_a^{\text{app}} = pK_a^w + \log \frac{\gamma_B^m}{\gamma_{\text{HB}}^m} - \frac{\Psi F}{2.30 RT} = pK_a^i - \frac{\Psi F}{2.30 RT}. \quad (2)$$

Here R is the gas constant, T is the absolute temperature, and F is the Faraday constant. The K_a^i parameter is the so-called intrinsic ionization constant [19,30,34]. The value of $pK_a^i = 4.23$ [30,32] was used in the calculations via Eq. (2). The Ψ value of -58.0 mV was found earlier for individual SDS micelles at 0.01 M SDS and total ionic strength $I_{\text{total}} = 0.053$ M [32]. As regards SDS–1-pentanol system, we have found surface electrical potential as -39.0 mV at $I_{\text{total}} = 0.060$ M by method described above. Hartland et al. [25] have reported that the surface potential equals -52 ± 5 mV for mixed 1-pentanol-containing SDS micelles ($c(\text{SDS}) = 0.02$ M, $c(1\text{-pentanol}) = 0.20$ M, $I = 0.003$ M) and -30 ± 5 mV ($c(\text{SDS}) = 0.05$ M, $c(1\text{-pentanol}) = 0.22$ M, $I = 0.103$ M).

For mixed micelles system the ionic strength is calculated according to Eq. (3) keeping in mind the dissociation of counter-ions:

$$I_{\text{total}} = I_{\text{salt}} + cmc + (1 - \beta) \cdot (c_{\text{SDS}} - cmc) \quad (3)$$

Here I_{salt} is the ionic strength of salt background (buffer + NaCl) ($= 0.05$ M), cmc – the critical micelle concentration, the β value is the degree of counter-ion binding (~ 0.50 , see Table 1), c_{SDS} – the analytical concentration of SDS ($= 0.02$ M). The cmc values are obtained using the dependence for the individual SDS systems, Eq. (4) [35]:

$$\log cmc = -3.50 - 0.67 \cdot \log c(\text{Na}^+) . \quad (4)$$

Here, $c(\text{Na}^+)$ stands for the analytical the concentration of the sodium ions in the buffer solution without the contribution of the counter-ions of micelles. Then, for mixed micelles the obtained cmc value should be multiplied by 0.25 , because 1-pentanol addition decreases the cmc value approximately fourfold (see Table 1).

Degree of the counter-ion binding, $\beta = 1 - \alpha$, as determined using the indicator method. It is well known that in the anionic micellar solutions, when the ionic strength increases, the shielding (screening) of the interfacial charge causes the decrease of pK_a^{app} value of cationic indicators. As indicator, we have chosen neutral red since this one was found rather suitable for the investigation of mixed micelles. In particular, the degree of counter-ion binding, β , for individual SDS micelles obtained by neutral red is similar to β value determined by electrometric measurements, so it is reasonable to investigation unknown systems [14].

The pK_a^{app} values are represented in Table 2. The ionic strength varied from 0.03 to 0.50 M for individual SDS micelles and from 0.02 to 0.35 M for mixed ones. In case the ionic strength exceeds 0.35 M, the 1-pentanol-containing micellar system becomes inhomogeneous. To determine the pK_a^{app} values of the indicator neutral red in individual SDS micelles, the carbonate – hydrocarbonate buffer was utilized for adjusting the pH. In the case of SDS–1-pentanol micelles, we normally used phosphate buffer. The absorption spectra of neutral red in individual SDS micelles system and mixed SDS–1-pentanol micelles system are exemplified in Figure 2 at ionic strength 0.35 M.

Table 2. The pK_a^{app} values of the dye neutral red in SDS micellar solutions without and with 1-pentanol.

0.02 M SDS			0.02 M SDS + 0.20 M 1-pentanol		
$I_{\text{salt}}, \text{M}$	$[\text{Na}_w^+]$	pK_a^{app}	$I_{\text{salt}}, \text{M}$	$[\text{Na}_w^+]$	pK_a^{app}
0.03	0.038	9.35 ± 0.03	0.02	0.028	8.04 ± 0.04
0.05	0.054	9.21 ± 0.01	0.05	0.055	7.89 ± 0.03
0.15	0.15	8.91 ± 0.05	0.1	0.11	7.74 ± 0.02
0.35	0.36	8.63 ± 0.02	0.2	0.21	7.60 ± 0.01
0.50	0.50	8.53 ± 0.03	0.35	0.36	7.46 ± 0.02

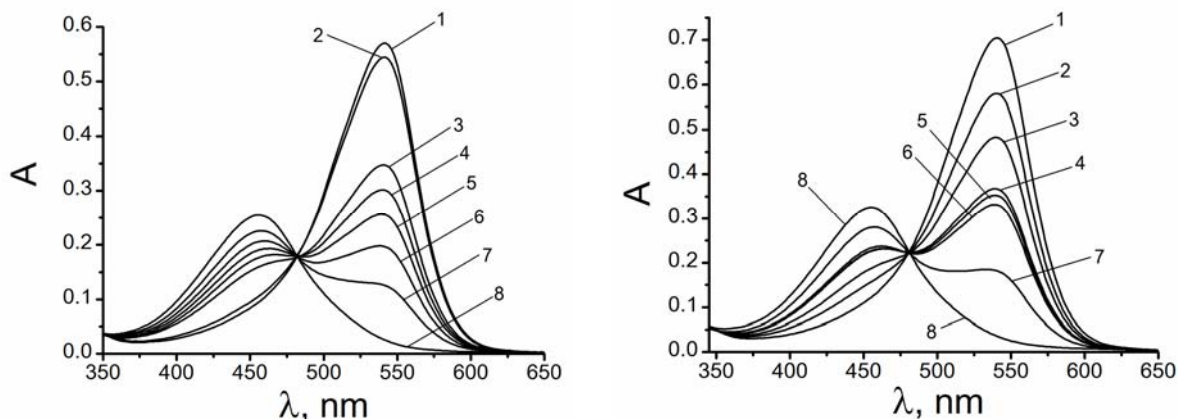


Figure 2. Left: the absorption spectra of neutral red at 0.02 M SDS; $I_{\text{salt}} = 0.35$ M; pH = 6.5 (1), 7.35 (2), 8.51 (3), 8.63 (4), 8.76 (5), 8.96 (6), 9.26 (7), 12.0 (8); HB^+ species: $\lambda_{\text{max}} = 542$ nm, pH = 6.5 (1); B species: $\lambda_{\text{max}} = 456$ nm, pH = 12.0 (8). Right: the absorption spectra of neutral red at 0.02 M SDS and 0.20 M 1-pentanol; $I_{\text{salt}} = 0.35$ M; pH = 4.0 (1), 6.80 (2), 7.17 (3), 7.48 (4), 7.52 (5), 7.55 (6), 8.02 (7), 12.0 (8); HB^+ species: $\lambda_{\text{max}} = 540.5$ nm, pH = 4.0 (1); B species: $\lambda_{\text{max}} = 454.5$ nm, pH = 12.0 (8).

The derivative $\partial(\text{p}K_a^{\text{app}})/\partial \log[\text{Na}_w^+]$ is considered to be equal to the degree of counter-ion binding, β , by the SDS micellar surface [13,30]. Here $[\text{Na}_w^+]$ is the equilibrium concentration of the sodium ions in the bulk (aqueous) phase and includes the counter-ions resulting from the dissociation of the micelles. To calculate the β value, the iterative method was used. At first, the dependence $\text{p}K_a^{\text{app}}$ vs. I_{salt} was obtained. The slope of this line is the rough value of β . Then, cmc values were found using Eq. (4) for corresponding Na^+ concentrations. The $[\text{Na}_w^+]$ values were calculated by an equation similar to Eq. (3), but I_{salt} was replaced by $c(\text{Na}^+)$. Next, the linear dependence of $\text{p}K_a^{\text{app}}$ vs. $\log[\text{Na}_w^+]$ was used to refine the β values. The iteration was repeated twice. The final dependences of $\text{p}K_a^{\text{app}}$ values vs. $\log[\text{Na}_w^+]$ are shown in Figure 3.

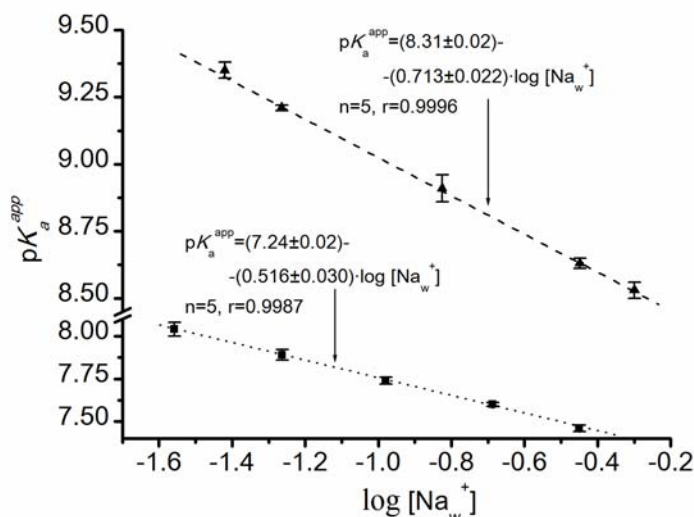


Figure 3. The dependence of the $\text{p}K_a^{\text{app}}$ value of neutral red in entire SDS solutions (dashed line) and in mixed solutions SDS + 1-pentanol (dotted line) on the logarithm of the Na^+ equilibrium concentration in the bulk (continuous) phase.

The β value is equal to 0.713 ± 0.022 for the entire SDS micelles, whereas $\beta' = 0.516 \pm 0.030$ for the mixed SDS–1-pentanol micelles. Our data are in a good agreement with the β and β' values obtained by different methods (Table 1). However, it should be kept in mind that using hexamethoxy red as indicator results in somewhat higher β and lower β' values. In this case, $\beta = 0.84 \pm 0.02$ for the entire SDS micelles and 0.43 ± 0.08 for the mixed SDS–1-pentanol micelles [36]. The questions about indicator choice will be discussed some later.

Results and discussion

The micellar surface charge density and the alcohol fraction in the micellar interface. The calculation of the micellar surface charge density for the pure and mixed SDS micelles, q_s and q'_s , respectively, was processed by the formulae obtained by Ohshima, Healy, and White for spherical and cylindrical colloidal particles with radius r [37] as it was represented in our previous paper [13]. The $r = 2$ nm value [22,25,38] for both individual and mixed micelles has been used in the calculations since the radii of mixed and individual SDS micelles are close [25]. The q_s and q'_s values were computed using the experimental Ψ values obtained by means of N,N' -di- n -octadecylrhodamine. For the spherical shape, the q_s and q'_s values are 0.352 and 0.231 charges per nm^2 for SDS and SDS–1-pentanol micelles, respectively, whereas for the cylindrical shape $q_s = 0.288$ and $q'_s = 0.189$ charges per nm^2 . Then, as we have determined earlier [14], the area of the anionic head group $s_- = 0.815$ and 0.996 nm^2 per charge for spherical and ellipsoidal (cylindrical) model, respectively, using the above q_s values for the pure SDS micelles. It should be underline that here s_- is the area of the micellar surface per the head group of the surfactant. In this case, s_- is equal to the a values, reported in the literature and compiled in Table 1. The calculations of s_- have been made for the β value obtained by neutral red.

After that, one can calculate the fractions of the 1-pentanol following two methods. According to first one, x_{ROH} is the function of q'_s and molecular areas, s_- and s_{ROH} :

$$x_{\text{ROH}} = \frac{q'_s s_- + \beta' - 1}{q'_s s_- - q'_s s_{\text{ROH}} + \beta' - 1}. \quad (5)$$

If the value $s_{\text{ROH}} = 0.21$ nm^2 [39] was used, the x_{ROH} values of 0.857 and 0.880 were obtained for the spherical and cylindrical models for the mixed SDS–1-pentanol micelles, respectively. In this case we assume that the alcohol molecules are directed with the OH group towards the water phase. The second method can be used if the location of alcohol molecules is undefined. Following to this method,

$$q'_s = \frac{1 - \beta'}{s'_-} \quad (6a) \quad \text{and} \quad s'_- = s_- + \frac{N_{\text{ROH}}}{N_{\text{SDS}}} \cdot s_{\text{ROH}}. \quad (6b)$$

Here, s'_- is the area of the micellar surface per head group of the surfactant in mixed micelles. If $\beta' = 0.516$, then from Eq. (6a) results $s'_- = 2.10$ or 2.56 nm^2 per charge for spherical and cylindrical model, respectively. Using the values of s_- and $N_{\text{ROH}} = 180$ ($x_{\text{ROH}} = 0.857$) or 210 ($x_{\text{ROH}} = 0.880$), the s'_- values are 2.08 nm^2 and 2.47 nm^2 for the spherical and cylindrical model, respectively, as obtained using Eq. (6b). This corresponds to 6–7 1-pentanol molecules per one $-\text{O}-\text{SO}_3^-$ group. Using the obtained above s'_- values and $s_- = 0.30$ nm^2 [40], the ratio $N_{\text{ROH}} / N_{\text{SDS}}$ is found to be 9 ($x_{\text{ROH}} = 0.900$) for spherical or 11 ($x_{\text{ROH}} = 0.917$) for cylindrical model. The schematic representation of the fragment of micellar surface in the case of individual and mixed micelles is shown in Figure 4.

It should be noted that our value of the molar fractions of the 1-pentanol is higher than some values reported in the literature. For instance, the molar fraction of 1-pentanol in the micelle was found by Hartland et al. [25] as 0.66 ($c(\text{SDS}) = 0.02$ M; $c(1\text{-pentanol}) = 0.20$ M, so $[\text{ROH}_m] = 0.035$ M) or 0.57 ($c(\text{SDS}) = 0.05$ M; $c(1\text{-pentanol}) = 0.22$ M, $I = 0.103$ M) or ~ 0.7 ($c(\text{SDS}) = 0.02$ M; $c(1\text{-pentanol}) = 0.20$ M) by Johnson et al. [24]. Probably, the higher x_{ROH} value means that mixed micelles are the “micelles of 1-pentanol stabilized SDS monomers”.

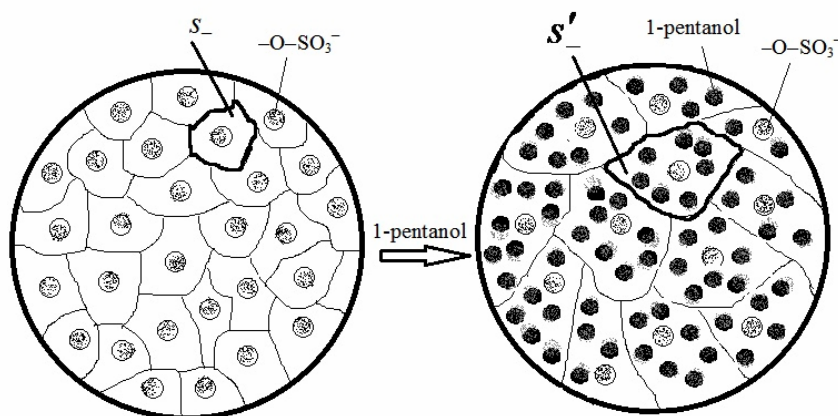


Figure 4. The schematic representation of the fragment of micellar surface in the case of individual SDS micelles (left) and SDS–1-pentanol mixed micelles (right). These schemes represent the calculations described in this paper.

The equilibrium constant of 1-pentanol partitioning. In terms of the ratio of molar interfacial fractions of 1-pentanol and SDS monomer, the equilibrium concentration of 1-pentanol in micelles (m) and aqueous phase (w) $[\text{ROH}_m]_f = 0.117 \text{ M}$, $[\text{ROH}_w]_f = 0.083 \text{ M}$ for spherical model, and $[\text{ROH}_m]_f = 0.143 \text{ M}$, $[\text{ROH}_w]_f = 0.057 \text{ M}$ for cylindrical model. The obtained values of the molar interface fraction and the equilibrium concentrations of 1-pentanol have allowed to estimate the equilibrium constant of alcohol partitioning between the continuous and micellar (SDS + 1-pentanol) phases following the method of Gettins et al. [13,15,41]:

$$K = \frac{[\text{ROH}_m]_f}{[\text{ROH}_w]_f \cdot ([\text{ROH}_m]_f + c_{\text{SDS}} - cmc)} = \frac{x_{\text{ROH}}}{[\text{ROH}_w]_f} \quad (7)$$

The obtained x_{ROH} values result in the K values 10.3 M^{-1} in terms of the spherical model and 15.4 M^{-1} on the assumption of cylindrical model. The partition of 1-pentanol may be represented as the distribution coefficient, K_x , the concentration distribution coefficient, K_r , as well as the fraction of the alcohols in the micellar pseudophase, p :

$$x_{\text{ROH}_{\text{water}}} = \frac{[\text{ROH}_w]_f}{55.6 \text{ mol/l}(\text{H}_2\text{O})}; \quad K_x = \frac{x_{\text{ROH}}}{x_{\text{ROH}_{\text{water}}}} = 570 \text{ (spherical model)} \quad \text{or} \quad 860 \text{ (cylindrical model)}$$

$$K_r = \frac{[\text{ROH}_m]_f}{[\text{ROH}_w]_f} = 140 \text{ (spherical model)} \quad \text{or} \quad 250 \text{ (cylindrical model)}$$

$$p = \frac{[\text{ROH}_m]_f}{c(\text{ROH})_f} = 0.59 \text{ (spherical model)} \quad \text{or} \quad 0.72 \text{ (cylindrical model)}$$

Here, the $[\text{ROH}_m]_f$ value is the concentration expressed in moles per 1 dm^3 of the pseudophase.

It should be noted that, when the β values of hexamethoxy red indicator was used for calculation, one can obtain the following results. The area of the anionic head groups, s_- , is 0.454 and 0.556 nm^2 per charge for spherical and ellipsoidal (cylindrical) model, respectively, as obtained using the above q_s values for the pure SDS micelles. Hence, the x_{ROH} values of 0.905 and 0.921 were obtained for the spherical and cylindrical models for the mixed SDS–1-pentanol micelles, respectively. Following the spherical model, $[\text{ROH}_m]_f = 0.186 \text{ M}$, $[\text{ROH}_w]_f = 0.014 \text{ M}$, the K value equals 67 M^{-1} . However, according to cylindrical model $[\text{ROH}_m]_f = 0.228 \text{ M}$. This value doesn't have physical meaning due to exceeding general 1-pentanol concentration. In this case, it can be assumed the K value is so great that all additive 1-pentanol is found in micelles pseudophase. However, the values of the area of anionic head group s_- are less than in literature data [4,27], so the K values obtained by hexamethoxy red are questionable.

Concluding remarks

In this study we have obtained the equilibrium constant of 1-pentanol partitioning between the continuous and micellar (SDS + 1-pentanol) phases following the method of Gettins. It equals 10.3 M^{-1} in terms of the spherical model and 15.4 M^{-1} on the assumption of cylindrical model. The respective distribution coefficients, K_x , are 570 and 860, the concentration distribution coefficients, K_r , are 140 and 250. The fraction of the alcohol in the micellar pseudophase, p , is 0.59 (spherical model) or 0.72 (cylindrical model). For instance, let us consider some data about mixed micelles composition obtained by more direct methods. The fraction (p) of the alcohol in the micellar pseudophase was determined from the measured self-diffusion coefficients as 0.35–0.40 by Førland et al. [22] ($c(\text{SDS}) = 0.04 \text{ mol kg}^{-1}$, $I = 0.4 \text{ mol kg}^{-1}$, $c(1\text{-pentanol}) = 0.16 \text{ mol kg}^{-1}$). It follows that $[\text{ROH}_m] \sim 0.06 \text{ M}$ at $c(1\text{-pentanol}) = 0.16 \text{ mol kg}^{-1}$. Nevertheless, the p value obtained by Stilbs by multicomponent self-diffusion studies [42] is 0.75 for the sample with weight fractions of alcohol, D_2O , and SDS, equal 0.027, 0.907, and 0.066. Hayase and Hayano determined the value $K_x = 722$ ($c(\text{SDS}) = 0.04 \text{ M}$) [7], whereas Muto et al. [9] determined the K_x of 1-pentanol in lithium dodecylsulphate system, the $K_x = 212$ (that corresponds to $K = 3.8 \text{ M}^{-1}$; $c(\text{SDS}) = 0.02\text{--}0.1 \text{ M}$, $c(1\text{-pentanol})$ in excess of its water solubility). According to Høiland et al. [10] the $K_x = 190$ at zero ionic strength, $=197$ at 0.0249 M NaCl and $=220$ at 0.2069 M NaCl ($c(\text{SDS}) = 0\text{--}0.05 \text{ M}$). The K_r is 87 ± 4 ($c(1\text{-pentanol}) = 0.03 \text{ M}$, $c(\text{SDS}) = 0.07\text{--}0.46 \text{ M}$) obtained by Lisi et al. [12]. The $K_x = 304$ value has been obtained by Rao and Ruckenstein [43] using the optimal micelle size approach at $x_{\text{ROH}} = 0.55$. Thereby, the various methods of estimation of the distribution of 1-pentanol between SDS micelles and continuous phase have resulted in K values from 3.5 M^{-1} to 13.0 M^{-1} [7-12,43]. It should be noted that higher K values were obtained at low 1-pentanol concentration. Our partition constants are rather high when determined via indicator method using neutral red and N,N' -di-*n*-octadecylrhodamine as indicators, but they are close to values of the distribution reported in the literature. It should be noticed that indicator method for SDS–1-pentanol system have given reasonable K values only in the case of neutral red but not hexamethoxy red, that may be related to special feature of dye solubilization. So, given method requires the careful selection of indicators as a rule by an experiment.

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А.Ю. Харченко. Определение состава смешанных мицелл *n*-додецилсульфат натрия – 1-пентанол с помощью кислотно-основных индикаторов.

Состав смешанных мицелл определяется параметрами распределения спирта между водной и мицеллярной фазами. В работе сообщается об индикаторном методе определения мольной доли 1-пентанола в смешанных мицеллах *n*-додецилсульфат натрия – 1-пентанол и константы распределения спирта. Этот метод основан на определении кажущихся констант ионизации, K_a^{app} , кислотно-основных индикаторов. Электрический поверхностный потенциал Ψ равен –58 мВ и –39 мВ для индивидуальных и смешанных

мицелл, соответственно, что было оценено с использованием значений pK_a^{app} индикатора *N,N*-ди-*n*-октадецилпродамина. Исходя из углового коэффициента линейной зависимости значений pK_a^{app} для индикатора нейтрального красного от $\log[Na_w^+]$, степень связывания противоионов индивидуальными мицеллами, β , составляет 0.71 ± 0.02 , тогда как соответствующее значение в присутствии 0.20 М 1-пентанола значительно ниже: $\beta' = 0.52 \pm 0.03$. Значения β , β' и Ψ позволяют оценить мольную долю 1-пентанола в смешанных мицеллах, используя уравнение Ошима – Хили – Вайта. В итоге установлено, что константа распределения 1-пентанола между водной и мицеллярной фазами, K , равна $10.3 M^{-1}$ и $15.4 M^{-1}$, исходя из сферической и цилиндрической модели смешанных мицелл, соответственно. Эти значения согласуются со значениями, полученными другими методами.

Ключевые слова: кислотнo-основнe индикаторы, мицеллы *n*-додецилсульфата натрия, 1-пентанол, электрический поверхностный потенциал, степень связывания противоионов, мольная доля спирта, константа распределения.

А.Ю. Харченко. Визначення складу змішаних міцел *n*-додецилсульфат натрію – 1-пентанол за допомогою кислотнo-основних індикаторів.

Склад змішаних міцел визначається параметрами розподілу спирту між водною та мицеллярною фазами. В роботі повідомляється про індикаторний метод визначення мольної частки 1-пентанолу в змішаних міцеллах *n*-додецилсульфат натрію – 1-пентанол і константи розподілу. Цей метод базується на визначенні уявних констант іонізації, K_a^{app} , кислотнo-основних індикаторів. Електричний поверхневий потенціал дорівнює -58 мВ і -39 мВ для індивідуальних і змішаних міцел, відповідно, що було оцінено з використанням значень pK_a^{app} індикатора *N,N*-ди-*n*-октадецилпродаміну. Виходячи з кутового коефіцієнту лінійної залежності значень pK_a^{app} для індикатора нейтрального червоного від $\log[Na_w^+]$, ступінь зв'язування протиіонів індивідуальними міцелами, β , дорівнює 0.71 ± 0.02 , відповідне значення в присутності 0.20 М 1-пентанолу значно нижче і становить $\beta' = 0.52 \pm 0.03$. Значення β , β' і Ψ дозволяють оцінити мольну частку 1-пентанолу в змішаних міцелах, використовуючи рівняння Ошіми–Хілі–Вайта. В результаті встановлено, що константа розподілу спирту між водною та мицеллярною фазами, K , дорівнює $10.3 M^{-1}$ і $15.4 M^{-1}$, виходячи з сферичної та циліндричної моделі змішаних міцел, відповідно. Ці значення узгоджуються зі значеннями, що отримані іншими методами.

Ключові слова: кислотнo-основні індикатори, міцели *n*-додецилсульфату натрію, 1-пентанол, електричний поверхневий потенціал, ступінь зв'язування протиіонів, мольна частка спирту, константа розподілу.

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