Effect of Nicotinic Acid on Micellization and Viscosity of Surfactants in Aqueous Solutions[1]

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Abstract—The effect of nicotinic acid on critical micelle concentration (CMC) and viscosity of sodium dodecyl sulfate, cetylpyridinium bromide, and hexadecyl poly[oxyethylene(20)] alcohol solutions is studied. The values of CMC and micelle ionization degree are obtained. The thermodynamic parameters of micellization are determined. The values of Jones–Dole coefficients are determined based on the results of viscosity measurements.

INTRODUCTION

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

The study of the effect of nicotinic acid on the properties of surfactants is of great importance because they can play the role of models for biological systems. In this paper, results of micellization and viscous flow studies of aqueous solutions of surfactants in the presence of nicotinic acid are reported.

EXPERIMENTAL

Materials

Anionic surfactant sodium dodecylsulfate ($C_{12}H_{25}SO_4Na$) (Sigma-Aldrich, ≥99.0%), cationic surfactant cetylpyridinium bromide ($C_{21}H_{38}NBr$) (Aldrich, 98.0%), nonionic surfactant polyoxyethylene (20) cetyl ether (OS 20, $C_{16}H_{33}O(C_2H_4O)_{20}H$)) (VEB-Leuna, ≥99.0%), and nicotinic acid (NicA) (vitamin PP, vitamin B_3) (Aldrich, ≥99.0%) were used as received. All the samples were prepared by directly mixing the appropriate amounts of both components using twice-distilled water.

Methods

A Jenway 4330 conductivity/pH meter was used for conductivity measurements at different temperatures.

The samples were thermostated for no less than 10 min and the temperature was controlled within ±0.05 K. The mean square error was no more than 2%. The critical micelle concentration (CMC) was found as the inflection point on the plots of conductivity versus the overall concentration of ionic surfactants.

Surface tension of solutions γ was determined using the method of maximum bubble pressure on a SITA Science Line t60 instrument (SITA Messtechnik GmbH, Germany). The samples were thermostated for at least 10 min and the temperature was controlled within ±0.05 K. The mean square error was no more than 2%. The CMC was determined as the inflection point in the plots of surface tension against the logarithmic concentration of the surfactant.

From the temperature dependence of the CMC, the thermodynamic parameters of micellization were obtained for surfactant–NicA–water solutions: the free energy of micellization ΔG_m°, the enthalpy of micellization ΔH_m°, and the entropy of micellization ΔS_m°.

The free energy of micellization ΔG_m°, was calculated by the following relationships [4, 5]:

for ionic surfactant

$$\Delta G_m^\circ = (2 - \beta) RT \ln \chi_{CMC}, \tag{1}$$

and for nonionic surfactant

$$\Delta G_m^\circ = RT \ln \chi_{CMC}, \tag{2}$$

where R is the gas constant and T is absolute temperature, χ_{CMC} is the molar fraction of the surfactant at

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[1] The article was translated by the authors.

the CMC, and β is the degree of ionization of the micelle.

The enthalpy of micellization ΔH_m° was determined as follows [4, 5]:

for ionic surfactant

$$\Delta H_m^\circ = -RT^2 (2 - \beta) \left(\frac{\partial \ln \chi_{CMC}}{\partial T} \right)_p, \qquad (3)$$

and for nonionic surfactant

$$\Delta H_m^\circ = -RT^2 \left(\frac{\partial \ln \chi_{CMC}}{\partial T} \right)_n. \qquad (4)$$

The entropy of micellization ΔS_m° was calculated from the equation [4, 5]:

$$\Delta S_m^\circ = \frac{\Delta H_m^\circ - \Delta G_m^\circ}{T}. \qquad (5)$$

The degree of ionization of ionic surfactants β for the surfactant−NicA−water system was obtained by Fraham's method [6] using the following equation:

$$\beta = S_2 / S_1, \qquad (6)$$

where S_2 and S_1 are the slopes above and below the CMC in the conductivity−concentration plots, respectively.

The efflux times of solutions and solvents were measured using an Ubbelohde-type viscometer. The samples were also thermostated for no less than 10 min, and the temperature was controlled within ±0.05 K. Relative viscosities η_r were calculated as the ratio of efflux times of solution t_{s-s} and solvent t_s:

$$\eta_r = t_{s-s} / t_s. \qquad (7)$$

The mean square error for viscosity measurements was no more than 2%.

The viscosity data were analyzed using the Jones−Dole equation [7]:

$$\eta_r = \frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc, \qquad (8)$$

$$\frac{(\eta/\eta_0 - 1)}{c^{1/2}} = A + Bc^{1/2}, \qquad (9)$$

where η_r is the relative viscosity of the solution; η and η_0 are the viscosities of the solution and the solvent, respectively; and A and B are the Falkenhagen [8] and Jones−Dole [7] coefficients, respectively.

RESULTS AND DISCUSSION

Effect of NicA on Micellization of Surfactants in Aqueous Solutions

The isotherms of conductivity and surface tension at different temperatures are analogous; therefore, isotherms at only 303.15 K are given in Figs. 1 and 2.
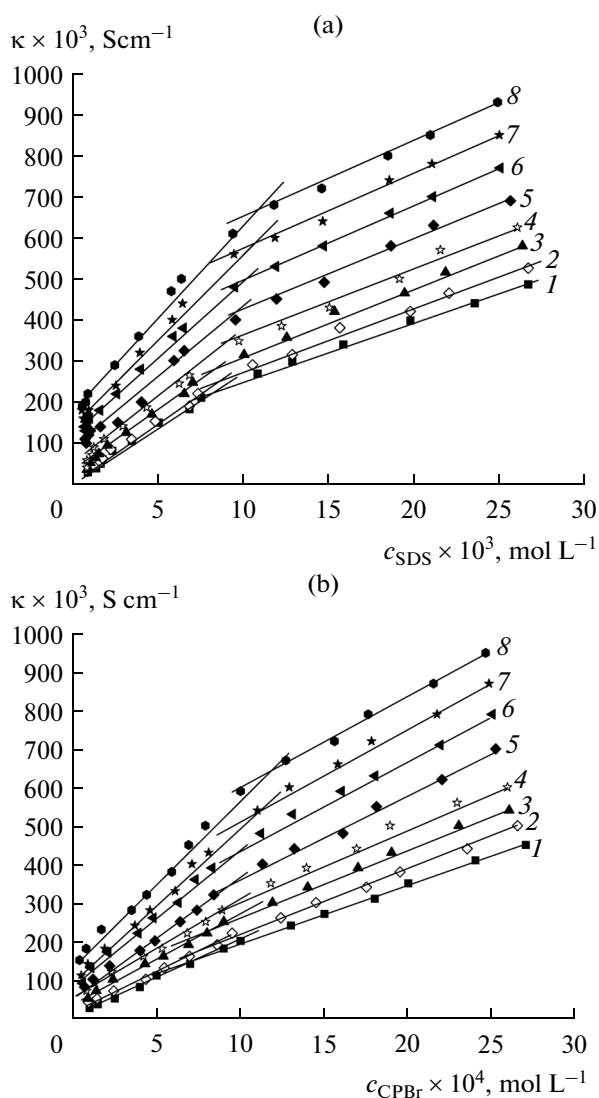
Fig. 1. Plots of conductivity of (a) SDS and (b) CPBr solutions vs. surfactant concentration at 303.15 K and at different concentrations of NicA: (*1*) 0, (*2*) 10^{-2}, (*3*) 2×10^{-2}, (*4*) 3×10^{-2}, (*5*) 4×10^{-2}, (*6*) 5×10^{-2}, (*7*) 7×10^{-2}, and (*8*) 8×10^{-2} mol L^{-1}.

The experimentally determined values of CMC of SDS, CPBr, and OS 20 in aqueous solutions in the absence and presence of NicA are given in Table 1. The experimentally determined CMC of studied surfactants in pure water at 303.15 K are in good agreement with the published values [9−11].

From the data presented in Table 1, it follows that the values of CMC were increased with temperature at the constant concentration of NicA. The effect of temperature on CMC of surfactant in aqueous solutions both in the absence and presence of an 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 disruption of the water structure sur-
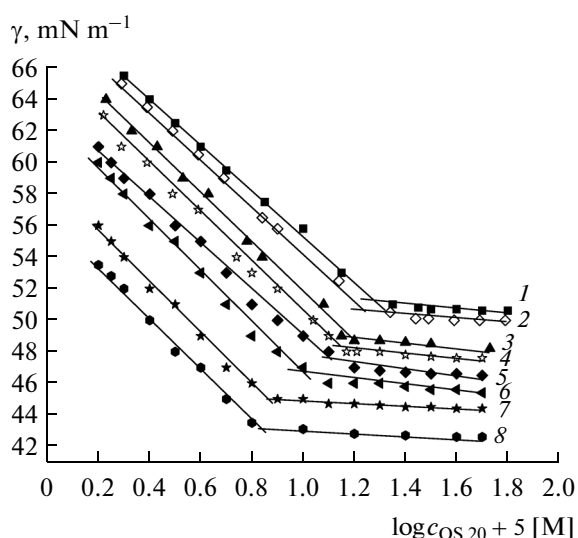
γ, mN m^{-1}

Fig. 2. Plots of surface tension of OS 20 solutions vs. surfactant concentration at 303.15 K and at different concentrations of NicA: (*1*) 0, (*2*) 10^{-2}, (*3*) 2 × 10^{-2}, (*4*) 3 × 10^{-2}, (*5*) 4 × 10^{-2}, (*6*) 5 × 10^{-2}, (*7*) 7 × 10^{-2}, and (*8*) 8 × 10^{-2} mol L^{-1}.

rounding the hydrophobic groups, which is unfavorable for micellization [12–14]. From the data in Table 1, it seems that this second effect is predominant.

From the data presented in Table 1, it also follows that the values of CMC of ionic SDS and CPBr increased with increase of NicA concentration. Thus, NicA acts as a structure-breaking solute in aqueous solutions of ionic surfactants. In micellar solutions, structure-breaking solutes are known to lower the hydrophobic effect, which is considered to be the driving force of micellization [13–16]. At the same time, the CMC values of OS 20 are decreased in the pres-

ence of NicA (Table 1). The CMC lowering of the OS 20 by addition of NicA may be a result of solubilization of NicA in the micelle [17–19].

Thus, from the data presented in Table 1, it can be concluded that the behavior of CMC upon increase of NicA concentration depends on type of surfactant.

The values of degree of ionization of SDS and CPBr micelles in the absence and presence of NicA are given in Table 2. The experimentally determined values of β of the SDS and CPBr micelles in aqueous solutions in the absence of NicA at 303.15 K are in good agreement with published data [16, 20].

The obtained data on thermodynamic parameters of micellization for the SDS−NicA−water, CPBr−NicA−water, and OS 20−NicA−water systems according to Eqs. (1)−(5) show the following. Free energy of micellization ΔG_m° is negative for all studied systems and becomes less negative with an increase in the concentration of NicA for the SDS−NicA−water and CPBr−NicA−water systems. This means that, in these systems, micellization becomes more difficult with increasing NicA concentration. The opposite behavior is detected for the OS 20−NicA−water system. The values of ΔG_m° increase with temperature for the systems studied, indicating that an increase of temperature favors micellization [21]. Negative values of ΔH_m° indicate that aggregation of NicA and surfactants is an exothermic processes.

The values of ΔH_m° are more exothermic at high concentrations of NicA. This suggests that, at high concentrations, NicA solubilized in studied surfactant solutions is located near the outer surface of a micelle [19]. ΔS_m° values are positive for all studied systems and show a decreasing trend with the increase of NicA concentration. The positive entropy change indicates

Table 1. Values of CMC of SDS, CPBr, and OS 20 in aqueous solutions in the absence and presence of NicA at different temperatures

	SDS				CPBr				OS 20			
T, K	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15
[NicA] × 10^2, mol/L	C_{CMC}× 10^3, mol/L											
0	7.9	8.2	8.5	8.7	0.75	0.78	0.81	0.84	0.188	0.200	0.225	0.254
1	8.2	8.3	8.8	9.0	0.77	0.81	0.83	0.86	0.174	0.191	0.218	0.241
2	8.5	8.6	9.0	9.4	0.80	0.84	0.87	0.90	0.156	0.179	0.200	0.228
3	8.8	9.2	9.4	9.9	0.85	0.88	0.93	0.96	0.141	0.158	0.187	0.210
4	9.2	9.5	9.9	10.4	0.89	0.93	0.97	1.02	0.122	0.131	0.154	0.192
5	9.7	10.1	10.4	10.8	0.94	0.98	1.07	1.07	0.108	0.114	0.141	0.179
7	10.2	10.7	11.0	11.5	1.03	1.05	1.09	1.13	0.087	0.099	0.133	0.160
8	10.6	11.2	11.2	12.2	1.08	1.08	1.15	1.15	0.070	0.082	0.121	0.148

Table 2. Degree of ionization β of SDS and CPBr micelles in aqueous solutions in the absence and presence of NicA at different temperatures

Surfactant	SDS				CPBr			
T, K	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15
[NicA] $\times 10^2$, mol/L	β							
0	0.27	0.30	0.32	0.35	0.33	0.32	0.28	0.25
1	0.32	0.34	0.35	0.36	0.34	0.33	0.29	0.26
2	0.37	0.39	0.40	0.41	0.36	0.34	0.32	0.28
3	0.42	0.43	0.44	0.45	0.39	0.37	0.35	0.31
4	0.47	0.45	0.46	0.47	0.43	0.40	0.38	0.35
5	0.53	0.49	0.50	0.51	0.57	0.43	0.41	0.39
7	0.58	0.55	0.56	0.57	0.51	0.46	0.44	0.43
8	0.63	0.59	0.60	0.61	0.55	0.49	0.47	0.45

that, in the systems studied, entropy dominates upon the micellization process. This observation may be explained by the reorganization of water molecules due to the interaction of NicA with micelles.

Effect of NicA on Viscous Flow of Aqueous Solutions of Surfactants

Electrolytes that are dissolved in water affect its viscosity. The viscosity of solution increases or decreases, depending on the type of ions, mainly on their size, and charge. In most cases, the viscosity of dilute solutions of electrolytes increases with an increase in their concentration. However, this dependence is nonlinear. The effect, which leads to a linear increase or decrease in the viscosity, depending on type of dissolved ions, occurs only in a certain, but not sharply limited, range of concentrations.

It is known [7, 22] that the B coefficient in Eq. (8) represents solute–solvent interactions and depends on various factors—the shape of dissolved ions, orientation of solvent molecules, and structure changes of solvent.

In the systems studied, the sign of the B coefficient can be either positive or negative, depending on the orientation of solvent molecules around the surfactant molecules/micelles and the solvent's structure-breaking effects. If the decrease of viscosity due to the structure-breaking effect is dominant over the increase of viscosity arising from the orientation effect of solvent molecules, the B coefficient will be negative. The studies showed that, with the addition of NicA, the B coefficients remain in most cases positive both for premicellar and postmicellar regions for studied surfactants. Only in the case of CPBr, at relatively small concentrations of NicA and especially at low temperatures,

the sign of the B coefficient is negative. It was shown in [23, 24] that, at very small concentrations of NicA (0–1×10^{-2} mol L^{-1}) and at different temperatures, the sign of the B coefficient is negative for both the premicellar and postmicellar regions for the CPBr–NicA–water system due to solvent's structure breaking. Thus, it can be concluded that NicA acts as a structure breaker at small concentrations in aqueous solutions of CPBr. However, with an increase of concentration of NicA and temperature, the orientation effect of solvent molecules the dominant, which may be a result of solubilization of NicA in micelles, and the B coefficient takes positive values.

REFERENCES

1. Kundu, A. and Kishore, N., *J. Solution Chem.*, 2003, vol. 32, p. 703.
2. Banipal, T.S., Singh, H., Banipal, P.K., and Singh, V., *Thermochim. Acta,* 2013, vol. 553, p. 31.
3. Ayranci, G., Sahin, M., and Ayranci, E., *J. Chem. Thermodyn.*, 2007, vol. 39, p. 1620.
4. Hoiland, H. and Blokhus, A.M., in *Handbook of Surface and Colloid Chemistry*, Birdi, K.S., Ed., Boca Raton: Taylor & Francis, 2009, p. 379.
5. Moroi, Y., *Micelles: Theoretical and Applied Aspects*, New York: Plenum, 1992, p. 98.
6. Gharbi, H., Palepu, R., Bloor, D.M., Hall, D.G., and Wyn-Jones, E., *Langmuir*, 1992, vol. 8, p. 782.
7. Jones, G. and Dole, M., *J. Am. Chem. Soc.*, 1929, vol. 51, p. 2950.
8. Falkenhagen, H. and Dole, M., *Z. Phys.*, 1992, vol. 30, p. 611.
9. Umlong, I.M. and Ismail, K., *Colloids Surf. A,* 2007, vol. 299, p. 8.

10. Bakshi, M.S. and Kaur, G., *J. Surfact. Deterg.*, 2000, vol. 3, p. 159.

11. Arutyunyan, N.G., Arutyunyan, L.R., Grigoryan, V.V., and Arutyunyan, R.S., *Colloid J.*, 2008, vol. 70, p. 666.

12. Rakshit, A.K. and Sharma, B., *Colloid Polym. Sci.,* 2003, vol. 281, p. 45.

13. Graciani, M., Munoz, M., Rodriguez, A., and Moya, M.L., *Langmuir*, 2005, vol. 21, p. 3303.

14. Mehta, S.K., Chaudhary, S., Bhasin, K.K., Kumar, R., and Aratono, M., *Colloids Surf. A*, 2007, vol. 304, p. 88.

15. Chauhan, M.S., Kumar, G., Kumar, A., Sharma, K., and Chauhan, S., *Colloids Surf. A*, 2001, vol. 180, p. 111.

16. Harutyunyan, L.R. and Markarian, S.A., *J. Mol. Liq.*, 2011, vol. 160, p. 136.

17. Chauhan, M.S., Kumar, G., Kumar, A., and Chauhan, S., *Colloids Surf. A,* 2000, vol. 166, p. 51.

18. Dubey, N., *J. Surf. Sci. Technol.*, 2008, vol. 24, p. 139.

19. Harutyunyan, L.R., Lachinyan, M.L., and Harutyunyan, R.S., *J. Chem. Eng. Data*, 2013, vol. 58, p. 2998.

20. Bales, B.L., *J. Phys. Chem. B*, 2001, vol. 105, p. 6798.

21. Alauddin, M., Rao, N.P., and Verrall, R.E., *J. Phys. Chem.*, 1988, vol. 92, p. 1301.

22. Erdey-Gruz, T., *Transport Phenomena in Aqueous Solutions*, Budapest: Akademia Kiado, 1974.

23. Lachinyan, M.L., *Khim. Zh. Armenii*, 2013, vol. 66, p. 561.

24. Lachinyan, M.L., Harutyunyan, L.R., and Harutyunyan, R.S.,*XIX Int. Conf. on Chemical Thermodynamics in Russia (RCCT-2013). Book of Abstracts*, Moscow: MITHT Publisher, 2013.