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# Thermodynamics of the Surfaces of Nonionic Spherical Micelles with Relatively Large Extensions of the Interfacial Layer

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**Abstract**—The structural properties of nonionic spherical micelles with relatively large extensions of the interfacial layer are investigated, and the size dependences of their adsorption, interfacial tension, and chemical potential are obtained. Such familiar thermodynamic relationships as the Gibbs and Laplace equations, the differential equation for the chemical potential, and the concept of hydrophilic–lipophilic balance are used. The method is applied to micelles formed in surfactant solutions of a homologous series of tetraethylene glycol alkyl ethers. The region of the existence of micellar solutions and the structural characteristics of the interfacial layer of micelles are determined. The interfacial tension minimum corresponding to ideal hydrophilic–lipophilic balance in the micelle interfacial layer is detected. The chemical potential is negative over the range of the homologous series, and its derivative with respect to the tension radius is also negative.

**Keywords:** structural and thermodynamic properties of non-ionic micelles, interfacial surface, interfacial tension

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## INTRODUCTION

The aim of this work was to study the thermodynamic and structural properties of the surfaces of nonionic micelles with relatively extended interfacial layers (ILs) comparable to micelle nuclei. This category of nanoobjects, especially spherical micelles with oligoxyethylene (E) groups, mimic the structure and properties of some morphological types of biological cells, simulations of which are important in investigating biological objects and physiological processes [1, 2]. In addition, colloidal solutions of surfactants with E groups are widely used in industrial applications [3]. Relatively well developed molecular–thermodynamic simulations of micellar systems can be used to analyze changes in the energy of supramolecular fibrous structures activated by, e.g., inclusions of highly coercive magnetic nanoparticles and nanocomposites [4].

Comparative studies of nonionic micelles in surfactant homologous series are rare; their importance is undoubted, however, since they allow us to identify and analyze size effects [5–9]. The experimental data on oxyethylene surfactants with a small numbers of polar E groups and calculations of molecular dynamics show that the conformation of E fragments with low dipole moments, weak hydration, and unfolded molecular structures most likely occurs at temperatures  $T \geq 300$  K [3, 10]. This allows us to use the quasi-droplet model of nonionic micelles [11]: unfolded

length  $\ell_0$  of a linear surfactant molecule can be considered the radius of a micelle; the  $\ell$  part of this length, as the radius of a micelle's compact nucleus and the radius of tension; and the  $(\ell_0 - \ell)$  part of the molecule, as the IL's thickness. Tension radius  $\ell$  thus cuts the surfactant molecule into two parts, lipophilic and hydrophilic [12], the equilibrium between which determines the forces of hydrophilic–lipophilic balance (HLB) in the IL [13]. Adsorption is determined by the excess of the  $(\ell_0 - \ell)$  parts of the surfactant molecules bound to a certain number of solvent molecules in the interfacial layer (per unit area of the micelle nucleus), compared to the similar value in the bulk phase [13].

## EXPERIMENTAL

### Interfacial Tension

If a surfactant molecule is biphilic and can be simultaneously present in two media on the boundary of which interfacial tension forces come into effect, chemical potential differential  $d\mu$  of the molecule under isochoric–isothermal conditions [12] is

$$d\mu = V_1 dp_1 + V_2 dp_2 - a_0 d\sigma, \quad (1)$$

where  $V_1$  and  $p_1$ , along with  $V_2$  and  $p_2$ , are the volumes of the molecule parts and the pressures in phases 1 and 2, respectively (in this case, index 1 corresponds to the

hydrocarbon nucleus of the molecule and index 2 to the interfacial layer);  $a_0$  is the dividing surface area per one molecule (the landing area); and  $\sigma$  is the interfacial tension coefficient.

As follows from the packing equation of the spherical micelle hydrocarbon nucleus, the  $a_0$  value is approximately equal to the tripled cross-sectional area of a hydrocarbon radical; i.e.,  $a_0 \approx 3a_c$  [14, 15]. It is known [14] that  $a_c = 21.24 \text{ \AA}^2$  and  $a_0 = 63.72 \text{ \AA}^2$ . The differentials of the chemical potential ( $d\mu$ ) and interfacial tension ( $d\sigma$ ) are associated with adsorption  $\Gamma$  in a IL by the Gibbs equation [8]

$$d\sigma = -\Gamma d\mu, \quad (2)$$

and the difference between pressures  $p_1$  and  $p_2$  (the Laplace pressure) for a spherical particle with radius  $\ell$  is determined by the corresponding Laplace equation [8]:

$$p_1 - p_2 = 2\sigma/\ell. \quad (3)$$

Let us consider external (with respect to the micelle nucleus) pressure  $p_2$  constant, as is typical of open systems [12]. Then  $dp_1 = 2(\ell d\sigma - \sigma d\ell)/\ell^2$  and, in view of  $V_1 = \ell a_c = \ell a_0/3$ , it follows from Eqs. (1)–(3) that

$$\frac{d\sigma}{\sigma} = -\frac{2d\ell}{\ell \left(1 - \frac{3}{\Gamma^*(\ell)}\right)}, \quad (4)$$

where  $\Gamma^*(\ell) = \Gamma a_0$  is the dimensionless unit adsorption.

$$\text{If } F(\ell) = -\frac{2}{\ell \left(1 - \frac{3}{\Gamma^*(\ell)}\right)}, \text{ then}$$

$$d\sigma/\sigma = F(\ell)d\ell. \quad (5)$$

The solution to this differential equation is

$$\sigma/\sigma^* = \exp\left(\int_{\ell^*}^{\ell} F(\ell)d\ell\right), \quad (6)$$

where  $\sigma^* = \sigma^*(\ell^*)$ . The  $\sigma^*$  and  $\ell^*$  parameters are determined from the boundary conditions. The  $\sigma^*$  and  $\ell^*$  parameters in the physics of curved surfaces are associated with zero-curvature surfaces. The  $\sigma^\infty$  values for them can be found from the surface tension isotherms of the corresponding solutions (if micellar systems are considered) and from the interfacial tension additivity rule [3], as was done in [16] for spherical micelles in solutions of sodium alkyl sulfates.

To a first approximation, the  $\Gamma$  value for diluted solutions (ignoring the adsorption of hydration solvent molecules in the IL) can be determined using the expression  $\Gamma = n(\ell_0 - \ell)/\ell_0 S$ , where  $S = 4\pi\ell^2$  is the area of the micelle nucleus surface,  $(\ell_0 - \ell)/\ell_0$  is the fraction of molecules inside the IL, and  $n$  is the aggre-

gation number. In turn,  $n = \frac{4\pi\ell^3}{3V_{1\ell}} = \frac{4\pi\ell^3}{3a_c\ell} = \frac{4\pi\ell^2}{a_0}$ ,

where  $V_{1\ell}$  is the volume of the part of the surfactant molecule inside the micelle's nucleus. Adsorption is then expressed as

$$\Gamma = \frac{1}{a_0} \left(1 - \frac{\ell}{\ell_0}\right); \quad \Gamma^* = \left(1 - \frac{\ell}{\ell_0}\right). \quad (7)$$

Here,  $\ell < \ell_0$ ,  $\Gamma > 0$ , and  $\Gamma^* > 0$ . In actual extreme cases,  $\Gamma \rightarrow \frac{1}{a_0}$  and  $\Gamma^* \rightarrow 1$  when  $\ell \ll \ell_0$ , and  $\Gamma \rightarrow 0$  and  $\Gamma^* \rightarrow 0$  when  $\ell \sim \ell_0$ .

At the ideal HLB equilibrium, the micelle nucleus contains only hydrocarbon (radical) fragments of surfactant molecules ( $\ell_c = \ell$ ); the IL, only hydrophilic parts with lengths  $\ell_{IL}$ . The length of a linear molecule is then  $\ell_0 = \ell + \ell_{IL}$ , and  $\Gamma^* = \ell_{IL}/(\ell + \ell_{IL})$ . After transformations, Eq. (4) takes the form

$$d\sigma/\sigma \approx -\ell_{IL}d\ell/(1.5\ell^2 + \ell_{IL}\ell). \quad (8)$$

With an increase in the surfactant homolog number, the  $\ell$  radius of the micelle nucleus increases by the length of a methylene group, while  $\ell_{IL} = \text{const}$ ; Eq. (8) must then be integrated from  $\sigma^\infty$  to  $\sigma$ , and from the extremely high  $\ell$  values (formally,  $\ell \rightarrow \infty$ ) to  $\ell$ , respectively:

$$\frac{\sigma}{\sigma^\infty} = \exp\left(\int_{\infty}^{\ell} \frac{\ell_{IL}}{\frac{3}{2}\ell^2 + \ell_{IL}\ell} d\ell\right). \quad (9)$$

The analytical solution to Eq. (9) is

$$\frac{\sigma}{\sigma^\infty} = \frac{\ell/\ell_{IL}}{(\ell/\ell_{IL}) + \frac{2}{3}} = \frac{\ell}{\ell + \frac{2}{3}\ell_{IL}}. \quad (10)$$

Here,  $(\sigma/\sigma^\infty) \rightarrow 1$  when  $\ell \rightarrow \infty$ , and  $(\sigma/\sigma^\infty) \rightarrow 0$  when  $\ell \rightarrow 0$ . For molecules of the  $C_m\text{OE}_4\text{H}$  series, aggregated into spherical micelles,  $\ell_{IL} = \ell(-\text{O}-)_{\text{eth}} + 4\ell(\text{E}) + \ell(\text{H}) = 17.84 \text{ \AA}$  (MM+ calculations using the HyperChem software package). The  $\sigma/\sigma^\infty$  ratio is 0.6 when  $\ell = \ell_{IL}$ . This value approximately corresponds to the tenth homolog of the  $C_m\text{OE}_4\text{H}$  series ( $m = 10$ ), as will be seen from further calculations. If  $\ell_{IL} = (\ell_0 - \ell)$ , then  $\ell = 0.5\ell_0$ .

The second approximation considers the adsorption of solvent molecules in the IL, which are bonded (albeit weakly) with the polar E groups of surfactant molecules [3, 13]. The adsorption of surfactant molecules is then determined by the familiar expression [17]

$$\Gamma = \left(n_2 - n_1 \frac{n_2^0}{n_1^0}\right) \frac{1}{S}, \quad (11)$$

where  $S = 4\pi\ell^2$ ;  $n_2$  is the number of parts of surfactant molecules in the IL;  $n_1$  is the number of solvent molecules in the IL;  $n_2^0$  and  $n_1^0$  are the numbers of surfactant and water molecules, respectively, in a certain volume ( $V_M$ ) of the micellar solution with a concentration of  $C^{\text{CMC}}(1 - \alpha)$  at  $T = \text{const}$ , where  $\alpha$  is the degree of solution micellization and CMC is the critical micelle concentration.

The first approximation for  $\Gamma$  (without water adsorption) should follow from the second approximation using Eq. (11) when  $n_1 = 0$ . It is then also true that  $\Gamma = n_2/S$  and, in light of the expression for  $n$ ,

$$n_2 = n \left( \frac{\ell_0 - \ell}{\ell_0} \right) = \frac{4\pi\ell^2}{a_0} \left( \frac{\ell_0 - \ell}{\ell_0} \right). \quad (12)$$

Let us consider  $V_{1w}$  to be the effective volume of a water molecule. Then  $n_1 = n \frac{V_w}{V_{1w}} = \frac{V_{1L} - V_{HG}}{V_{1w}}$ , where  $V_{1L} = \frac{4}{3}\pi(\ell_0^3 - \ell^3)$  is the volume of the IL, and  $V_{HG} = na_c(\ell_0 - \ell) = \frac{4}{3}\pi\ell^2(\ell_0 - \ell)$  is the volume of the hydrophilic groups in the IL (assuming they are closely packed in the IL ( $a_0 \approx 3a_c$ ) and the mean cross-sectional area of the hydrophilic groups is approximately that of a hydrocarbon radical).

We then have

$$n_1 = \frac{\frac{4}{3}\pi(\ell_0^3 - \ell^3) - \frac{4}{3}\pi\ell^2(\ell_0 - \ell)}{V_{1w}} = \frac{\frac{4}{3}\pi\ell_0(\ell_0^2 - \ell^2)}{V_{1w}}. \quad (13)$$

When the  $V_{HG}$  value approaches that of  $V_{1L}$ ,  $n_1 \rightarrow 0$  (which corresponds to the transition from the second approximation to the first approximation). The nucleus sizes are in this case greater than the IL sizes, and the  $(\ell_0 - \ell)$  value is less than  $\ell$ .

The number of surfactant molecules in a solution volume of  $V_M$  is

$$n_2^0 = C^{\text{CMC}}(1 - \alpha)V_M. \quad (14)$$

These molecules occupy volume  $V_M' = n_2^0 a_c \ell_0$  and, in light of Eq. (14),

$$n_1^0 = \frac{V_M - V_M'}{V_{1w}} = V_M \frac{1 - \frac{1}{3}C^{\text{CMC}}(1 - \alpha)a_0\ell_0}{V_{1w}}. \quad (15)$$

Returning to Eq. (11) and considering Eqs. (12)–(15), we obtain the formula

$$\Gamma = \frac{1}{a_0} \left( 1 - \frac{\ell}{\ell_0} \right) - \frac{\ell_0}{a_0} \left( \frac{\ell_0^2}{\ell^2} - 1 \right) \frac{C^{\text{CMC}}A}{1 - \frac{1}{3}\ell_0 C^{\text{CMC}}A}, \quad (16)$$

where  $A = (1 - \alpha) \frac{N_A}{10^{27}} \text{ dm}^3/(\text{mol } \text{Å})$  (we consider that molecular parameters  $\ell_0$ ,  $\ell$ , and  $a_0$  are given in Å and Å<sup>2</sup>, respectively; and that the  $C^{\text{CMC}}$  concentration is in mol/dm<sup>3</sup>). In its simplest form, the degree of micellization is calculated using the formula [13]

$$\alpha = \frac{n - 2}{(n - 1)(\sqrt{2n} + 2)} \quad (17)$$

and ranges from 0.07 to 0.15 for the aggregation numbers corresponding to this case ( $10 < n < 50$ ). If we assume that  $\alpha \approx \text{const} = 0.11$ , then  $A = 5.36 \times 10^{-4} \text{ dm}^3/(\text{mol } \text{Å})$ . Estimating the  $\ell_0 C^{\text{CMC}}A/3$  term in Eq. (16) gives a value of  $0.0053 \ll 1$  for the worst case of high parameter values (e.g.,  $\ell_0 = 100 \text{ Å}$  and  $C^{\text{CMC}} = 0.3 \text{ mol/dm}^3$ ). Therefore,

$$\Gamma \approx \frac{1}{a_0} \left( 1 - \frac{\ell}{\ell_0} \right) - \frac{\ell_0}{a_0} \left( \frac{\ell_0^2}{\ell^2} - 1 \right) C^{\text{CMC}}A, \quad (18)$$

$$\Gamma^* = a_0\Gamma = 1 - \frac{\ell}{\ell_0} - \ell_0 \left( \frac{\ell_0^2}{\ell^2} - 1 \right) C^{\text{CMC}}A. \quad (19)$$

The  $C^{\text{CMC}}$  value for nonionic surfactants depends especially strongly on homolog number  $m$ , and on the  $\ell$  value, since  $C^{\text{CMC}} = C^{\text{CMC}}(\ell)$ . Experimental surface tension isotherms at 298 K for the homologous series of  $C_m\text{OE}_4\text{H}$  with  $m = 5, 6, 7, 8$ , and 10, which include regions with  $C \geq C^{\text{CMC}}$ , were presented in [18, 19]. Surface tension isotherms  $\gamma(\log C)$  of the solutions show that the  $C^{\text{CMC}}$  concentrations fall by two orders of magnitude (from 0.190 to 0.002 mol/dm<sup>3</sup>) after raising the  $m$  number from 5 to 10 (i.e., with an increase in the  $\ell$  value). Processing these data yields the following  $C^{\text{CMC}}(\ell)$  dependence (at least within the specified limits):

$$C^{\text{CMC}} = 4.861 \exp(-0.477\ell), \quad (20)$$

where  $C^{\text{CMC}}$  and  $\ell$  are expressed in mol/dm<sup>3</sup> and in Å, respectively.

The concept of HLB in IL micelles is used to determine the  $\ell_0(\ell)$  or  $\ell(m)$  dependences.

#### *Hydrophilic–Lipophilic Balance and Structural Characteristics of Interfacial Layers*

In the absence of sufficiently precise data on the aggregation numbers of nonionic micelles with E-fragments in a molecule, the HLB is apparently the only way of determining their structural characteristics, particularly the  $\ell$  and  $\ell_{1L}$  lengths and the  $\ell_0(\ell)$  dependence [3, 13]. The HLB is based on the additivity of experimentally determined work  $w_i$  of the transfer of

individual molecular groups  $i$  from the polar to the nonpolar phase. Group HLB numbers  $g_i$  are used in practical calculations for this transfer work [13]:

$$g_i = 0.36w_i/kT. \quad (21)$$

For hydrophilic groups,  $g_i > 0$ ; for lipophilic groups,  $g_i < 0$ . Knowing the chemical composition of the molecules and group numbers  $g_i$  taken from [13], we can calculate hydrophilic–lipophilic balance numbers  $G$ :  $G = 7 + \sum_i g_i$ . Number 7 is a conditional number. It was assumed in [13] that surfactant molecules are mostly soluble in water when  $G > 0$ , and mostly soluble in the nonpolar phase when  $G < 7$ . With an ideal balance,

$$\sum_i g_i = 0; \quad G = 7. \quad (22)$$

The values of the group numbers needed to calculate the properties of micelle ILs in the homologous series of  $C_m\text{OE}_4\text{H}$  are

$$\begin{aligned} g(-\text{CH}_2-) &= -0.475, \\ g(-\text{CH}_2-\text{CH}_2-\text{O}-) &= 0.33, \\ g(-\text{O}-) &= 1.3. \end{aligned} \quad (23)$$

Partial work  $w_i$  of transfer through flat and curved surfaces has virtually no effect on the values of the group numbers  $g_i$  [13]. With an ideal HLB in the micelle interfacial layer (where the alkyl radical is completely immersed in the nucleus),  $\sum_i g_i = 0$ ,  $G = 7$ , and  $\bar{\ell} \equiv \bar{\ell} = \ell_c$ . With a nonideal balance, the deviation of  $\ell$  from  $\ell_c$  is determined by the  $\bar{\ell} \sum_i g_i/7$  value:

$$\ell = \ell_c - \bar{\ell} \sum_i g_i/7. \quad (24)$$

The  $\sum_i g_i$  value can in this case be either positive or negative. In accordance with Eqs. (22) and (23), the following expression is valid for the homologous series of  $C_m\text{OE}_4\text{H}$ :  $\sum_i g_i = 0.33 \times 4 + 1.3 - 0.475(m - 1) = 0$ . Hence,  $m \equiv \bar{m} = 6.52$  and  $\bar{\ell} = \ell_c = 1.5 + 1.265\bar{m} = 9.74 \text{ \AA}$ . Here,  $\bar{m}$  and  $\bar{\ell}$  are relevant structural characteristics for an ideally balanced system. If  $m < \bar{m} = 6.52$ , then  $\sum_i g_i > 0$ ,  $\ell < \bar{\ell} = 9.74 \text{ \AA}$ , and  $\ell < \ell_c$  (some parts of the methylene fragments protrude from the micelle nucleus), but  $\sum_i g_i < 0$  and  $\ell > \ell_c$  when  $m > \bar{m}$ , owing to nonhydrocarbon molecular fragments (in this case, the oxygen atoms of ether groups) inverted in the micelle nucleus.

## RESULTS AND DISCUSSION

The colloidal properties of solutions in the homologous series of  $C_m\text{OE}_4\text{H}$  become apparent starting from butyl ether. If  $m = 1-3$ , then  $\ell < \ell(\text{CH}_3-)$ . A stable micelle nucleus is formed only at  $m = m_{\min} = 4$ , once  $\ell = \ell_{\min} = 4.90 \text{ \AA}$ . In this case,  $\ell_c = 6.56 \text{ \AA}$ ,  $\ell_0 = 24.4 \text{ \AA}$ ,  $n = n_{\min} = (4\pi\ell_{\min}^2/a_0) = 4.74$ , and  $(\ell_{\min} - \ell_c) = -1.66 \text{ \AA}$ . The last value means that on average, 1.3 the methylene group length of each surfactant molecule is pulled from the micelle nucleus into the IL by the forces of hydrophilic interactions.

As follows from the familiar Tanford equation,  $\ell_c = 1.5 + 1.265m$ , and equations  $\ell = \ell_c - \bar{\ell} \sum_i g_i/7 = \ell_c - 1.39 \sum_i g_i$ ,  $\sum_i g_i = 3.095 - 0.475m$ , and  $\ell_0 = \ell_c + 17.84$  (all lengths are in  $\text{\AA}$ ), obtained earlier from HLB for the considered series, yield the relations

$$\ell = 1.925m - 2.802, \quad (25)$$

$$\ell_0 = 21.19 + 0.658\ell = 19.346 + 1.267m. \quad (26)$$

These are valid only at relatively low  $m$  and  $\ell$  values (within the considered homologous series) and are incorrect at high  $\ell$  values, if these are possible. Note that according to Eq. (26),  $\ell_0 \lesssim \ell$  when  $\ell \gtrsim 62 \text{ \AA}$ , which makes no physical sense. If we therefore consider that the  $(-\text{OE}_4\text{H})$  groups of surfactant molecules can be completely immersed in a micelle's nucleus, we may assume that  $\ell_0 \rightarrow \ell$ .

Linear graphs  $\ell_0 = \ell$  and  $21.19 + 0.568\ell$  intersect at point  $\ell = \ell' \approx 62 \text{ \AA}$ . A smooth transition from the  $\ell$  value in Eq. (25) to the  $\ell_0$  value in Eq. (26) can be achieved by using an exponential relaxation term with an exponent value  $(-\lambda_0\ell)$  such that Eqs. (25) and (26) are valid when  $\ell \rightarrow 0$  and  $\ell \rightarrow \infty$ , respectively. To accomplish this, we must assume that  $\lambda_0 = (1/\ell') \approx 0.016 \text{ \AA}^{-1}$ . The general  $\ell_0(\ell)$  dependence then takes the form

$$\ell_0 = \ell + 21.19\exp(-0.016\ell). \quad (27)$$

It is obvious that  $\exp(-0.016\ell) \approx (1 - 0.016\ell)$  at  $\ell \ll (1/0.016) \approx 62 \text{ \AA}$ , and we can derive from Eq. (27) that  $\ell_0 \approx 21.19 + 0.658\ell$ , which coincides with Eq. (26). In accordance with Eq. (27),  $\ell_0 \approx \ell$  when  $\ell \gg 62 \text{ \AA}$ . The value  $\ell' = 62 \text{ \AA}$  formally corresponds to the number of carbon atoms in the alkyl chain of a  $C_m\text{OE}_4\text{H}$  molecule; i.e.,  $m \equiv m' \approx 34$ . However, it is unlikely that such a homolog exists, since not only does the  $C^{\text{CMC}}$  concentration fall as the  $m$  number of carbon atoms in an alkyl chain rises at a constant number of 4 for E fragments in the molecule, but the solubility diminishes as well. The maximum possible  $\ell$  and  $m$  values in the  $C_m\text{OE}_4\text{H}$  series are thus determined by the minimum solubility and  $C^{\text{CMC}}$  values. According to [3], the  $m$

Structural characteristics of micelles and the critical micelle concentrations of surfactant solutions in the homologous series of tetraethylene glycol alkyl ethers  $C_mOE_4H$  ( $m = 4-18$ ) at 298 K

Characteristics	4	5	6	7	8	10	12	14	16	18
$l_c, \text{\AA}$	6.56	7.83	9.09	10.35	11.62	14.16	16.68	19.21	21.74	24.27
$l, \text{\AA}$	4.90	6.82	8.75	10.67	12.60	16.45	20.30	24.15	28.00	31.99
$l_0, \text{\AA}$	[31]	24.42	25.68	26.95	28.21	29.47	32.02	34.55	37.08	42.15
	[33]	24.49	25.82	27.17	28.53	29.92	32.74	35.61	38.54	44.50
$n$	4.7	9.2	15.1	22.4	31.3	53.3	81.2	114.9	154.4	199.8
$C^{CMC}, \text{mol/dm}^3$	0.469	0.188	0.075	0.030	0.012	0.0019	0.0003	$4.83 \times 10^{-5}$	$7.70 \times 10^{-6}$	$1.24 \times 10^{-6}$

numbers at room temperature do not exceed 16 to 18 at a constant small number (4 to 6) of E fragments in the molecule. If the asymptotic formula given by Eq. (20) is also valid in the area of very low concentrations, then  $l = l_{\max} \approx 32 \text{\AA}$ ,  $C^{CMC} \approx 1.3 \times 10^{-6} \text{ mol/dm}^3$ ,  $l_c = 24.3 \text{\AA}$ ,  $l_0 = 42.2 \text{\AA}$ ,  $n \approx 200$ , and  $(l_{\max} - l_c) \approx 7.7 \text{\AA}$  at  $m = 18$ . The last means that ethereal oxygen atoms are in this case immersed in the micelle nucleus and, on average, 1.5 of the E groups of all micelle molecules.

The results from calculating the structural characteristics of the ILs of micelles in the  $C_mOE_4H$  series are presented in the table. The  $C^{CMC}$  values for  $m = 5, 6, 7, 8, 10$  are taken from the surface tension isotherms of the corresponding solutions [18, 19] and were calculated using Eq. (20) for the rest of the homologs.

As can be seen from table,  $l_c < l$ , and HLB is shifted toward the lipophilic micelle nucleus starting from the homolog with  $m = 7$ . Thus,  $(l_c - l) = -2.29 \text{\AA}$  in the micelle with  $m = 10$ ; i.e., the ethereal oxygen atoms, the effective diameters of which are  $2.0 \text{\AA}$ , are completely transferred to the nucleus. For this homolog ( $m = 10$ ),  $l \approx 0.5 l_0$ ; i.e., the IL thickness is approximately equal to the radius of a nucleus:  $l_{IL} \approx l$ . The length of an unfolded surfactant molecule is balanced:  $l_0 = l_c + l_{HG} \approx l_c + 17.84 \text{\AA}$ . For any two homologs (1 and 2),  $n_1 l_2^2 = n_2 l_1^2$ . The variation in the  $C^{CMC}$  value in the homologous series is over five orders of magnitude, in agreement with the experimental data [3]. This finding, along with the strong dependence of the properties (micelle sizes,  $C^{CMC}$  concentration, packing parameters in micelles, the sequence of phase structures, etc.) of colloidal solutions of surfactants with E groups on temperature, which is not discussed in detail in this work, relies is based on the experimental data in [3, 10].

Dimensionless adsorption  $\Gamma^* = \Gamma a_0$  in the ILs of micelles with nucleus radii equal to  $l$  for the  $C_mOE_4H$  homologous series ( $l_{\max} = 32 \text{\AA}$ ) is given Fig. 1 (in the (I) first and (II) second approximations produced using Eqs. (7) and (19), respectively). These equations

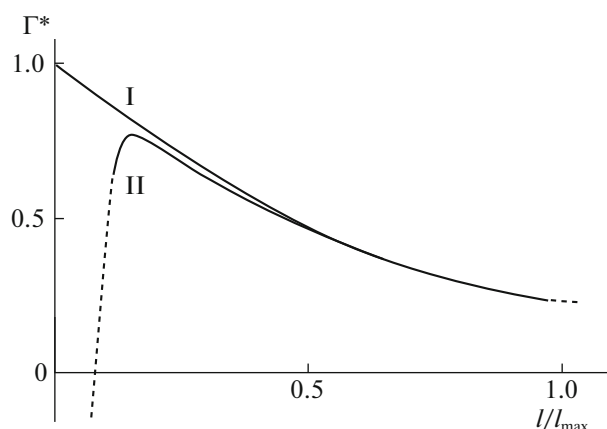
show that  $\Gamma_{II}^* = \Gamma_I^* - l_0 \left( \frac{l_0^2}{l^2} - 1 \right) C^{CMC} A$ , and

$\Gamma_{II}^* \rightarrow \Gamma_I^*$  at the lowest possible parameters,  $m \approx 4.1$  and  $l \approx 5.08 \text{\AA}$ , for this homologous series, as can be seen from Fig. 1. These values are almost identical to the HLB calculation results ( $m = 4$  and  $l = 4.9 \text{\AA}$ ). We found that  $\Gamma_{II}^* \approx \Gamma_I^*$  when  $m \gtrsim 8$ . When  $m \lesssim 3$  and  $l \approx 2.97 \text{\AA}$ ,  $\Gamma_{II}^* \leq 0$ . Micelles cannot exist in this area in principle, since adsorption cannot assume a negative value for surfactants. Those states of the system are thus shown by the dotted lines in Figs. 1 and 2; they were not attained in the objects investigated in this work.

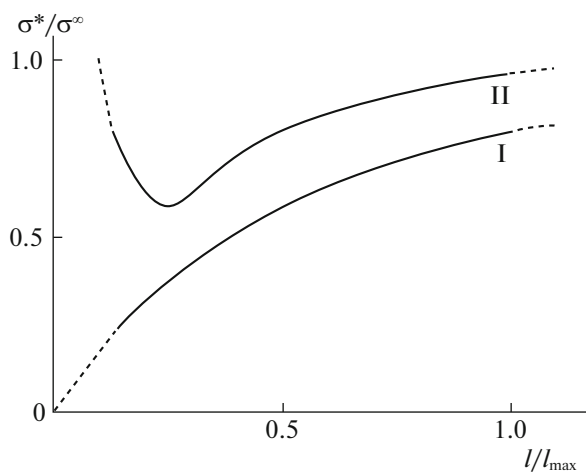
Let us compare Eq. (10) of the first approximation to the familiar Tolman equation [20]

$$\sigma/\sigma^\infty = R/(R + 2\delta), \quad (28)$$

where  $R$  is the nanoparticle radius and  $\delta$  is the Tolman parameter. When  $R = l$ , this parameter is  $\delta = l_{IL}/3$ . As follows from Eqs. (25) and (26),  $\delta(l) = (l_0 - l)/3 =$



**Fig. 1.** Adsorption  $\Gamma^* = a_0\Gamma$  in the interfacial layers of micelles in solutions of homologs of a tetraethylene glycol series, depending on the radius of a spherical micelle nucleus in the (I) first (Eq. (7)) and (II) second (Eq. (9)) approximations when  $l_{\max} = 32 \text{\AA}$ .



**Fig. 2.** Interfacial tensions in spherical micelles in solutions of homologs of a tetraethylene glycol series, depending on the radius of a spherical micelle nucleus in the (I) first (Eq. (10)) and (II) second (Eqs. (4), (6), (19), (20), and (25)) approximations.

7.06 – 0.11 $\ell$ . The Tolman formula was derived by assuming that  $\delta \ll R = \ell$ , so the variation of this parameter can be analyzed only qualitatively. Tolman parameter  $\delta$  is the difference between radius  $R_{\text{eq}}$  of an equimolecular surface and surface tension radius  $R$ .

At all acceptable  $\ell$  values ( $4.9 \lesssim \ell \lesssim 32 \text{ \AA}$ ), parameter  $\delta$  diminishes linearly, from 6.5 to 3.5  $\text{\AA}$ . For the fourth homolog of the  $C_m\text{OE}_4\text{H}$  series, it exceeds surface tension radius  $\ell$ . In this case,  $R_{\text{eq}} \approx 11.4 \text{ \AA}$  and extends approximately to the middle of the IL. At  $\ell = 6.36 \text{ \AA}$ , we find that  $\delta = \ell$  and  $R_{\text{eq}} = 2\ell$ . The state of an IL with  $\delta \rightarrow 0$  is a criterion of the nondependence of adsorption and surface tension on size effects. This state ( $\delta \rightarrow 0$ ,  $R_{\text{eq}} = \ell$ ) can be achieved only when  $\ell \gtrsim 2\ell_{\text{max}} = 64 \text{ \AA} \approx \ell'$ . According to our finding, this cannot be attained by this particular homologous series.

The considered case of  $C_m\text{OE}_4\text{H}$  micelles is a classic description of the thermodynamics of nanoparticle surfaces in the first approximation [3, 8, 21]. At the same time, a drop in adsorption in the ILs of micelles (Fig. 1) increases the dipole interaction energy of the E fragments of molecules, leading to an asymptotic increase in surface tension (Fig. 2, approximation I). However, a potential well is observed in the  $\sigma(\ell)$  dependence with approximation II, which considers the adsorption of water and the HLB changes in IL (Fig. 2, approximation II). This minimum corresponds to radius  $\ell \approx 8.2 \text{ \AA}$ , which is close to the  $\ell$  value for the system with ideal HLB. With an ideal HLB,  $(\sigma/\sigma^\infty)_{\text{min}} = 0.60$ . For the  $\ell$  value specified in approximation I,  $(\sigma/\sigma^\infty) \approx 0.42$ . The difference between the  $\sigma/\sigma^\infty$  values (0.18) for these two approximations is preserved when  $\ell \geq 8.2 \text{ \AA}$  ( $\ell/\ell_{\text{max}} \approx 0.26$ ) (Fig. 2).

Naturally, the interfacial tension in an IL with adsorbed water (approximation II) is indeed nominally higher than when water is removed (approximation I). The interfacial tension in an IL naturally grows when deviating from the equilibrium state with minimal surface tension in one direction or another (extracting lipophilic fragments from the nucleus or pulling in hydrophilic fragments).

The chemical potential and its dependence on size are also important factors in the thermodynamics and kinetics of nanoparticle surfaces [12, 21]. At  $p_2 = \text{const}$ , Eq. (1) takes the form  $d\mu = V_1 dp_1 - a_0 d\sigma$ . With the expressions found earlier for the  $V_1$  and  $dp_1$  values, we easily obtain the equation

$$\frac{d\mu}{d\ell} = -\frac{a_0}{3} \left( \frac{d\sigma}{d\ell} + 2\frac{\sigma}{\ell} \right). \quad (29)$$

The  $d\sigma/d\ell$  derivative is  $d\sigma/d\ell < 0$  at low  $\ell$  values within the limits  $4.9 \lesssim \ell \lesssim 8.2 \text{ \AA}$  and  $d\sigma/d\ell > 0$  at  $\ell > 8.2 \text{ \AA}$  ( $\ell/\ell_{\text{max}} > 0.26$ ) (Fig. 2). However, calculations show that  $|d\sigma/d\ell| < 2\sigma/\ell$  for the appropriate  $\ell$  values in the area of negative  $d\sigma/d\ell$  values. For example,  $d\sigma/d\ell \approx -0.15$  and  $2\sigma/\ell \approx 0.26$  for the fourth  $C_4\text{OE}_4\text{H}$  homolog (Fig. 2). The chemical potential thus falls as the  $\ell$  value rises ( $d\mu/d\ell < 0$ ) for all acceptable  $\ell$  values.

The general formula for the chemical potential of the micelle surface in the considered homologous series is derived from Eqs. (2) and (4):

$$\mu = -\int \frac{\sigma(\ell) F(\ell) d\ell}{\Gamma} = 2a_0 \int \frac{\sigma(\ell) d\ell}{\ell(\Gamma^* - 3)}. \quad (30)$$

However, we need not calculate the integral given in Eq. (30), since there are no specific points in the  $\mu(\ell)$  dependence. It is simpler to use Eq. (10). After the substitution in Eq. (29) and transformations, we obtain the expression

$$\begin{aligned} \mu^* &\equiv \frac{\mu}{a_0 \sigma^\infty} = -\frac{2}{3} \int \frac{(\ell + \ell_{\text{IL}}) d\ell}{\left(\ell + \frac{2}{3}\ell_{\text{IL}}\right)^2} \\ &= -\frac{6}{25} \left( -\frac{\ell_{\text{IL}}}{\ell} + \ln \ell \right) + \text{const}, \end{aligned}$$

where the IL thickness is  $\ell_{\text{IL}} = \text{const} = 11.89 \text{ \AA}$  (approximation I). The change in the chemical potential of a  $C_m\text{OE}_4\text{H}$  molecule in a micelle upon transitioning from the homolog with  $(m-1)$  to one with  $m$  is expressed by the formula

$$\Delta\mu_{(m-1)}^{*m} = -\frac{6}{25} \left[ \frac{\ell_{\text{IL}} + (\ell^m - \ell^{(m-1)})}{\ell^m \ell^{(m-1)}} + \ln \frac{\ell^m}{\ell^{(m-1)}} \right].$$

This value includes not only the work of the transfer of the methylene group to the micelle nucleus, and of the E groups to IL, but that associated with changes in

curvature, HLB, adsorption, and the conformation of E fragments. This value changes from  $-0.24$  for  $\Delta\mu_{4}^{*5}$  and to  $-0.022$  for  $\Delta\mu_{17}^{*18}$ .

## CONCLUSIONS

A way of calculating the structural and thermodynamic properties of nonionic surface micelles in a homologous series of surfactant was proposed that uses the classical equations of thermodynamics, the concept of HLB, and one experimental parameter: the critical micelle concentration. The adsorption of water in an IL affects the dependence of interfacial tension on micelle nucleus size, creating a minimum corresponding to the size of a micelle nucleus with ideal HLB. For  $C_mOE_4H$  homologs that can produce colloidal solutions, the chemical potential of a molecule in a micelle is negative and diminishes in absolute value upon an increase in the nucleus radius (and the homolog number, as a result).

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