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TEMPERATURE EFFECT ON MICELLIZATION OF NONIONIC SURFACTANT HEXADECYL POLY[OXYETHYLENE(25)] ALCOHOL IN AMINO ACIDS AQUEOUS SOLUTIONS

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Influence of amino acids (L-glycine, L-alanine, L-phenylalanine, L-serine, L-aspartic acid, L-lysine and L-leucine) on the critical micelle concentration (cmc) and thermodynamic of micellization of nonionic surfactant hexadecyl poly[oxyethylene(25)] alcohol ($C_{16}A_{25}$) in aqueous solutions at different temperatures was studied. It was shown that with the increase of amino acids concentration cmc of $C_{16}A_{25}$ decreased, and with the increase of the temperature cmc of $C_{16}A_{25}$ increased.

***Keywords*:** nonionic surfactant, amino acids, micellization.

Introduction. Amino acids, the building blocks of peptides and proteins, have a broad spectrum of applications. These substances are widely used as additives in food industry as buffers or acid correctors, plant growth regulators, and in the production of medicines, either in injection solution as nutritional infusion or as a raw material for making L-Dopa, a pharmaceutical for treating Parkinson's disease [1, 2]. On the other hand, the study of interactions between proteins and amphiphiles is of great importance from both fundamental and technological points of view [3]. However, due to the complexity of these interactions, an alternative strategy used, consists of studying the interactions in simpler systems [4–7].

In this paper the effect of a number of amino acids on micellization of aqueous solutions of nonionic surfactant hexadecyl poly[oxyethylene(25)] alcohol ($C_{16}A_{25}$) at different temperatures is studied.

Materials and Methods. Nonionic surfactant $C_{16}A_{25}$ (Shostkinsk, Russia, ≥99.0%) and amino acids L-glycine, L-alanine, L-phenylalanine, L-serine, L-aspartic acid, L-lysine and L-leucine ("Sigma", ≥99.0%) were used without further purification. All the samples were prepared by directly mixing the appropriate amounts of both components, using twice-distilled water.

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 the critical micelle concentration (cmc) for each solvent composition at each temperature 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 (see Figure).

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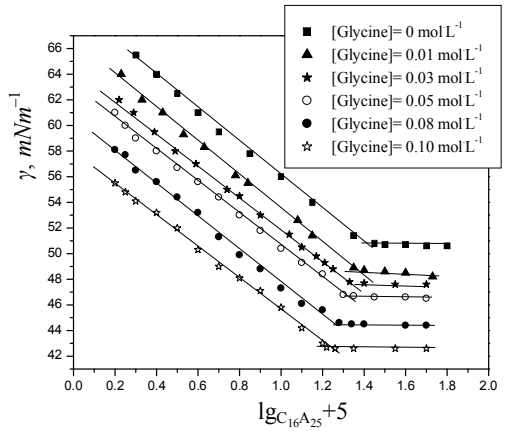

Plots of surface tension vs [$C_{16}A_{25}$] in the presence of glycine at 303.15 *K*.

Results and Discussion. The experimentally determined cmc values of $C_{16}A_{25}$ in aqueous solutions in the absence and presence of amino acids (AAs) at four temperatures are reported in Tab. 1. The cmc values of $C_{16}A_{25}$ in the presence of AAs are increased by temperature. The effect of temperature on cmc of surfactant in aqueous solutions both in the absence and presence of additive is usually analyzed in terms of two opposing factors. First, as the temperature increases, the degree of hydration of the hydrophillic groups decreases, which favors micellization; however, an increase in temperature also causes the disruption of the water structure surrounding the hydrophobic group and this is unfavorable for micellization [8, 9].

From the data in Tab. 1 it seems, that this second effect is predominant in the temperature range studied. Estimated precision in the cmc is better than ± 2%.

As seen from Tab. 1, the cmc values of $C_{16}A_{25}$ are decreased in the presence of AAs. The cmc lowering of $C_{16}A_{25}$ by adding AAs may be the result of solubilization (penetration) of AAs in micelles [7, 9].

It is also seen from Tab. 1 that the cmc values of $C_{16}A_{25}$ are decreased in the order glycine–alanine–leucine–phenylalanine. It is known as longer alkyl chain in the molecule of AA as higher hydrophobicity of AA. Thus phenylalanine destroys the structure of water stronger and the micellization becomes easier in the presence of phenylalanine in compare with glycine.

From temperature dependence of the cmc the thermodynamic parameters of micellization were obtained. The free energy of micellization (ΔG_m^0) is calculated by the following relationship [10, 11]:

$$\Delta G_m^0 = RT \ln \chi_{\text{cmc}}, \tag{1}$$

where R is the gas constant, χ_{cmc} is the ratio of molar concentration of the surfactant in the liquid phase at the cmc and that of the solvent in the liquid phase. The enthalpy of micellization (ΔH_m^0) is determined as follows [10, 11]:

$$\Delta H_m^0 = -RT^2 \left(\frac{\partial \ln \chi_{\text{cmc}}}{\partial T} \right)_p. \tag{2}$$

The entropy of micellization (ΔS_m^0) was calculated by the equation [10, 11]

$$\Delta S_m^0 = (\Delta H_m^0 - \Delta G_m^0)/T. \tag{3}$$

The obtained thermodynamic parameters of micellization are reported in Tab. 2. Estimated uncertainties are $\pm$ 0.05 $kJ{\cdot}mol^{-1}$ in ΔG_m^0, $\pm$ 0.05 $kJ{\cdot}mol^{-1}$ in ΔH_m^0 and $\pm$ 0.1 $J{\cdot}mol^{-1}K^{-1}$ in ΔS_m^0.

Table 1

Cmc of $C_{16}A_{25}$ in aqueous solution of AAs at different temperatures

	[AAs], $mol{\cdot}L^{-1}$	cmc$\cdot 10^4$, $mol{\cdot}L^{-1}$			
		298.15 *K*	303.15 *K*	308.15 *K*	313.15 *K*
	0.00	2.20	2.40	2.68	2.89
Glycine	0.01	2.13	2.25	2.49	2.64
	0.03	2.02	2.15	2.29	2.47
	0.05	1.87	2.00	2.11	2.32
	0.08	1.63	1.90	2.00	2.20
	0.10	1.51	1.80	1.91	2.07
Alanine	0.01	2.03	2.20	2.57	2.71
	0.03	1.83	1.98	2.33	2.54
	0.05	1.69	1.82	2.07	2.39
	0.08	1.44	1.70	1.90	2.11
	0.10	1.28	1.52	1.73	1.96
Phenylalanine	0.01	1.51	1.60	1.69	1.81
	0.03	0.88	0.95	1.07	1.25
	0.05	0.25	0.30	0.37	0.44
	0.08	0.05	0.06	0.07	0.08
	0.10	0.05	0.06	0.07	0.08
Serine	0.01	2.00	2.20	2.43	2.66
	0.03	1.87	2.06	2.29	2.42
	0.05	1.61	1.89	2.04	2.27
	0.08	1.43	1.71	1.89	2.08
	0.10	1.32	1.58	1.74	1.91
Leucine	0.01	2.00	2.10	2.18	2.30
	0.03	1.68	1.80	2.05	2.21
	0.05	1.32	1.48	1.65	1.93
	0.08	1.03	1.21	1.43	1.74
	0.10	0.78	0.93	1.19	1.30
Aspartic acid	0.01	1.93	2.20	2.44	2.67
	0.03	1.70	2.00	2.31	2.48
	0.05	1.55	1.80	2.07	2.23
	0.08	1.36	1.60	1.84	2.06
	0.10	1.17	1.40	1.66	1.84
Lysine	0.01	1.95	2.15	2.29	2.41
	0.03	1.58	1.90	2.20	2.53
	0.05	1.31	1.55	1.84	2.15
	0.08	0.87	1.10	1.27	1.47
	0.10	0.87	1.10	1.27	1.47

The standard Gibbs free energy of micellization, enthalpy of micellization and entropy of micellization have been used to obtain information about the solubilization site of AAs in the micelle. From Tab. 2 it is evident that in all cases ΔG_m^0 is negative and becomes more negative with the increase of [AAs] indicating that micellization of $C_{16}A_{25}$ is more favorable in the presence of AAs.

Table 2

Thermodynamic parameters (kJ·mol^{-1}) of micellization of $C_{16}A_{25}$ in aqueous solutions of AAs at different temperatures

[AAs], *mol·L*$^{-1}$	ΔG_m^0	ΔH_m^0	ΔG_m^0	ΔH_m^0	ΔG_m^0	ΔH_m^0	ΔG_m^0	ΔH_m^0	ΔS_m^0, *J·mol*$^{-1}$*K*$^{-1}$
	298.15 *K*		303.15 *K*		308.15 *K*		313.15 *K*		
Glycine									
0.00	–30.857	–47.359	–31.155	–47.853	–31.386	–48.359	–31.698	–48.946	55.08
0.01	–30.937	–50.235	–31.317	–51.010	–31.574	–51.591	–31.934	–52.276	64.96
0.03	–31.068	–51.855	–31.423	–52.568	–31.789	–53.273	–32.108	–53.941	69.72
0.05	–31.260	–51.636	–31.615	–52.332	–31.999	–53.058	–32.271	–53.672	68.34
0.08	–31.601	–48.393	–31.744	–48.817	–32.136	–49.491	–32.409	–50.046	56.32
0.10	–31.790	–47.938	–31.880	–48.299	–32.254	–48.943	–32.568	–49.528	54.16
Alanine									
0.01	–31.056	–46.256	–31.374	–46.829	–31.493	–47.202	–31.866	–47.830	50.98
0.03	–31.313	–44.891	–31.640	–45.445	–31.744	–45.777	–32.035	–46.297	45.54
0.05	–31.511	–44.731	–31.852	–45.294	–32.048	–45.711	–32.193	–46.078	44.34
0.08	–31.908	–44.269	–32.024	–44.593	–32.267	–45.043	–32.518	–45.501	41.46
0.10	–32.200	–42.522	–32.307	–42.802	–32.508	–43.176	–32.710	–43.551	34.62
Phenylalanine									
0.01	–31.790	–54.282	–32.177	–47.359	–32.568	–39.386	–32.917	–49.652	75.44
0.03	–33.130	–55.622	–33.492	–48.674	–33.740	–40.618	–33.882	–50.617	50.08
0.05	–36.251	–58.743	–36.399	–51.581	–36.462	–43.340	–36.602	–53.337	22.32
0.08	–40.244	–62.736	–40.459	–56.142	–40.731	–47.609	–41.044	–57.779	53.44
0.10	–40.244	–62.736	–40.459	–56.142	–40.731	–47.609	–41.044	–57.779	53.44
Serine									
0.01	–31.093	–47.348	–31.374	–47.902	–31.637	–48.437	–31.914	–48.987	54.52
0.03	–31.260	–46.179	–31.540	–46.710	–31.789	–47.209	–32.161	–47.831	50.04
0.05	–31.631	–46.038	–31.757	–46.395	–32.085	–46.975	–32.327	–47.458	48.32
0.08	–31.925	–44.215	–32.110	–44.606	–32.281	–44.986	–32.555	–45.463	41.22
0.10	–32.124	–44.187	–32.279	–44.544	–32.493	–44.961	–32.777	–45.447	40.46
Leucine									
0.01	–31.093	–55.088	–31.491	–55.885	–31.915	–56.715	–32.293	–56.693	80.48
0.03	–31.526	–48.258	–31.880	–48.893	–32.073	–48.539	–32.397	–49.454	56.12
0.05	–32.124	–44.843	–32.374	–45.306	–32.629	–45.056	–32.750	–46.733	42.66
0.08	–32.739	–40.224	–32.882	–40.503	–32.996	–40.360	–33.120	–40.755	25.14
0.10	–33.429	–40.430	–33.546	–40.664	–33.667	–40.547	–33.780	–40.899	23.48
Aspartic acid									
0.01	–31.182	–45.618	–31.374	–46.053	–31.626	–46.547	–31.905	–47.068	48.42
0.03	–31.496	–44.644	–31.615	–44.984	–31.767	–45.356	–32.097	–45.907	44.10
0.05	–31.725	–44.337	–31.880	–44.703	–32.048	–45.083	–32.374	–45.620	42.30
0.08	–32.050	–42.563	–32.177	–42.866	–32.350	–43.215	–32.580	–43.622	35.26
0.10	–32.423	–41.105	–32.514	–41.342	–32.614	–41.587	–32.875	–41.994	29.12
Lysine									
0.01	–31.424	–35.222	–31.482	–35.344	–31.543	–35.469	–31.616	–35.606	12.74
0.03	–31.678	–39.126	–31.744	–39.317	–31.892	–39.590	–32.045	–39.867	24.98
0.05	–32.143	–40.318	–32.257	–40.569	–32.350	–40.799	–32.469	–41.056	27.42
0.08	–33.158	–42.007	–33.122	–42.219	–33.300	–42.446	–33.460	–42.754	29.68
0.10	–33.158	–42.007	–33.222	–42.219	–33.300	–42.446	–33.460	–42.754	29.68

From Tab. 2 is also evident that ΔG_m^0 becomes more negative with the increase of temperature, which indicates that the hydrophobic effect increases in magnitude with increasing temperature, which in turn shows that penetration of AAs into the micelle is more favorable at high temperature [12].

The ΔH_m^0 data show that the process of solubilization of AAs in aqueous micelle solutions is exothermic. The negative values of ΔH_m^0 indicate that strong interactions are occurring between AAs and the micellar system and these interactions are stronger at the lowest concentration of glycine, alanine, serine, leucine, aspartic acid and at the highest concentrations of phenylalanine and lysine. This suggests that AAs solubilized in $C_{16}A_{25}$ are located near the outer surface of the micelle at low concentrations of glycine, alanine, serine, leucine, aspartic acid and at the high concentrations of phenylalanine and lysine. ΔS_m^0 values are positive for all studied systems. The positive entropy values indicate that in the systems studied the entropy is dominating over the micellization process. This observation may be explained as due to the reorganization of water molecules at the micellar solubilization of AAs [13].

Conclusion. The effect of amino acids (L-glycine, L-alanine, L-serine, L-phenylalanine, L-aspartic acid, L-lysine and L-leucine) on micellar and viscosity properties of nonionic surfactant $C_{16}A_{25}$ in aqueous solutions at different temperatures was studied. The addition of AAs in water decreases the cmc values of $C_{16}A_{25}$. The obtained values of ΔH_m^0 and ΔS_m^0 indicate that in the studied systems the entropy is dominating over the micellization process. The micellization parameters of the studied systems indicate that AAs are solubilized (penetrated) in $C_{16}A_{25}$.

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