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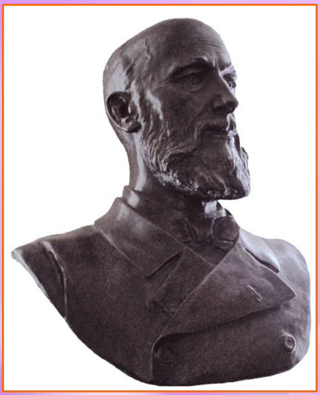

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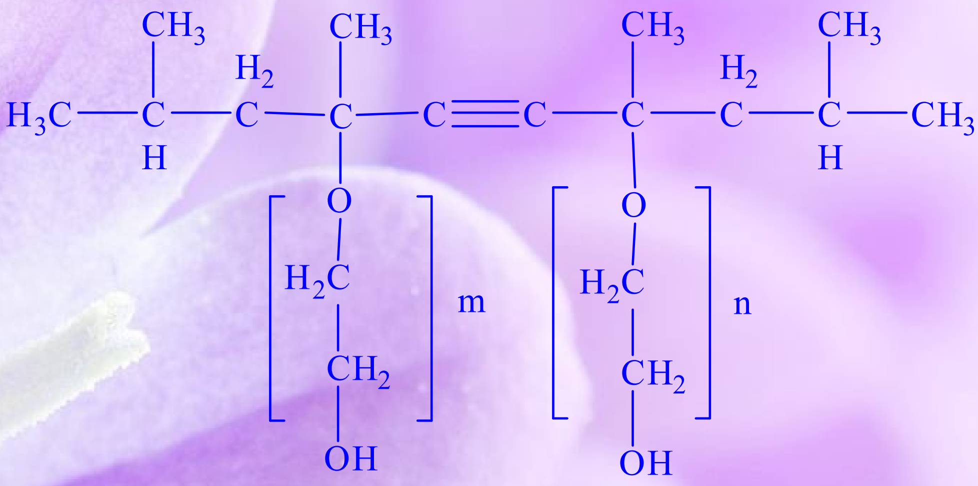

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Colloid-chemical properties of nonionic gemini surfactants Surfynol® 400 series with different degrees of oxyethylation

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Keywords: gemini surfactants, oxyethylated surfactants, Surfynol® 400 series, surface tension, micelle formation, wetting.

Abstract

Adsorption at water – air interface and micelle formation in water for nonionic gemini surfactants *Surfynol® 400 series* with different degree of oxyethylation (30, 10, 3.5 и 1.3, respectively) was investigated. Colloid-chemical properties of surfactants given were studied, their adsorption characteristics and critical micelle concentration (CMC) values were experimentally determined. Decrease of the oxyethylation degree results in increase of the surface activity and decrease of CMC values. The gemini surfactants examined had higher surface activities in comparison with monomeric surfactants (sodium laurylsulphate and sodium laurethsulphate). The less ethoxylated gemini surfactants showed the lowest CMC values (2.1 и 4.6 mmol/l) whereas more ethoxylated gemini surfactants had CMC values close to that of monomeric surfactants (10.0 mmol/l).

The values of average hydrodynamic radius of micelles were determined, the micellar mass and average aggregation number values for gemini surfactants were calculated. The average hydrodynamic radius was slightly dependent of the oxyethylation degree of surfactant whereas aggregation number increased with decreasing of the oxyethylation degree.

The wetting ability of Surfynol® 400 series on teflon surface was studied. The decrease of the surfactant oxyethylation degree resulted in improvement of wetting properties. The wetting ability of highly ethoxylated gemini surfactants was almost equivalent to that of ethoxylated monomeric surfactants (ethoxylated nonylphenols Neonol AF9-10 and Neonol AF9-12).

For gemini surfactants examined cloud point dependence from the oxyethylation degree was typical for ethoxylated nonionic surfactants.

Introduction

Dimeric or gemini surfactants are a special class of surfactants with their own particular chemical structure: two amphiphile parts, similar to monomeric surfactant molecule, connected by a bridge or a spacer. Spacer can be both hydrophobic or hydrophilic, it can have different flexibility and length. This feature of gemini surfactant structure causes their specific physical and chemical properties such as high surface activity, solubilizing effect, low Krafft temperature, extremely low values of CMC (much lower than appropriate monomeric surfactant has) [1-4], and, also, variety of micelle and aggregate forms in bulk phase or adsorption on solid surfaces [1-9]. Due to these properties the surfactants given are very promising for use and are of special interest for researchers.

The aim of the present work was to research colloid chemical properties of nonionic gemini surfactants Surfynol® 400 series, which have the form of oxyethylated tetramethyldecyndiols. They have different oxyethylation degrees their hydrocarbonic radicals being equal. These surfactants meet Food and Drug Administration (FDA) and Environmental Protection Agency (EPA) requirements and are used as efficient molecular defoamers and wetting agents being a part of water-soluble coatings, inks and glue systems. Though there is no open-source data about their colloid chemical properties. In this connection this research is of great importance and practical interest.

Experimental part

1. Materials

Gemini surfactants *Surfynol® 400 series* (Air Products and Chemicals Inc., USA) (fig. 1) were used. Surfynol 485W, 465, 440 и 420 species have different oxyethylation degrees their hydrocarbonic radicals being equal (table 1). In order to establish the regularities that depend on their oxyethylation degrees the adsorption properties of the surfactants given were examined.

For comparison the following wide-spread monomeric surfactants were used:

- sodium laurylsulphate $C_{12}H_{25}SO_4Na$, trademark *Texapon K 12 G (BASF*, Germany). The basic substance concentration is 95-99%;
- sodium laurethsulphate $C_{12}H_{25}(OCH_2CH_2)SO_4Na$, trademark *Texapon 70 N* (*BASF*, Germany). The basic substance concentration is 67-72%;
- Neonol AF9-10 $C_9H_{19}C_6H_4O(C_2H_4O)_{10}H$ (*Nizhnekamskneftekhim*, RF). The basic substance concentration is 98-99 %;
- Neonol AF9-12 $C_9H_{19}C_6H_4O(C_2H_4O)_{12}H$ (*Nizhnekamskneftekhim*, RF). The basic substance concentration is 98-99%.

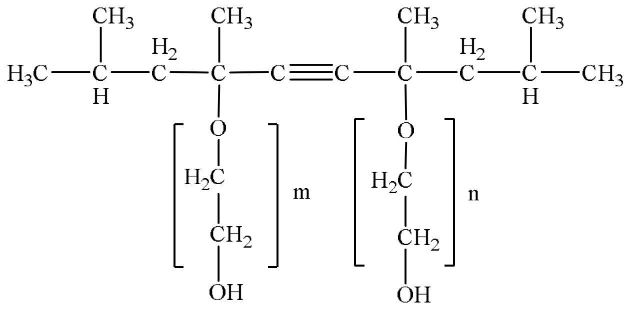

Fig. 1. *Surfynol® 400 series* structural formula

Table 1. Oxyethyl groups content in *Surfynol® 400 series*

Gemini surfactant	Surfynol 485W	Surfynol 465	Surfynol 440	Surfynol 420
Amount of oxyethyl groups (m+n), mol	30	10	3.5	1.3
Molecular weight, g/mol	1546	666	380	283.2
GLB	17	13	8	4
Density, kg/m^3	1079	1038	982	943
Water-solubility at concentration of 1.0 %	soluble	soluble	insoluble	insoluble
Basic substance content, % m./vol.	75	100	100	100

2. Methods

Surfactant solution surface tension was studied by standard du Nouy method using analog tensiometer (*KRÜSS GmbH*, Germany) [10].

Average hydrodynamic radius of micelles was determined by dynamic light scattering method using photocorrelation spectrometer *Photocor Complex* [11], where the light source is a semiconducting laser with wavelength of 654 nm. Scattered light was registrated at 90° angle. The auto-correlation function of scattered light intensity fluctuations and particle size were analyzed using DynaLS program included to the software package of *Photocor Complex*.

Contact angle values of surfactant solutions with different concentrations were determined on a teflon plate, previously defatted with acetone, using cathetometer KM-8 by standard method [10].

Cloud point of 1% surfactant water solutions was determined by standard method [12]. Solution opacity was fixed visually or using photoelectrocolorimeter at wavelength of 420 nm. *Surfynol 440* solution had 0.7-0.8% concentration that is the highest concentration of its water solubility. If the surfactant cloud point was above 100 °C then the surfactant was soluted in sodium chloride solutions with concentration from 3 to 7%, respectively, and the dependence $T_{cp} = f(c_{NaCl})$ was plotted. Cloud point values were determined by extrapolation to zero concentration of sodium chloride.

Results and discussion

1. Adsorption properties of gemini surfactant Surfynol® 400 series

Surface activity values were determined using surface tension isotherms in σ = f(C) coordinates (fig. 2), CMC values were determined using surface tension isotherms in σ = f(lgC) coordinates (table 2, fig. 3, 4).

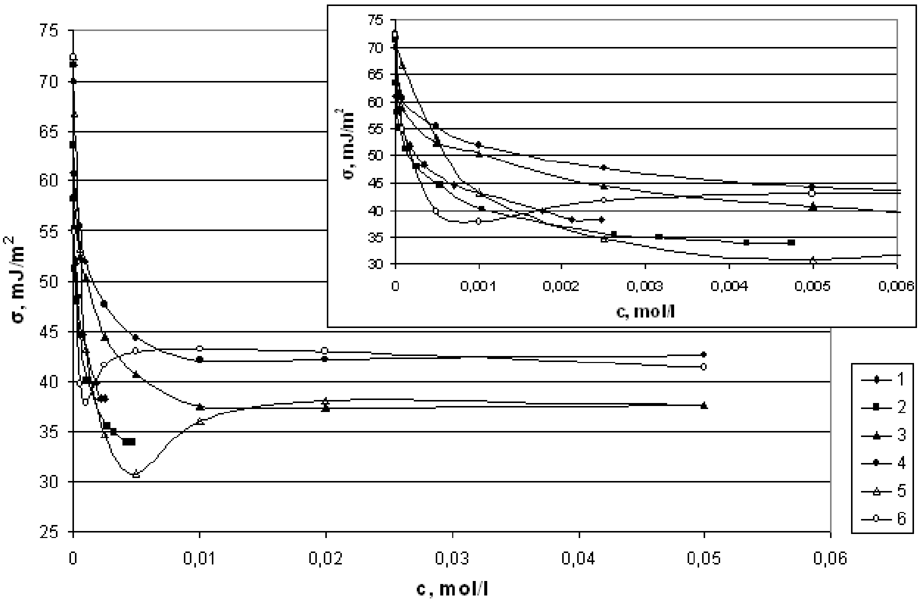

Fig. 2. Surface tension isotherms: 1 – Surfynol 420, 2 – Surfynol 440, 3 – Surfynol 465, 4 – Surfynol 485W, 5 – sodium laurylsulphate, 6 – sodium laurethsulphate

The isotherms plotted were typical for colloid surfactants. There was a fall-off of surface tension when increasing of the concentration up to the region of very low concentrations corresponding to true solubility (10^{-3}-10^{-6} моль/л). Surface tension remained constant after reaching CMC value and at higher concentrations.

There was the legible minimum on surface tension isotherms of sodium laurylsulfate and sodium laurethsulphate. That means the presence of lauryl alcohol impurity formed by the surfactant hydrolyzis that has higher surface activity and adsorbs on the phase border. Lauryl alcohol concentrates in the surface layer with an increase of surfactant concentration. When surfactant concentration is high enough, lauryl alcohol returns back to the bulk phase. This process accounts for the presence of minimum on the surfactant tension isotherms [13].

Also this effect may be caused by alcohol solubilization into surfactant micelles when surfactant concentration is near CMC.

Gemini surfactants CMC values were determined in the ordinary way for nonionic surfactants: as a concentration coinciding with a fracture on surface tension isotherm in σ = f(lg c) coordinates (fig. 3, 4). CMC values of monomeric surfactants were determined in the ordinary way for ionic surfactants using dependence of conductivity on surfactant concentration. The results obtained are shown in table 2.

According to the gained data the obtained CMC values of gemini surfactants with high oxyethylation degree (Surfynol 485W and Surfynol 465) were similar to monomeric surfactants (sodium lauryl- and laurethsulphate). With the further increase of the gemini surfactant oxyethylation degree the CMC value decreased due to lowering of the surfactant water solubility. Thuswise, the ability to form micelles at low concentrations raises with the decrease of the oxyethylation degree. Gemini surfactants with short oxyethylic chains confirmed their high micellization ability at concentrations much lower than monomeric surfactants.

Adsorption properties of gemini surfactants were determined using surface tension isotherms and plot of Shishkovsky`s equation linear form [14] (1). When the development of Shishkovky`s equation, there was an assumption that for substances with high surface activity $\Gamma_{\max} \approx A_{\infty}$.

$$\sigma_0-\sigma = RT\Gamma_{max}\ln(1+Kc) = B\ln(1+Kc) \qquad (1)$$

where $B = RT\Gamma_{max}$ – constant for homologous series, that doesn`t depend on surfactant nature at 20 °C $A \approx 0{,}2$; K – constant that shows raise of surface activity when transition to the next homologous member, $K_{n+1}/K_n = 3\text{-}3.5$.

If surfactant concentration is high enough and therefore Kc>>1, then the summand of 1 in Shishkovky`s equation can be neglected and the equation would be:

$$\Delta\sigma = \sigma_0-\sigma = B\ln K + B\ln c \qquad (2)$$

Thereafter the graphs $\Delta\sigma = f(\ln c)$ were plotted (fig. 5). Value of $B = RT\Gamma_{max} = RTA_\infty$ were determined using slope of the line to X-axis. The results are shown in table 3.

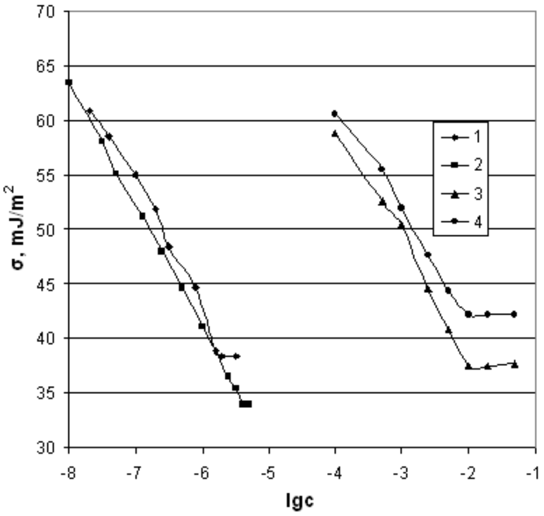

Fig. 3. Surface tension isotherms in $\sigma = f(\lg c)$ coordinates: 1 – Surfynol 420, 2 – Surfynol 440, 3 – Surfynol 465, 4 – Surfynol 485W

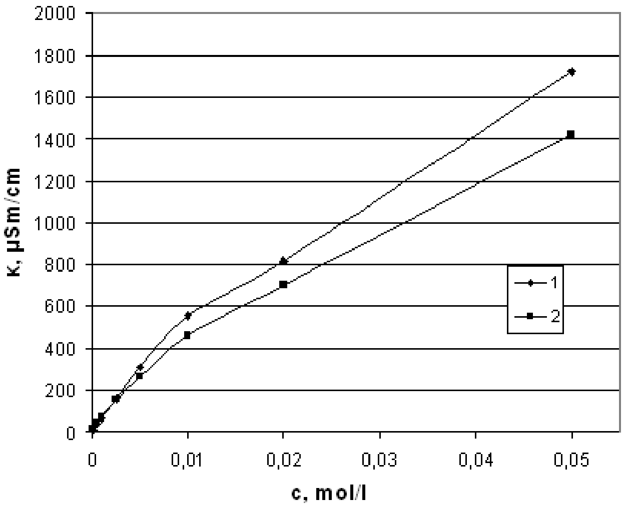

Fig. 4. Dependence of electric conductivity on surfactant water solution concentration: 1 – sodium laurylsulphate, 2 – sodium laurethsulphate

Table 2. CMC values for monomeric and gemini surfactants

	Sodium laurylsulfate	Sodium laurethsulfate	Surfynol 485W	Surfynol 465	Surfynol 440	Surfynol 420
CMC, mmol/l	10	10	10	10	4.6	2.1

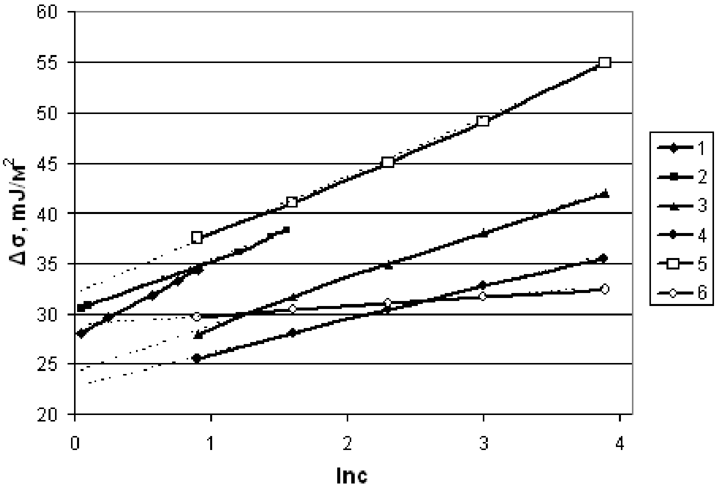

Fig. 5. The plot of Shishkovsky`s equation linear form: 1 – Surfynol 420, 2 – Surfynol 440, 3 – Surfynol 465, 4 – Surfynol 485W, 5 – sodium laurylsulphate, 6 – sodium laurethsulphate

According to the results obtained the conclusions about connection between oxyethylation degree and adsorption properties could be made. Decreasing of the average oxyethylation degree from 30 to 1.3 led to sharp raise of surface activity (54 times) because of decreasing of the surfactant water-solubility.

The absence of free rotation around triple bond –C≡C– is one of the features of molecule spatial structure of these surfactants. That causes restrictions in mutual spatial layout of functional groups. In this case Surfynol® 400 series form stretched liquid-phase pellicle of L_1 type instead of traditional Langmuir`s palisade, caused by two oxyethyl fragments aspiring to lay horizontally and making the whole molecule get oriented parallel to the air-water interface. Thus the higher the oxyethylation degree the higher the value of landing site S_0 and, relatively, lower limited adsorption value A_∞. Such suggestion is proved by literature data [15, 16].

Table 3. Adsorption properties of gemini surfactants *Surfynol® 400 series*

Surfactant Property	Sodium laurylsulphate	Sodium laurethsulphate	Surfynol 485 W	Surfynol 465	Surfynol 440	Surfynol 420
$A_\infty \cdot 10^6$, mol/m^2	2.2	3.1	1.6	2.1	1.9	3.1
$S_0 \cdot 10^{19}$, m^2	55.0	54.0	10.4	8.1	8.7	5.4
δ, Å	6.3	11.0	22.8	13.2	7.4	9.3
g, mN/m·mol	5.6	38.0	10.0	15.7	264	538

When calculating ($\delta = MA_\infty/\rho$) thickness of adsorption layer there was an assumption that surfactant molecule has cylinder form and adsorbed molecule volume equals to δS_0 [14]. Because of molecule spatial structure of surfactant Surfynol® 400 series calculated volumes of adsorbed molecule δS_0 and adsorption layer $\delta S_0 N_A$ are higher than real ones. Hence "cylinder volume" model has an error for surfactants of this kind which makes it difficult to correctly interpret the results obtained.

2. Micellar weight and aggregation value of gemini surfactants Surfynol® 400 series

Hydrodynamic radius of micelles was determined with dynamic light scattering method. Micellar weight values of gemini surfactants were calculated using the following equation:

$$M = \frac{4}{3}\pi r^3 \rho N_A, \tag{3}$$

where M – surfactant micellar weight, g/mol; r – average hydrodynamic radius of micelles, m; ρ – surfactant density, kg/m^3; N_A – Avogadro`s value, mol^{-1}.

Average aggregation number was calculated using the equation:

$$N = \frac{M}{M_r} \tag{4}$$

where M – surfactant micellar weight, M_r – surfactant molecular weight.

The results obtained are shown in table 4.

Table 4. Hydrodynamic radius of micelles, micelle weight and average aggregation number of gemini surfactants Surfynol® 400 series

	Surfynol 485W	Surfynol 465	Surfynol 440	Surfynol 420
r, nm	262.2	295.8	293.9	275.5
$M \cdot 10^{-10}$, g/mol	4.90	6.77	6.28	4.97
$N \cdot 10^{-6}$	31.7	101.7	165.3	175.5

According to experimental data it is obvious that decreasing of surfactant oxyethylation degree led to higher average aggregation value. The reason is that in case of decreasing of surfactant oxyethylation degree, and relative decreasing of surfactant water-solubility it`s energetically beneficial for surfactant molecules to be in micellar form, rather than in molecular form, so molecules tend to unite into large aggregates. Raising of surfactant oxyethylation degree led to decrease of average aggregation number.

Another factor affecting average aggregation number in micelles is features of surfactant molecule spatial structure. Increasing length of oxyethyl fragments in the surfactants examined leads to decrease of average aggregation value due to steric difficulties caused by free spin absence around triple bond –C≡C–, leading to restrictions in spatial layout of functional groups (perpendicular to hydrocarbonic radicals). This factor prevents tight packing of gemini surfactant`s molecules in micelle and leads to decrease of average aggregation number due to raise of oxyethylation degree.

Calculations were made for gemini surfactant solutions with concentrations several times higher than CMC. There was made an assumption that micelles have spherical form. But the measured values of micelles hydrodynamic radius let us know that gemini surfactant`s molecules form not spherical micelles but extended lamellar structures as phospholipids do. It correlates with literature basis that raising concentration of gemini surfactant leads to transformation of aggregate forms from spherical to lamellar or formation of cylindric micelles and rod-like ones or loosely-packed stretched structures like three dimensional grid [1-9]. Form and structure of aggregates depends on many factors like surfactant concentration, polar groups and hydrocarbonic radicals structure (particularly saturation or branching), spacer`s length and flexibility.

3. Gemini surfactants Surfynol® 400 series wetting ability

Wetting isotherms of the examined gemini surfactants were made (fig. 6). Two monomeric surfactants of oxyethylated alkylphenols were used for comparison (Neonol AF9-10 and Neonol AF9-12).

Measuring of contact angles showed that even small concentrations of surfactants led to decrease of contact angle Θ value, increasing surface`s hydrophilization. Till surfactant concentration raises up to CMC, raising of contact angle cosine and wetting ability was observed.

The results of the investigation displayed that gemini surfactants with lower oxyethylation degree gave higher values of contact angle cosine at lower concentrations than gemini surfactants with longer oxyethylation chain. Comparing Surfynol 420 and Surfynol 440 between each other let us notice that their wetting ability varied slightly and sometimes similar, but in general gemini surfactant with lower oxyethylation degree (Surfynol 420) showed better wetting ability.

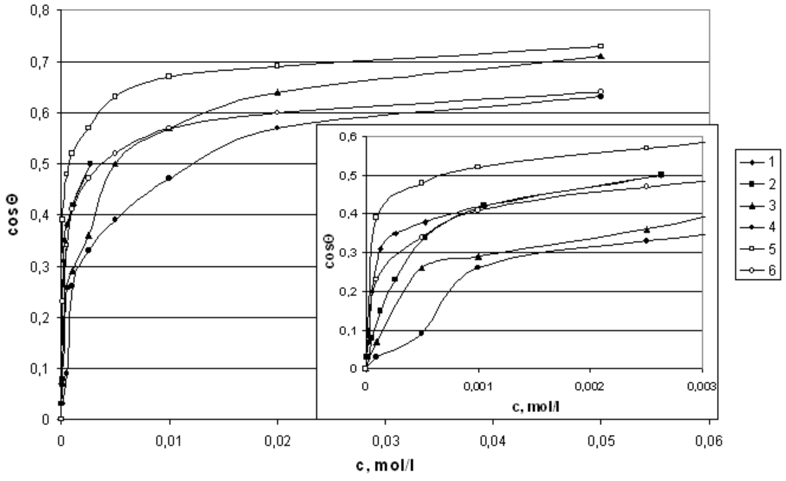

Fig. 6. Teflon wetting isotherms for investigated surfactants: 1 – Surfynol 420, 2 – Surfynol 440, 3 – Surfynol 465, 4 – Surfynol 485W, 5 – Neonol AF9-10, 6 – Neonol AF9-12

Wetting isotherms of gemini surfactant with high oxyethylation degree display that their wetting ability is a bit lower than Neonol`s wetting ability (at the same concentrations).

Wetting ability of the examined surfactants grew with oxyethylation degree decrease, which can be explained by surface activity raise. This fact accords with literature data for oxyethylated nonionic surfactants [17; 18]. Gemini surfactant`s wetting ability tends to grow this way: Surfynol 485W < Surfynol 465 < Surfynol 440 < Surfynol 420, and for monomeric surfactants Neonol AF9-12 < Neonol AF9-10. Comparing gemini surfactant`s wetting ability to Neonol`s one it could be shown that Neonol AF9-12 had higher contact angle cosine than Surfynol 465 or Surfynol 485W, and Neonol AF9-10 had higher contact angle cosine than Surfynol 420 or Surfynol 440.

4. Gemini surfactant Surfynol® 400 series cloud point

Cloud point of the examined gemini surfactants was determined. Cloud points of Surfynol 465 and Surfynol 485W were fixed visually. Surfynol 485W had its cloud point above 80 °C. That fact hinders the experiment so it was necessary to reduce the cloud point value with low-molecular electrolyte. Thus Surfynol 485W was dissolved in 3-7 % sodium chloride water solutions. Cloud point value was determined by the dependence $T_{cp} = f(c_{NaCl})$ extrapolation to zero concentration (fig. 7).

Surfynol 440 has limited water solubility with 1 % concentration. It was difficult to determine the cloud point visually so photoelectrocolormeter was used. Sharp raise of the solution optical density with temperature corresponds to the cloud point (fig. 8). Cloud point for Surfynol 420 is still unknown. It may be connected with fact that at high concentrations (several times higher than CMC) surfactant`s molecules tend to associate and segregate from system as separate drops. The results obtained are shown in table 5.

The experimental data showed us that cloud point`s dependence on oxyethylation degree is typical for oxyethylated surfactants [19-21]. Oxyethylation degree raise led to cloud point increase because surfactant molecule forms higher amount of hydrogen bonds with water molecules, the higher temperature value is required to destroy hydrogen bonds and extraction of the surfactant-enriched phase from the solution.

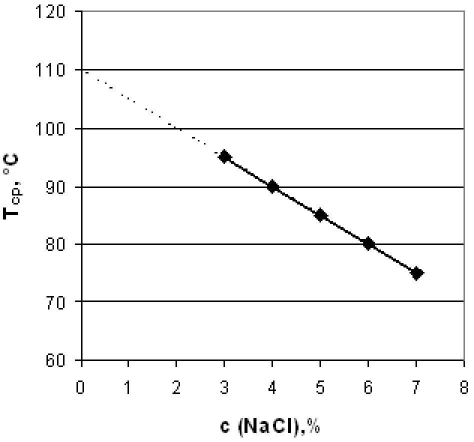

Fig. 7. The dependence of the 1 % Surfynol 485W water solution cloud point on sodium chloride concentration

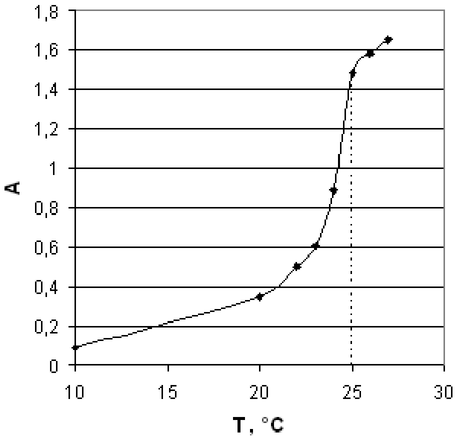

Fig. 8. The dependence of the 1 % Surfynol 440 water solution optical density on temperature

Table 4. Cloud point values for Surfynol® 400 series

	Surfynol 485W	Surfynol 465	Surfynol 440	Surfynol 420
T_{cp}, °C	110	63	25	-

Conclusions

1. Colloid-chemical properties of the gemini surfactant Surfynol® 400 series at water – air interface were studied. Surface tension isotherms were scheduled, CMC values were determined. CMC values decreased while decreasing of surfactant oxyethylation degree. Comparing to monomeric surfactants displayed that only Surfynol 420 and Surfynol 440 had the ability to form micelles at very low concentrations. At the same time Surfynol 465 and Surfynol 485W had CMC values similar to monomeric surfactants. Surface activity grew with reduction of oxyethylation degree. Surfynol 420 and Surfynol 440 showed highest surface activity values.

2. Adsorption properties of the oxyethylated gemini surfactants Surfynol® 400 series were determined: highest monolayer capacity A_∞, landing site value S_0 and monolayer thickness δ. The higher is the oxyethylation degree the higher is the landing site value and, accordingly, the lower is limited adsorption value.

3. Micellar weight and average aggregation number values were determined for Surfynol® 400 series. Raising oxyethyle fragment led to higher micellar weight values, but average aggregation number reduced because of higher water-solubility and steric hindrances caused by surfactant molecule spatial structure.

4. Wetting ability of the Surfynol® 400 series was studied on a teflon surface. It tends to raise at oxyethylation degree diminition because of increasing surface activity. Gemini surfactant`s wetting ability tends to grow this way: Surfynol 485W < Surfynol 465 < Surfynol 440 < Surfynol 420, and for monomeric surfactants Neonol AF9-12 < Neonol AF9-10. Comparing gemini surfactant`s wetting ability to Neonol`s one shows that Neonol AF9-12 had higher contact angle cosine than Surfynol 465 or Surfynol 485W, and Neonol AF9-10 had higher contact angle cosine than Surfynol 420 or Surfynol 440.

5. Dependence of the cloud point on oxyethylation degree of the examined gemini surfactants is typical for oxyethylated surfactants.

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Коллоидно-химические свойства неионогенных gemini-ПАВ марки Surfynol® 400 series с различной степенью оксиэтилирования

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Ключевые слова: димерные поверхностно-активные вещества, gemini-ПАВ, оксиэтилированные ПАВ, *Surfynol® 400 series*, поверхностное натяжение, мицеллообразование, смачивание, температура помутнения.

Аннотация

Исследованы процессы адсорбции на границе вода-воздух и мицеллообразования в водной среде для неионогенных gemini-ПАВ марки Surfynol® 400 series с различной степенью оксиэтилирования (30, 10, 3.5 и 1.3, соответственно). Изучены коллоидно-химические свойства указанных ПАВ, экспериментально определены их адсорбционные характеристики и значения критической концентрации мицеллообразования (ККМ). Уменьшение степени оксиэтилирования приводит к росту поверхностной активности и снижению величины ККМ gemini-ПАВ, а сравнение с мономерными ПАВ (лаурилсульфат натрия и лауретсульфат натрия) показывает, что gemini-ПАВ обладают лучшей поверхностной активностью. Gemini-ПАВ с наименьшими степенями оксиэтилирования показывают самые низкие значения ККМ (2.1 и 4.6 ммоль/л), в то время как gemini-ПАВ с более длинными оксиэтильными участками имеют близкие значения ККМ с мономерными ПАВ (10.0 ммоль/л).

Определены значения гидродинамического радиуса мицелл, рассчитано значение мицеллярной массы и среднего числа агрегации в мицеллах gemini-ПАВ. Гидродинамический радиус практически не зависит от степени оксиэтилирования ПАВ, в то время как число агрегации в мицеллах gemini-ПАВ увеличивается с уменьшением степени оксиэтилирования.

Изучена смачивающая способность Surfynol® 400 series на поверхности тефлона. Смачивание улучшается с уменьшением степени оксиэтилирования ПАВ. Смачивающая способность gemini-ПАВ с высокими степенями оксиэтилирования и мономерных оксиэтилированных НПАВ (оксиэтилированные нонилфенолы Неонол АВ9-10 и Неонол АФ9-12) не имеет существенных различий.

Зависимость температуры помутнения водных растворов данных gemini-ПАВ от степени оксиэтилирования имеет классический вид для оксиэтилированных НПАВ.