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Original Russian Text © 2017 V. S. Kuznetsov, N. V. Usol'tseva, A. P. Blinov, N. V. Zharnikova, A. I. Smirnova, V. G. Badelin.

STRUCTURAL, ELECTROSTATIC, AND THERMODYNAMIC PROPERTIES OF THE SURFACE OF SPHERICAL MICELLES IN SOLUTIONS OF SODIUM *n*-ALKYL SULFATE HOMOLOGUES. II. ELECTROSTATIC AND THERMODYNAMIC CHARACTERISTICS

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The structural characteristics of micelles from our previous work (Part I) are used to calculate the electrostatic energy of ions in the electric double layer on the surface of spherical ionic micelles in solutions of sodium *n*-alkyl sulfate homologues with the following number of carbon atoms in the molecule: $n_C = 8$, 10, 12, and 14. This energy is found to depend on the thickness of the electric double layer and its average radius on the surface of a micelle, the aggregation number, the degree of binding of counterions, and the dielectric constant. The developed semi-empirical method is used to calculate interfacial tensions in spherical micelles for the said homologues in solutions at their critical micellar concentrations and $T = 303$ K. These values are split into the contributions from the hydrophobic and electrostatic components. The electrostatic component of the interfacial tension in spherical micelles is compared with the expression for the ion–ion repulsion energy to obtain the values of static permittivity (dielectric constant) in the surface layer of micelles.

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Keywords: spherical ionic micelles, electrostatic energy, electric double layer, interfacial tension.

INTRODUCTION

In our previous article (Part I), we calculated the structural characteristics of spherical micelles in solutions of sodium *n*-alkyl sulfate homologues with the following number of carbon atoms in the molecule: $n_C = 8$, 10, 12, and 14. In this work, we use these data to calculate the electrostatic energy of ions in the electric double layer (EDL) on the surface of micelles, dielectric constant, and interfacial tension as a function of the homologue number.

THEORETICAL

In this work, the electrostatic energy of a system of single charged ions in the EDL on the surface of micelles is expressed as a sum of two terms: the interaction energy of all ions (both the surfactant heads and counterions) that have, in

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a first approximation, a total charge of $e_0 n_{\exp}(1 - \beta)$ and are placed on a sphere of radius $l_{(-)}$ where there were originally only negative polar heads (a bare micelle), and the work associated with the transfer of positive hydrated counterions on a sphere of radius $l_{(+)}$, i.e., at a distance of $\Delta l = l_{(-)} - l_{(+)}$. As is known, the first term is given by the equation [1, 2]:

$$W_{l_1} = \frac{1}{4\pi\varepsilon_0} \cdot \frac{e_0^2 n_{\exp}^1 (1-\beta)^2}{2\varepsilon l_{(-)}}. \tag{1}$$

The second term is the work associated with the charge transfer $(q_1 - q_2)$; after the transfer, the charge that remains on a sphere of radius $l_{(-)}$ is q_2. This work is

$$A = \frac{1}{4\pi\varepsilon_0\varepsilon} \int_{q_1}^{q_2} \int_{l_{(-)}}^{l_{(+)}} q dq \frac{dr}{r^2} = \frac{1}{4\pi\varepsilon_0} \cdot \frac{1}{2\varepsilon} \int_{q_1}^{q_2} d(q^2) \int_{l_{(-)}}^{l_{(+)}} \frac{dr}{r^2} = \frac{1}{4\pi\varepsilon_0} \cdot \frac{1}{2\varepsilon} (q_2^2 - q_1^2) \left(\frac{1}{l_{(-)}} - \frac{1}{l_{(+)}} \right).$$

If $q_1 = e_0^2 n_{\exp}(1-\beta)$ and $q_2 = e_0 n_{\exp}$ then

$$A = \frac{1}{4\pi\varepsilon_0} \cdot \frac{e_0^2 n_{\exp}^2}{2\varepsilon} \beta(2-\beta) \left(\frac{1}{l_{(-)}} - \frac{1}{l_{(+)}} \right). \tag{2}$$

The total electrostatic energy of ions in EDL is

$$W_l = W_{l_1} + A = \frac{1}{4\pi\varepsilon_0} \cdot \frac{e_0^2 n_{\exp}^2}{2\varepsilon} \left[\frac{(1-\beta)^2}{l_{(-)}} + \beta(2-\beta) \left(\frac{\Delta l}{l_{(+)} l_{(-)}} \right) \right], \tag{3}$$

where e_0 is the elementary charge; ε_0 is the electric constant; $\Delta l = (l_{(+)} - l_{(-)})$ is the EDL thickness; and ε is the static permittivity in the EDL. In addition, $l_{(-)} = l_C + r_r$; $l_{(+)} = l_{(-)} + \Delta l$, r_r is the radius of the head part of the surfactant ion; this part concentrates the charge of the ion.

Dependence (3) is verified using limiting transitions for the degree of binding and the micelle size. Obviously, at $\beta = 1$, relation (1) becomes zero and relation (2) is the same as (3). In this case, both (2) and (3) represent a formula for the energy of a spherical capacitor as applied to ionic micelles [1, 3]. At $\beta = 0$, formula (3) transforms into the corresponding relation for a bare micelle (i.e., a micelle without counterions). Given a sufficiently large size of the micelle (large $n_{\exp}$, n_C, and l_C) and, hence, large values of $l_{(-)}$ and $l_{(+)}$, at real values of close to unity, $\beta(2 - \beta) \approx \beta$ and $l_{(+)} l_{(-)} \approx l^2 = S/4\pi$, where S is the average surface area of a spherical EDL. Then, given that a planar EDL has the same area, its energy will transform, as follows from (3), into the energy of a planar EDL: $W_l \to W_{l\infty} \approx \dfrac{e_0^2 n_{\exp}^2 \beta \Delta l}{2\varepsilon\varepsilon_0 S}$, where the charges of the negative and positive EDL are $(e_0 n_{\exp})$ and $(e_0 n_{\exp}\beta)$, respectively.

The average surface density of the electrostatic energy of an EDL is $\omega_l = W_l/4\pi l^2$, where $l \approx (l_{(+)} + l_{(-)})/2$.

Thus, considering the approximation $l_{(+)} \cdot l_{(-)} \approx l^2$, we have:

$$\omega_l = \frac{e_0^2 n_{\exp}^2}{32\pi^2 \varepsilon_0 l^4} \cdot \frac{1}{\varepsilon} [(1-\beta)^2 l_{(+)} + \beta(2-\beta)\Delta l]. \tag{4}$$

At the same time, the electric layer (EL) density of a planar layer of the same area is

$$\omega_{l\infty} = \frac{W_{l\infty}}{4\pi^2 l^2} = \frac{e_0^2 n_{\exp}^2}{32\pi^2 \varepsilon_0 l^4} \cdot \frac{\beta \Delta l}{\varepsilon}. \tag{5}$$

The dimensionless relationship

$$\frac{\omega_l}{\omega_{l\infty}} = \frac{(1-\beta)^2}{\beta} \cdot \frac{l_{(+)}}{\Delta l} + 2 - \beta \tag{6}$$

does not depend on the permittivity ε.

Previously, there was a brief communication [4] about the use of a semi-empirical method to calculate interfacial tension in spherical micelles in solutions of sodium alkyl sulfate homologues with the following number of carbon atoms in the molecule: $n_C = 8$, 10, 12, and 14 (at their CMC and $T = 303$ K). The method is based on a comparison of the transitions from one homologue to another with a change in the size of spherical micelles and the use of experimental interfacial tension isotherms of the corresponding solutions at their CMCs and the Laplace equation of interfacial tension [4]. The idea of the method is as follows.

The main thermodynamics equation for the specific free energy of the surface of a spherical micelle has the form

$$\gamma_r + \omega_L = \gamma_\infty, \tag{7}$$

where γ_r is the interfacial tension in a spherical micelle in a solution at the CMC and at a given temperature; γ_∞ is the interfacial tension for a planar dividing surface; and ω_L is the specific work to identify the potential barrier in the transfer of a surfactant ion into a micelle due to the surface curvature (the work to overcome the Laplace pressure difference [5]).

The relationship between ω_L and γ_r can be found from the Laplace equation for the interfacial tension of a spherical particle

$$\left(\frac{2\gamma_r}{r}\right) = \Delta P_L, \tag{8}$$

where r is the tension radius and ΔP_L is the Laplace difference of pressures.

Under isochoric conditions, $\Delta P_L = W_L/V$, where W_L is the full work to overcome the Laplace pressure difference per a micelle with a volume V. Therefore, the work per surface area is

$$\omega_L = \frac{2}{3}\gamma_r. \tag{9}$$

It follows from equations (7), (8), and (9) that

$$\gamma_r / \gamma_\infty = 3/5 \tag{10}$$

and

$$\omega_L / \gamma_\infty = 2\gamma_r / 3\gamma_\infty = 2/5. \tag{11}$$

The interfacial tension for a planar surface γ_∞ dividing the condensed film of SAS hydrocarbon molecules (ions) on the surface of a solution and the aqueous phase of the solution is found from interfacial tension isotherms at the CMC and from the known additivity rule: interfacial tension is the difference of the surface tensions of the corresponding phases. This is the approximate Antonov rule; the lower the mutual solubility of the hydrocarbon and aqueous phases and the lower the pressure of saturated vapors, the better the rule is observed [6, 7]. At low SAS concentrations in an aqueous solution, which is the case of the CMC, this rule is written as follows:

$$\gamma_\infty = \gamma^0 - \gamma^{\mathrm{CMC}}, \tag{12}$$

where γ_∞ is the interfacial tension at the planar boundary between the hydrocarbon layer and water; γ^0 is the surface tension of water at a given temperature; and γ^{CMC} is the surface tension of solutions of SAS homologues at their CMCs from the corresponding isotherms.

The data on γ^{CMC} at $T = 303$ K for sodium alkyl sulfate homologues ($n_C = 8$, 10, 12, and 14) were taken from [8]. The thus derived dependence $\gamma_\infty(l_C)$ can be approximated by an asymptotic function with a deviation from experimental points no worse than 2%:

$$\frac{\gamma_\infty}{\tilde{\gamma}} = \exp\left(a - \frac{b}{l_C}\right), \tag{13}$$

where $\tilde{\gamma} = 1$ mJ/m^2 is a unit nondimensionalizing factor (further we omit it); the constants are $b = 6.77$ Å and $a = 3.59$ Å. The boundary condition $b << l_C$ gives an asymptote of curve (13)

$$\gamma_\infty \to \gamma_\infty^{\max} = \exp(a) = 51.98 \text{ mJ/m}^2 = \text{const}. \tag{14}$$

The extended length l_C of the hydrocarbon radical of the SAS molecule can be used as the average tension radius of the surface layer of the micelle: $l_C \approx r$ [1, 4, 6]. Then, taking into account (10), (11), and (13), we derive

$$\gamma_r / \gamma_\infty^{\max} = 3/5 \exp(-b/l_C) \tag{15}$$

and

$$\omega_l / \gamma_\infty^{\max} = 2/5 \exp(-b/l_C). \tag{16}$$

There are hydrophobic intermolecular forces in the spherical layer of the micelle between the core ($l_0 \le l_C$) and the average EDL radius ($l_C < l$); however, interfacial tension depends on the repulsive Coulomb energy of EDL ions as well as these intermolecular interactions [3, 5]. Therefore, it is adequate to divide the effective interfacial tension γ_r into a hydrophobic γ_h and electrostatic γ_e component. Then, the original equations have the form

$$\gamma_h + \gamma_e = \gamma_r; \quad \gamma_h + \gamma_e + \omega_L = \gamma_\infty; \quad \omega_L = 2/3(\gamma_h + \gamma_e) \tag{17}$$

and

$$5/3\gamma_h + 5/3\gamma_e = \gamma_\infty. \tag{18}$$

It can be assumed (and it is shown below) that the term γ_e, which is a specific characteristic of the surface, is almost independent of l_C:$\gamma_e \approx$ const given that the degree of binding β of counterions and the EDL thickness Δl are constant. Then, 5/3 of this value can be considered as the integration constant C_1 of the equation derived from (18): $(5/3)(d\gamma_h/dl_C) = d\gamma_\infty/dl_C$ and $C_1 + (5/3)\gamma_h = \gamma_\infty$. The boundary condition $b << l_C$ implies that $\gamma_h \to \gamma_h^{\max} \to \gamma_\infty^{\max}$ and $\gamma_\infty \to \gamma_\infty^{\max}$; this gives us $C_1 = -2/3\gamma_\infty^{\max} = 5/3\gamma_e$. Hence, it follows that

$$\gamma_e / \gamma_\infty^{\max} = -2/5. \tag{19}$$

Using equations (18) and (19), we derive

$$\gamma_h / \gamma_\infty^{\max} = 2/5 + 3/5 \exp(-b/l_C). \tag{20}$$

In this case, $(\gamma_h / \gamma_\infty^{\max}) = 1$ at $b << l_C$. The equations derived here allow us to make some important conclusions about the thermodynamic properties of the surface of micelles of sodium alkyl sulfate homologues in solutions, e.g., about the lower and higher members of the homological series, which demonstrate surfactant and micellization abilities, about a possibility to neglect the curvature of the micelle surface in calculating interfacial tension, about the ways to estimate the Tolman parameter, etc. However, these conclusions are beyond the scope of this article. Here we focus on comparing the electrostatic energy density ω_l and the component γ_e of interfacial tension to calculate the static permittivity ε in the EDL on the surface of micelles.

It is known that the energy of a system is equal to its free energy, strictly speaking, at $T = 0$. Since it was shown previously that the energy of hydrated EDL ions is free energy, we can write the following relation for the corresponding surfaces:

$$\omega_l = \gamma_e. \tag{21}$$

Then, comparing (4), (14), (19), and (21), we obtain the values of the dielectric constant ε in the EDL on the surface of a micelle:

$$\varepsilon = \frac{5e_0^2 \cdot n_{\exp}^2}{64\pi^2 \varepsilon_0 \cdot l^4 \cdot \gamma_\infty^{\max}} \cdot [(1-\beta)^2 l_{(+)} + \beta(2-\beta)\Delta l]. \tag{22}$$

RESULTS AND DISCUSSION

The description of the EDL in the neighborhood of a spherical ionic micelle in a SAS solution by the theory of strong electrolytes (including the Poisson–Boltzmann equation) and the calculation of the electrostatic potentials of micellar systems have been the subject of many studies [1, 2, 9-12], including comparative calculations for micelles of sodium *n*-alkyl sulfate homologues [13].

Abstracting from the diffuse part of the EDL in solution, ionic micelles have their own EDL on the outer part of the micelle surface (the Stern layer). This layer is formed by the surfactant head parts of ions and counterions in the dense layer. The focus of this article is precisely on this EDL because the strong electrostatic repulsion of closely located similar ions (although weakened by the interaction of different ones) produces additional tangential pressure. The latter loosens the surface layer of the micelle to decrease its interfacial tension, which is a major property of surfactant systems. It is this EDL that is discussed below.

The electrostatic properties of ionic micelles are typically calculated using statistical models where the distribution of charges, as well as volume and temperature, are considered invariable. However, the charges of hydrated ions located at distances of about two (or slightly more) diameters of water molecules cannot be treated as point charges [1]. There are two different static models (both are solved approximately): the first one is based on the proportionality of the charge density and surface potential of a spherical particle (Poisson equation); the second one is an analogue of a spherical capacitor [1]. The first model considers the EDL thickness and gives overestimated results for electrostatic energy. The spherical capacitor model as applied to ionic micelles corresponds only to full binding of counterions ($\beta = 1$) and gives underestimated results compared to those obtained from experimental data (potentiometry, conductometry, the fluorescent probe method, etc.) [1, 9, 14].

To calculate the electrostatic properties of ionic micelles, one needs to know, apart from the structural parameters of their surface, which were calculated in Part I of this study [15], the aggregation numbers and the degree of binding of counterions. In this work (Part II), we use experimental values of the aggregation numbers n_{exp} [15, Table 1]. Although the degree of binding of counterions β can be determined experimentally [16-18], the determinations are rather inaccurate [1, 9]; therefore, the degree of binding is used here as a preset parameter.

The dependence ($\omega_l/\omega_{l\infty}$) vs. n_C β is plotted in Fig. 1. It is evident from the plot that the higher the degree of binding, the lower the number of counterions and the higher their repulsion energy. This pattern is true for micelles of each homologue ($n_{\text{exp}} = \text{const}$). At this value and with increasing n_C $l_{(+)}$ increases more than Δl ([15], Fig. 4), which explains the dependence of ($\omega_l/\omega_{l\infty}$) on n_C.

We can show that (3) is the free energy of the EDL. Indeed, one of the main postulates in the electrostatics of dielectrics is that the bulk density of the free energy *f* of a system of (free) charges generating an electrostatic field *E* and placed in a medium with a dielectric constant is given by the relation [19]

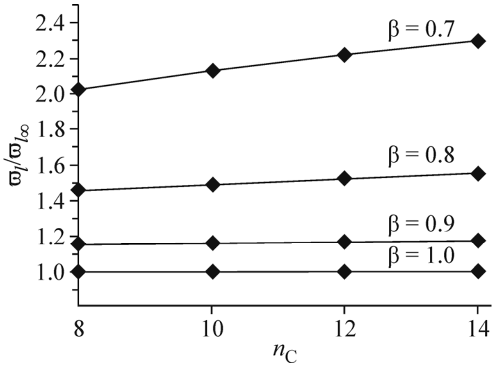

Fig. 1. Surface density of the electrostatic energy in EDL of spherical micelles of sodium alkyl sulfate homologues as compared with the density of the planar layer, depending on n_C and the degree of binding of counterions.

$$f = 1/2\varepsilon_0\varepsilon E^2. \quad (23)$$

It is known [1] that the electrostatic field of a spherical ionic micelle is determined by the field of surfactant ions and its intensity at $l_{(-)} \approx l$ is

$$E = \frac{n_{\exp} e_0}{4\pi\varepsilon_0\varepsilon l^2}. \quad (24)$$

The volume of the EDL at $l_{(+)}^2 \approx l_{(-)}^2 \approx l^2$ is

$$V = 4\pi\Delta l \cdot l^2. \quad (25)$$

Considering (23)-(25), the free energy of the EDL is

$$F \approx \frac{n_{\exp}^2 e_0^2 \Delta l}{8\pi\varepsilon_0\varepsilon l^2}, \quad (26)$$

which is the same as relation (3) at $\beta = 1$.

Fig. 2 shows the interfacial tension in the surface layer of micelles of sodium alkyl sulfate homologues in solutions at the respective CMCs and at a temperature of $T = 303$ K (equation 15). The values in Fig. 2 are normalized to asymptote (14).

The absolute values of γ_r in the homologue series ($n_C = 8$, 10, 12, and 14) are 17.42 mJ/m^2, 19.33 mJ/m^2, 20.78 mJ/m^2, and 21.98 mJ/m^2, which is less than the literature estimates for sodium dodecyl sulfate (30÷40 mJ/m^2) [1, 3, 14]. Moreover, the literature sources give no comparative calculations or even estimates for interfacial tension for members of a homological series.

It follows from Fig. 2 that the lower the homologue, the higher its surface activity (the larger decrease in tension) at the curved interfacial boundary between the water solution and hydrocarbon as opposed to the surface tension of the planar boundary between the hydrocarbon layer in a solution and air.

The values of the static permittivity ε in the surface layer of ionic micelles of sodium alkyl sulfates, depending on n_C and β, were calculated from (22) and are shown in Fig. 3. The literature data on ε in the EDL of ionic micelles are highly contradictory, ranging from 2 to 50 [1, 6, 9]. Therefore, in electrostatic calculations for micelles, this value is most often used as a fitting parameter [9].

As follows from (22), with decreasing β and increasing n_C, the squared charge of a micelle increases much greater than the fourth power of its size. This pattern explains the small change in ε with changing parameters (Fig. 3).

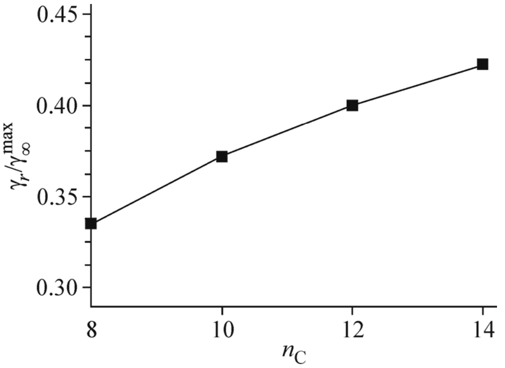

Fig. 2. Reduced effective interfacial tensions of micelles of sodium alkyl sulfate homologues in solutions at their CMCs and at $T = 303$ K. $\gamma_\infty^{\max} = 51.98$ mJ/m^2.

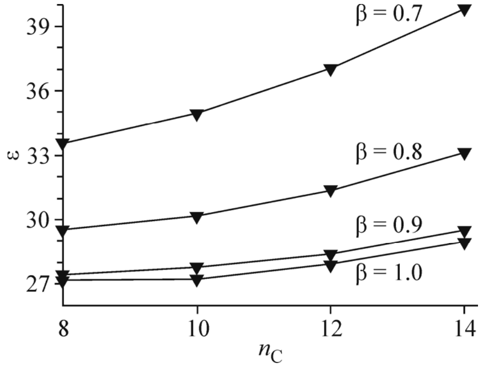

Fig. 3. Static permittivity values in the surface layer of micelles of sodium alkyl sulfate homologues in solutions at their CMCs and at $T = 303$ K.

Taking into account (6) and (24) and at large β ($1 \geq \beta > 0.8$), ε the relationship between and the asymptotic value of interfacial tension in the EDL on the surface of ionic micelle is written as follows:

$$\varepsilon \approx (4/5)\gamma_{\infty}^{\max} / (\varepsilon_0 E^2 \Delta l). \tag{27}$$

CONCLUSIONS

Thus, in this study we have developed and applied a semi-empirical method for determining hydrophobic interactions and the interfacial tension in the surface layer of ionic micelles in surfactant solutions. Together with geometric and electrostatic calculations of an ionic structure, this method allows one to find major surface characteristics for micelles in homological series of surfactants and, importantly, compare these characteristics. If surface tension isotherms are available or experiments for finding these isotherms are relatively simple and inexpensive, the proposed method can also be used to study non-ionic micelles and other nanoscale molecular or ionic clusters in solutions such as, e.g., proteins or biopolymers.

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REFERENCES

1. A. I. Rusanov, *Micelle Formation in Solutions of Surfactants* [in Russia], Khimiya, St. Petersburg (1992).
2. H. Ohshima, T. W. Healy, and L. R. White, *J. Colloid Interface Sci.*, **90**, 17 (1982).
3. A. I. Rusanov, A. P. Grinin, F. M. Kuni, et al., *Zhurn. Obshch. Khim.*, **72**, No. 4, 651 (2002).
4. V. S. Kuznetsov, N. V. Usoltseva, and V. P. Zherdev, *Abstracts. XIX Internat. Conf. on Chemical Thermodynamics in Russia (RCCT-2013). June 24-28, 2013*, M.: MJ THT Publisher, Moscow (2013).
5. A. P. Grinin, A. I. Rusanov, F. M. Kuni, et al., *Kolloid. Zhurn.*, **65**, No. 2, 168 (2003).
6. K. Holmberg, B. Jönsson, B. Kronberg, and B. Lindman, *Surfactants and Polymers in Aqueous Solution*, 2nd Edition, Wiley (2000).
7. A. A. Abramzon, *Surface Active Substances: Properties and Applications* [in Russian], Khimiya, Leningrad (1981).
8. K. Tajima, *J. Chem. Soc. Jpn.*, No. 5, 883 (1973).
9. O. G. Us'yarov, *Kolloid. Zhurn.*, **69**, No. 1, 102 (2007).
10. V. Sanghiran and K. S. Schmitz, *Langmuir.*, **16**, No. 20, 7566 (2000).
11. V. Vlachy, *Annu. Rev. Phys. Chem.*, **50**, 145 (1999).
12. V. A. Andreev, A. Yu. Vlasov, and N. A. Smirnova, *Zhurn. Fiz. Khim.*, **80**, No. 1, 39 (2006).
13. V. S. Kuznetsov, N. V. Usol'tseva, and V. V. Bykov, *J. Struct. Chem.*, **53**, No. 1, 82 (2012).
14. A. I. Rusanov, F. M. Kuni, A. P. Grinin, et al., *Kolloid. Zhurn.*, **64**, No. 5, 670 (2002).
15. V. S. Kuznetsov, N. V. Usol'tseva, A. P. Blinov, et al., *J. Struct. Chem.*, **57**, No. 8, 1577 (2016).
16. D.-H. Kim, S.-G. Oh, and C.-G. Cho, *Colloid Polym. Sci.*, **279**, 39 (2001).
17. G. Gunnarsson, B. Jönsson, and H. Wennerström, *J. Phys. Chem.*, **84**, No. 23, 3114 (1980).
18. E. S. Podchasskaya and O. G. Us'yarov, *Kolloid. Zhurn.*, **67**, No. 2, 213 (2005).
19. I. E. Tamm, *Fundamentals of the Theory of Electricity* [in Russian], Nauka, Moscow (1976).