Chemistry

EFFECT OF VITAMINS NICOTINIC ACID, PYRIDOXINE AND Co^{2+}, Mn^{2+}, Cu^{2+} METAL-IONS ON CRITICAL MICELLE CONCENTRATION OF ANIONIC, CATIONIC AND NONIONIC SURFACTANTS IN AQUEOUS SOLUTIONS

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Effect of aqueous soluble vitamins nicotinic acid, pyridoxine and biologically active ions Co^{2+}, Mn^{2+}, Cu^{2+} on critical micelle concentration (cmc) of anionic surfactant sodium pentadecylsulfonate, cationic surfactant cetylpyridinium bromide and nonionic surfactant hexadecylpoly[oxyethylene(20)] alcohol (C$_{16}$A$_{20}$) in aqueous solutions at 303.15 *K* was studied. It was shown that with increase of vitamins concentration the cmc of studied anionic sodium pentadecylsulfonate increases and cmc of C$_{16}$A$_{20}$ decreases. In the presence of metal-ions cmc of the studied surfactants decreases.

***Keywords*:** micellization, sodium pentadecylsulfonate, cetylpyridinium bromide, hexadecylpoly[oxyethylene(20)] alcohol.

Introduction. Enzymes catalyze a variety of reactions in biofluids, cell metabolism. For catalyzing oxidation-reduction reactions and many types of group transfer processes, enzymes require a cofactor, which may be metal-ion or organic molecule (coenzyme). Vitamins, the essential micronutrients of animal diet, are precursors for various coenzymes [1, 2]. Therefore, these coenzymes are required in almost metabolic pathways [3].

In this paper the effect of vitamins nicotinic acid (NicA), pyridoxine (PO) and metal-ions Co^{2+}, Mn^{2+}, Cu^{2+} on critical micelle concentration (cmc) of sodium pentadecylsulfonate (SPDS), cetylpyridinium bromide (CPBr) and hexadecylpoly[oxyethylene(20)] alcohol (C$_{16}$A$_{20}$) in aqueous solutions at 303.15 *K* was studied.

Materials and Methods. Anionic surfactant SPDS ("VEB-Leuna", $\geq$ 98%), cationic surfactants CPBr ("Aldrich", $\geq$ 9.5%), nonionic surfactant C$_{16}$A$_{20}$ (Shostkinsk, Russia, $\geq$99.0%), NicA ("Aldrich", $\geq$99.5%), pyridoxine ("Aldrich", $\geq$99.5%), MnSO$_4 \cdot$5H$_2$O, CuSO$_4 \cdot$5H$_2$O and CoCl$_2$ ("Krasniy Khimik", S. Peterburg) were used without further purification. All samples were prepared by directly mixing the appropriate amounts of both components using twice-distilled water.

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A Conductivity/pH meter Jenway 4330 was used for conductivity measurements at temperature 303.15 *K*. The temperature was controlled within ±0.05 *K*. The determination of cmc for each solvent composition was carried out by plotting conductivity against the total concentration of the surfactant.

Surface tension of solutions was determined using the method of maximum bubble pressure (SITA science line t60). The temperature was controlled within ±0.1 *K*. The determination of cmc for each solvent composition at 303.15 *K* was carried out by plotting surface tension against the logarithm of total concentration of the surfactant. The cmc is defined as the break point on these plots.

Results and Discussion. Experimentally determined values of cmc of SPDS in the presence of studied metal-ions in aqueous solutions are presented in Tab. 1. From the data in Tab. 1 it follows, that with increase of metal-ions concentration the cmc values of SPDS decrease.

Table 1

Critical micelle concentration values of SPDS in the presence of metal-ions in aqueous solution at 303.15 K

$[CuSO_4]\cdot10^2$, M	cmc$\cdot10^3$, M	$[MnSO_4]\cdot10^2$, M	cmc$\cdot10^3$, M	$[CoCl_2]\cdot10^2$, M	cmc$\cdot10^3$, M
0.00	1.60	0.00	1.60	0.00	1.60
0.20	0.95	0.20	0.90	0.20	0.80
0.35	0.60	0.35	0.50	0.35	0.33
0.60	0.35	0.60	0.26	0.60	0.20
1.00	0.22	1.00	0.19	1.00	0.12

It is well known from literature [4], that in the presence of metal-ions cmc of surfactant decreases and that behavior is described by the equation

$$\lg cmc = const - K \ln C_i,\qquad(1)$$

where C_i is concentration of ions and K is experimentally determined constant.

Based on Tab. 1 data and according to Eq. (1), $\lg cmc = f(\lg C_i)$ dependences are presented in Fig. 1, which confirms that obtained data are satisfying for Eq. (1).
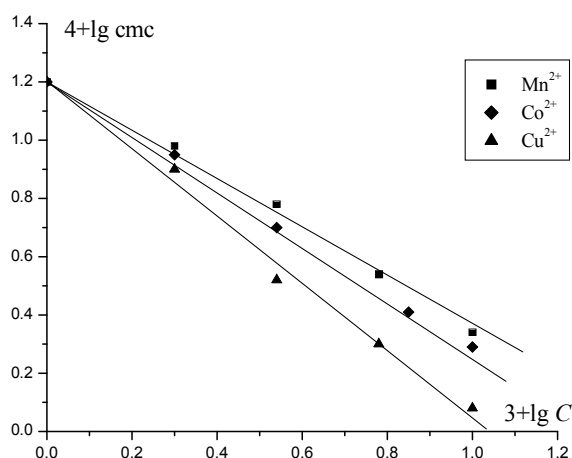
Fig. 1. Dependence of cmc of SPDS vs. metal-ions concentration at 303.15 *K*.

The decrease of SPDS cmc in the presence of metal-ions (electrolyte) is the result of different factors, acting together. The cmc of ionic surfactant can decrease due to introduction of ions into Stern layer and effect on the summary charge of electrical layer [4–6]. In the presence of electrolytes the hydration degree of surfactant decreases [7, 8], which favors micellization, and the cmc of surfactant also decreases. Electrolytes change the structure of water [9]. If the electrolyte acts as structure-making, the solubility of surfactant decreases and as a result the cmc also decreases. It must be noted that there is a possibility of interaction between metal-ion and SPDS. In the case of Cu^{2+} ions it is described by Eq. (2) and Fig. 2:

$$Cu^{2+} + X C_{15}H_{31}SO_3^- \leftrightarrow Cu\left(C_{15}H_{31}SO_3\right)_X, \qquad (2)$$
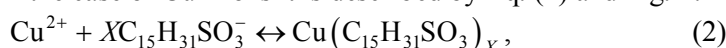
where X can be 1 or 2. From Fig. 2 it follows, that X is equal to 2. The generated $Me\left(C_{15}H_{31}SO_3\right)_2$ molecules can interact with SPDS molecules and form mixed micelles. As a result, the surface charge of micelles will be decreased, the micellization will take place easily, and the cmc of anionic surfactant will be decreased.
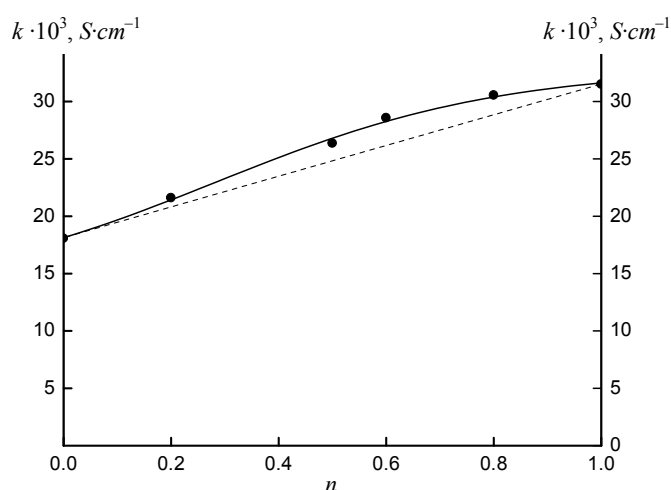

Fig. 2. Plots of conductivity of CuSO$_4$–SPDS system vs. molar fraction of CuSO$_4$ at 303.15 K.

The effect of Ca^{2+} and Mn^{2+} ions on micellization of cationic surfactant CPBr and nonionic surfactant $C_{16}A_{20}$ was also studied. In the case of CPBr all the ions of systems studied have the same sign charges and, therefore, the formation of new molecules between metal ions and CPBr is practically impossible. There is only one break point on the isotherms $k = f\left(C_{CPBr}\right)$ in the absence of electrolytes which is obtained as cmc of CPBr and in good agreement with literature data ($7.5 \cdot 10^{-4}$ M) [10]. But in the presence of electrolytes the second break pint is obtained on the isotherms $k = f\left(C_{CPBr}\right)$ (Fig. 3), which is cmc$_2$ [11, 12]. The obtained results of cmc$_1$ and cmc$_2$ of CPBr in the presence of studied electrolytes are given in the Tab. 2. It is known from literature that there is possibility for changing micelles' forms from spherical to ellipsoidal in the presence of electrolytes [11] and as a result there are two break points (cmc$_1$ and cmc$_2$) on the physicochemical isotherms.

*The values of cmc$_1$ and cmc$_2$ of CPBr in aqueous solutions in the presence
of studied electrolytes, [Electrolyte]=1·10^{-3} M, T=303.15 K*

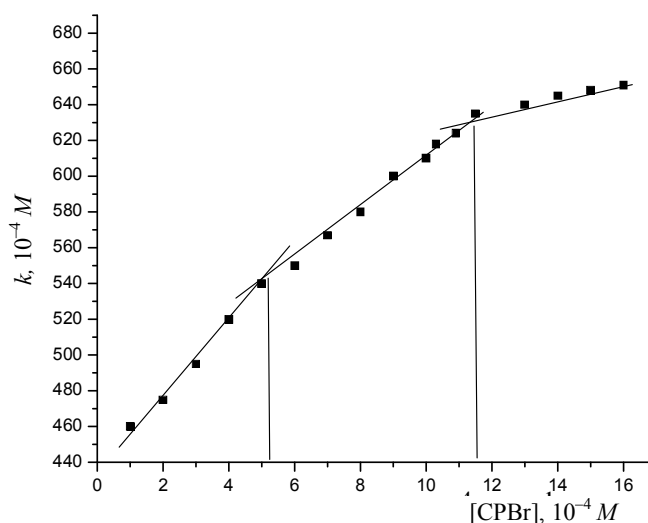|	CaCl$_2$	MnSO$_4$
cmc$_1$, 10^{-4} M	5.25	6.50
cmc$_2$, 10^{-4} M	11.25	10.00

Fig. 3. The isotherms of conductivity of aqueous solutions of CPBr in the presence
of Ca^{2+} ion. [Ca^{2+}]=1·10^{-4} M, *T*=303.15 *K*.

In the case of C$_{16}$A$_{20}$ it is obtained that the surface tension of C$_{16}$A$_{20}$ solutions and the cmc of C$_{16}$A$_{20}$ in aqueous solutions decrease in the presence of electrolytes (Tab. 3).

*The values of cmc and surface tension at cmc of C$_{16}$A$_{20}$ in aqueous solutions
in the presence of studied electrolytes at 303.15 K, [Electrolyte]=4·10^{-4} M*

	Without electrolyte	CaCl$_2$	MnSO$_4$
cmc,10^{-4} M	1.99	1.20	1.25
γ_{cmc}, mN·m^{-1}	46.0	42.5	42.5

Direct interaction between metal ions and cationic surface active cation molecule C$_{16}$A$_{20}$ in the presence of CPBr and C$_{16}$A$_{20}$ is impossible, and the decrease of cmc surfactants studied is a result of changes of volumetric properties of solution and reduction of dehydration degree of molecules (ions) of CPBr and C$_{16}$A$_{20}$. The hydrophobic interactions are enhanced due to reduction of hydration degree of molecules (ions) of CPBr and C$_{16}$A$_{20}$, which is led to induction of surfactants molecules (ions) ability to associate, and as a result the cmc of studied surfactants decreases. The reduction of surface tension of C$_{16}$A$_{20}$ solutions is also the result of above studied factors.

From our studies it is obtained, that the used vitamins (NicA, PO) affect the cmc of anionic SPDS and nonionic $C_{16}A_{20}$. The experimentally obtained values of cmc of SPDS and $C_{16}A_{20}$ in the presence of vitamins in aqueous solutions are presented in Tab. 4. From data in Tab. 4 it follows, that the values of cmc SPDS in the presence of NicA–PO increased. Thus, NicA–PO is acting as a cosolvent and also as a structure-breaking solute. In micellar solutions structure-breaking solutes are known to lower the hydrophobic effect, which is considered to be the driving force of micellization [13–17]. From Tab. 4 it also follows, that the cmc values of $C_{16}A_{20}$ are decreased in the presence of NicA–PO (Tab. 4). The cmc lowering of the $C_{16}A_{20}$ by addition of NicA–PO may be a result of solubilization of NicA–PO in micelle [18–20]. The values of surface tension at cmc of $C_{16}A_{20}$ are also presented in Tab. 4, and show that the surface activity of $C_{16}A_{20}$–vitamin–water systems are enhanced in the presence of vitamins. It is suggested the degree of hydrophobicity of $C_{16}A_{20}$–vitamin–water systems are enhanced in the presence of vitamins, which leads to enhance the $C_{16}A_{20}$ solubility, and as a result the transfer of molecules (ions) of $C_{16}A_{20}$ from bulk phase to surface becomes easier and the surface tension of $C_{16}A_{20}$–vitamin–water systems decreases.

Table 4

Values of cmc of SPDS and $C_{16}A_{20}$ and surface tension at cmc of $C_{16}A_{20}$ aqueous solutions in the presence of NicA and PO in aqueous solutions at 303.15 K

$C_{vit}, 10^{-2} M$	NicA		PO	
	cmc of SPDS, $10^{-3} M$			
0.00	1.59		1.59	
1.00	1.63		1.83	
2.00	1.68		2.39	
4.00	1.89		3.31	
8.00	2.30		5.57	
	cmc of $C_{16}A_{20}$, $10^{-4} M$	γ_{cmc}, $mN \cdot m^{-1}$	cmc of $C_{16}A_{20}$, $10^{-4} M$	γ_{cmc}, $mN \cdot m^{-1}$
0.00	1.99	46.0	1.99	46.0
0.25	1.60	45.0	2.00	45.5
0.50	1.58	40.0	2.25	42.5
1.00	1.25	38.0	2.60	40.0

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