

Original articles

Research article

<https://doi.org/10.17308/kcmf.2022.24/9260>**Surface-active and chemical properties of alkylbenzenesulfonic acid – nitric acid – water composites**S. A. Zabolotnykh¹✉, A. D. Solovyev², A. S. Sofronov², M. G. Shcherban²¹*Institute of Technical Chemistry of the Ural Branch of the Russian Academy of Sciences,
3 ul. Akademika Koroleva, Perm 614013, Russian Federation*²*Perm State National Research University,
10 ul. Bukireva, Perm 614068, Russian Federation***Abstract**

Industrially produced anionic surfactant alkylbenzenesulfonic acid is proposed as a reagent for the ionic flotation of metals from acidic media. To establish the possibility of its application using this method, it is necessary to study the surface-active (surface tension, adsorption, cross-sectional area of a molecule in the adsorption layer) and colloidal (particle size, critical micelle concentration, solubilisation) properties of its aqueous and nitric acid solutions.

In this study, a series of solutions with various concentrations of alkylbenzenesulfonic acid and containing various amounts of nitric acid (from 1 to 10 wt%) were prepared. The surface tension of the obtained solutions was determined by the hanging drop method using a DSA 25E tensiometer. The introduction of HNO₃ led to a decrease in the surface tension of alkylbenzenesulfonic acid solutions and in its CMC value in comparison with aqueous solutions. On surface tension isotherms with a nitric acid content of 5 and 10 wt%, the presence of several inflections was found, which indicates a stepwise micelle formation. The values of surface activity and Gibbs energies of micelle formation of alkylbenzenesulfonic acid in aqueous and nitric acid solutions were calculated. Adsorption isotherms were constructed from the results of processing the curves of the surface tension of alkylbenzenesulfonic acid solutions. With small amounts of HNO₃ (1 and 2%), the limiting adsorption value of the anionic surfactant significantly increased as compared to the aqueous solution. A further increase in the acidity of the medium led to a decrease in the maximum on the adsorption isotherm. In the presence of an inorganic acid, the monomolecular layer of the surfactant first significantly loosened and then gradually became denser with an increase in acidity. The values of the limiting adsorptions, the adsorption equilibrium constants and the Gibbs energies of adsorption at the liquid-gas interface were calculated using the obtained isotherms. The solubilising ability of alkylbenzenesulfonic acid in relation to the Sudan I dye was determined photometrically using a UNICO 1201 spectrophotometer. With an increase in the solution acidity and the surfactants content the amount of solubilised dye increased.

Keywords: Alkylbenzenesulfonic acid, Surfactant properties, Nitric acid, Adsorption, Solubilisation**Funding** This work was performed in accordance with the state task, state registration No. AAAA-A18-118032790022-7.**Acknowledgements:** This work was carried out using the equipment of the Core Facilities Centre “Research of materials and matter” of Perm Federal Research Centre of the Ural Branch of the Russian Academy of Sciences (PFRC UB RAS).**For citation:** Zabolotnykh S. A., Solovyev A. D., Sofronov S. A., Scherban M. G. Surface-active and chemical properties of alkylbenzenesulfonic acid – nitric acid – water composites. *Condensed Matter and Interphases*. 2022;24(2): 204–210. <https://doi.org/10.17308/kcmf.2022.24/9260>**Для цитирования:** Заболотных С. А., Соловьев А. Д., Софронов А. С., Щербань М. Г. Поверхностно-активные и химические свойства композиций алкилбензолсульфокислота – азотная кислота – вода. *Конденсированные среды и межфазные границы*. 2022;24(2): 204–210. <https://doi.org/10.17308/kcmf.2022.24/9260>✉ Svetlana A. Zabolotnykh, zabolotsveta@mail.ru

© Zabolotnykh S. A., Solovyev A. D., Sofronov S. A., Scherban M. G., 2022



The content is available under Creative Commons Attribution 4.0 License.

1. Introduction

Solutions of surfactants are widely used in various industries: the production of detergents and cosmetics, food products and dyes, oil production and refining technology, various chemical, biochemical and pharmaceutical industries, where surfactants can be used to influence the speed and direction of processes, to synthesize mesoporous materials, etc.

A feature of surfactants is the ability to spontaneously form structured aggregates (micelles) in solution, which determines the particular practical importance of such systems. The size and shape of surfactant aggregates in solution is determined by the balance of interactions between the hydrophilic and hydrophobic parts of surfactant molecules. While hydrophobic interactions of surfactant molecules promote the growth of micelles, the repulsion between hydrophilic groups on the micelle surface limits their growth. The addition of low molecular weight inorganic compounds (salts, acids), ions of which shield the electrostatic repulsion of surfactant hydrophilic groups on the micelle surface, increases surface activity and enhances surfactant adsorption at the interphase boundary. In addition, inorganic electrolytes affect the entire complex of colloid-chemical properties of surfactants, increase their micelle-forming ability, solubilising effect, wetting, and promote, in particular, the transition of spherical micelles to cylindrical ones. If cylindrical micelles already exist in the solution, then the addition of an inorganic low molecular weight salt can lead to an increase in their length. In this case, the effect is determined not only by the amount of salt added to the surfactant solution, but also by the chemical structure of the ions formed during its dissociation. Thus, since the structure of surfactant micelles is highly sensitive to the type and amount of the inorganic low molecular weight salt added to the solution [1–3], for the control of the surface active and rheological properties of surfactant solutions electrolytes are used [4].

The anionic surfactant alkylbenzenesulfonic acid (ABSA) was proposed as a reagent for ionic flotation. ABSA mixes well with water, forms a stable foam, forms precipitates with metal ions, and it is also a fairly accessible reagent.

To establish the possibility of using ABSA as a flotation agent in acidic solutions, it is necessary to study the effect of the concentration of inorganic acids on the surfactant and micellar properties of ABSA solutions [5]. Previously, the effect of hydrochloric acid on the colloidal properties of alkylbenzenesulfonic acid was studied [6]. This study is devoted to the investigation of the colloidal properties of aqueous solutions containing ABSA and nitric acid.

2. Experimental

Reagents. Anionic surfactant alkylbenzenesulfonic acid (general formula $C_nH_{2n+1}C_6H_4SO_3H$, where $n = 10–14$, the content of the main substance is 96.8%, the average molecular weight is 320.9 g/mol, OOO KINEF). The initial ABSA solution was prepared by dissolving an accurate weighed quantity in distilled water. Solutions with lower concentrations were prepared by appropriate dilution. Sudan I dye (1-(phenylazo)-2-naphthol, chemically pure reagent, Sigma-Aldrich). Nitric acid, concentrated ($\rho = 1.49 \text{ g/cm}^3$, chemically pure reagent, RM Engineering). HNO_3 content of 1, 2, 5, and 10% in mixtures were created by introducing the calculated amount of concentrated acid.

All experiments were performed at a temperature of 25 °C.

Devices. The surface tension of ABSA – HNO_3 – H_2O systems at the liquid-gas interface was determined by the hanging drop method using a DSA 25E tensiometer manufactured by KRUSS.

The critical micelle concentration (CMC) of ABSA at different HNO_3 content was determined based on surface tension isotherms: the content of surfactant, at which the curvilinear section of the graph become straight line parallel to the abscissa axis was determined in semilogarithmic coordinates [7, 8]. The surface tension value at the water-air boundary at a given temperature was taken from the reference book [9]. All data presented in the study were obtained by averaging the results of three measurements. Surface activity was calculated as the slope of the initial section of the surface tension isotherm:

$$g = -\lim_{c \rightarrow 0} \frac{d\gamma}{dc}, \quad (1)$$

C is the concentration of the ABSA solution (kg/m^3); γ is the surface tension of the solution (N/m).

Based on the CMC values obtained, the Gibbs energies of micelle formation were calculated using the formula:

$$\Delta_m G = RT \ln \text{CMC}, \quad (2)$$

$R = 8.314 \text{ J}/\text{mol}\cdot\text{K}$ is the universal gas constant; $T = 298 \text{ K}$ is the absolute temperature; CMC is the critical micelle concentration (mol/m^3).

Adsorption G ($\mu\text{mol}/\text{m}^2$) of ABSA at the liquid-gas boundary was calculated based on the surface tension isotherms according to the equation:

$$G = -\frac{1}{RT} \frac{d\gamma}{d \ln C}, \quad (3)$$

C is the concentration of the ABS solution (kg/m^3); $R = 8.314 \text{ J}/\text{mol}\cdot\text{K}$ is the universal gas constant; $T = 298 \text{ K}$ is the absolute temperature; γ is the surface tension of the solution (N/m).

Based on the obtained adsorption data, the C/G values were calculated and the dependence $C/G - f(C)$ was plotted. According to the graph, the values of the limiting adsorption G_m (as the slope α) and adsorption equilibrium constant K (m^3/mol), as the Y-interception is equal to $1/(G_m K)$ were determined. The determination of limiting adsorption value allows to calculate the parameters of the monomolecular layer: the cross-sectional area of a molecule S (nm^2) and axial length d (nm) of the molecule according to the following formulas:

$$S = \frac{1}{G_m N_A}, \quad (4)$$

$$\delta = \frac{G_m M}{\rho}, \quad (5)$$

G_m is the limiting Gibbs adsorption (mol/m^2); $N_A = 6.02 \cdot 10^{23} \text{ mol}^{-1}$ is the Avogadro number; M is the molar mass of the surfactant (kg/mol); ρ is the surfactant density (kg/m^3).

The Gibbs energies $\Delta_{\text{ads}} G$ of adsorption at the liquid-gas interface were calculated based on the values of the adsorption equilibrium constants K according to the equation:

$$\Delta_{\text{ads}} G = -RT \ln K, \quad (6)$$

$R = 8.314 \text{ J}/\text{mol}\cdot\text{K}$ is the universal gas constant; $T = 298 \text{ K}$ is the absolute temperature; K is the adsorption equilibrium constant (m^3/mol).

The solubilising ability S (mg/dm^3) of ABSA – HNO_3 – H_2O compositions was studied by absorption photometry in relation to the oleophilic dye Sudan I [10, 11], which is insoluble in water but soluble in the hydrophobic part of micelles. The dye content in the solution was determined by measuring the optical density of the solution in 0.5 cm cuvettes using a UNICO 1201 spectrophotometer at $\lambda = 400 \text{ nm}$. In prepared solutions of surfactant compositions with a volume of 20 cm^3 dye (20 mg) was added. The flasks were stoppered, mixed using Millab Unimax 1010 shaker for 60 min until equilibrated, then the contents were filtered through filter paper. According to the calibration chart ($A = 0.0147 \cdot C$ (mg/dm^3), $R^2 = 0.9983$) [6] the amount of solubilised dye per unit volume of the solution was determined.

Molar solubilising ability S_m (mg/g) was calculated as the ratio of the obtained value of S to the ABSA concentration (c , g/dm^3) [12]:

$$S_m = \frac{S}{c}. \quad (7)$$

3. Results and discussion

3.1. Surface tension and micellization

The introduction of alkylbenzenesulfonic acid leads to a sharp decrease in the surface tension of both water and aqueous solutions of nitric acid (Fig. 1). The decrease in the value of γ reflects the process of filling the surface layer with surfactant molecules and reaching the

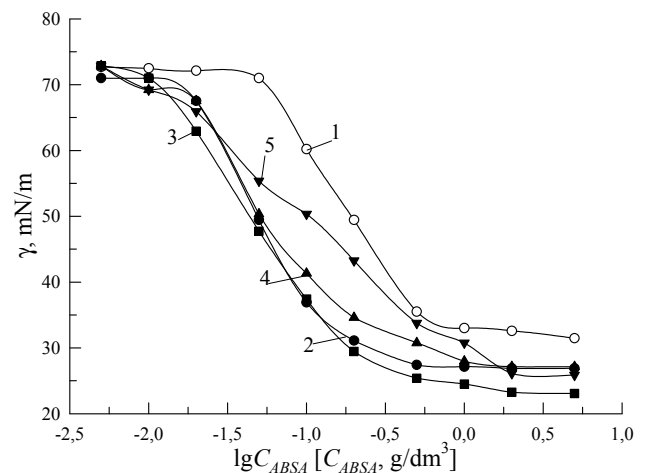


Fig. 1. Surface tension isotherms of ABSA acid compositions: 1 – without acid; 2 – 1% HNO_3 ; 3 – 2% HNO_3 ; 4 – 5% HNO_3 ; 5 – 10% HNO_3

limiting value of adsorption. After the critical micelle concentration is reached, the decrease in surface tension with an increase in the ABSA content slows down, which is associated with the formation of micelles in the solution [13].

In the presence of an inorganic acid, the decrease in surface tension is more significant than in pure water. The introduction of nitric acid at concentrations of 1 and 2 wt. % led to an increase in micelle-forming ability, expressed in a decrease in CMC values and surface tension during CMC, which was caused by dehydration of the polar groups of surface-active ions in the presence of an electrolyte. Also, with an increase in the concentration of inorganic acid, a decrease in the surface tension of the solution started at a lower content of ABSA.

An increase in the content of HNO_3 up to 5 and 10% led to the appearance of two inflections on the surface tension curves (Fig. 1, curves 4 and 5). Probably, with an increase in the concentration of the inorganic acid, the dissociation of ABSA, as a weaker acid, is suppressed ($pK_a = 2.17$ [14]), as a result it behaves similarly to a nonionic surfactant and forms pre-micellar structures at lower concentration regions [15]. With an increase in the surfactant content, the amount of ABSA anions increased, and mixed micelles were formed. This formation was accompanied by the appearance of another step on the surface tension isotherm. The obtained CMC_1 values and values of the surface activity and Gibbs energy of micellization calculated using formulas (1) and (2) depending on the ionic strength of the medium are presented in Table 1. Negative values of the Gibbs energy indicated the spontaneity of the micelle formation process. The introduction of HNO_3 led to a sharp increase in the surface activity of ABSA,

the negative value of $\Delta_m G$ slightly increased in absolute value with increasing acidity.

3.2. Adsorption at the liquid-gas interface

The increase in the acidity of the medium in the transition from water to 10 wt% HNO_3 changed the conditions for the formation of a monomolecular layer, compared with an aqueous solution, which was expressed as the change in the height and position of the maximum of adsorption isotherms, calculated based on surface tension isotherms (Fig. 2). The initial increase in acidity sharply increased the value of the limiting adsorption, however, a subsequent increase in the acid content lowered the value of G_m .

The introduction of nitric acid at concentrations of 1 and 2% led to a “loosening” of the monomolecular layer, which was expressed by an increase in the area occupied by one surfactant molecule (Table 2). In this case, the adsorption equilibrium constants (K) and the absolute values of the Gibbs energies

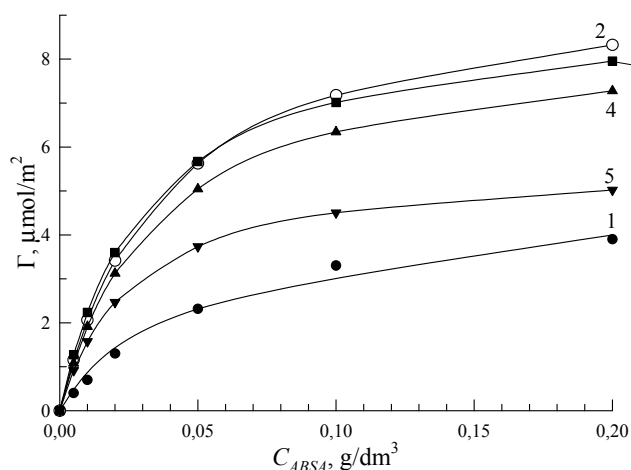


Fig. 2. ABSA adsorption isotherms at the liquid-gas interface: 1 – without acid; 2 – 1% HNO_3 ; 3 – 2% HNO_3 ; 4 – 5% HNO_3 ; 5 – 10% HNO_3

Table 1. Influence of the ionic strength of the solution on the surface-active characteristics of ABSA – HNO_3 – water compositions

C_{HNO_3} , %	I , mol/dm ³	CMC, g/dm ³	γ , mN·m ² /kg	$\Delta_m G$, kJ/mol
0.00	0.00	0.50	74.72	–33.17
1.00	0.16	0.15	252.83	–36.15
2.00	0.32	0.20	217.05	–35.44
5.00	0.79	0.20 ($\text{CMC}_2 = 0.80$)	217.05	–35.44
10.00	1.59	0.02 ($\text{CMC}_2 = 0.1$)	347.00	–41.11

Table 2. Influence of the ionic strength of the solution on the parameters of the ABSA monomolecular layer at the liquid-gas interface

C_{HNO_3} , %	I , mol/dm ³	G_m , mmol/m ²	K , m ³ /mol	$\Delta_{\text{ads}} G$, kJ/mol	S , nm ²	δ , nm
0.00	0.00	5.09	9.65	-5.62	1.96	1.58
1.00	0.29	9.90	26.31	-8.10	1.01	3.07
2.00	0.58	9.19	32.17	-8.60	1.09	2.85
5.00	1.45	8.54	28.89	-8.33	1.17	2.65
10.00	2.92	5.67	38.49	-9.04	1.76	1.76

of adsorption, which characterize the adsorption, increased. With an increase in the content of inorganic acid, the transfer of 1 mol of surfactant from the solution to the surface layer requires less energy than in an aqueous solution.

3.3. Solubilisation

The mechanism of solubilisation is largely determined by the nature of the surfactant. In the case of ionic surfactants, an oleophilic dye containing polar groups is introduced into the surface layer of micelles, where its molecules are located between surfactant molecules, orienting parallel to them and turning polar groups into the aqueous phase. In this case, the solubilisate can dissolve both in the core and in the hydrophilic shell of micelles [16].

In the initial section, the amount of solubilised dye slowly increased with increasing surfactant concentration. Solubilisation isotherms in aqueous solution and in the presence of 1 and 2% HNO₃ almost coincided (Fig. 3). In a medium with 5 and 10% inorganic acid, the solubilisation of the dye increased abruptly with an increase in the ABSA content, which was probably due to the transition from one type of micelles to another.

At high concentrations of nitric acid, an increase in the solubilising capacity was also observed, which was probably due to the protonation of the dye and the formation of an ion associate with the ABSA anion. Various additives especially affect colloidal dissolution, contributing to the enlargement of micelles due to their hydrophobization (i.e., lowering the effective degree of dissociation and hydration). The molar solubilisation curves of Sudan I have maxima at an ABSA content of 0.01 g/dm³, only the degree of the manifestation of the maximum changed with increasing acidity (Fig. 4). With a further increase in the concentration of ABSA, the

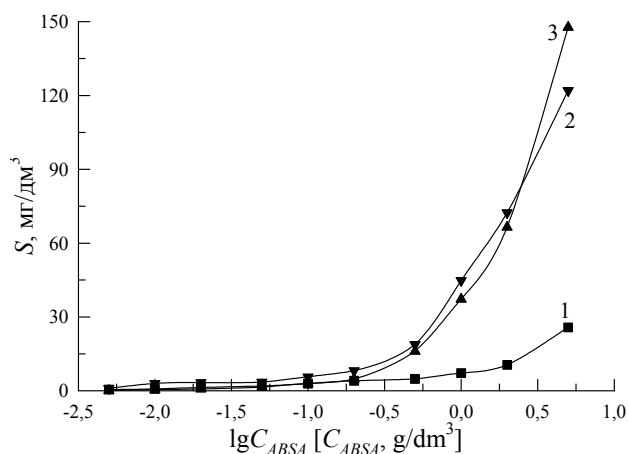


Fig. 3. Effect of nitric acid concentration on the solubilisation of the Sudan I dye in ABSA solutions: 1 – without acid, 1 and 2% HNO₃; 2 – 5% HNO₃; 3 – 10% HNO₃

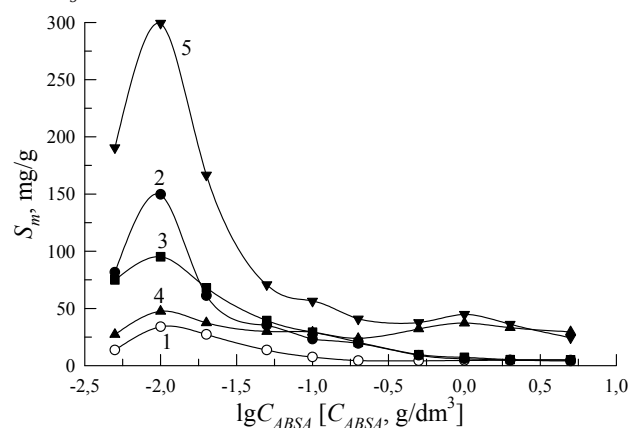


Fig. 4. Effect of nitric acid concentration on the molar solubilisation of the Sudan I dye in ABSA solutions: 1 – without acid; 2 – 1% HNO₃; 3 – 2% HNO₃; 4 – 5% HNO₃; 5 – 10% HNO₃

number of moles of solubilised dye per 1 mole of surfactant remained constant.

4. Conclusions

The introduction of nitric acid into aqueous solutions of alkylbenzenesulfonic acid changed the structure of surfactant monomolecular layers

and led to an increase in the surface activity of ABSA, expressed in a decrease in the CMC value. In more concentrated nitric acid solutions (5 and 10%), micelle formation proceeded in several stages. The processes of micellization and adsorption of surfactants at the liquid-gas interface proceeded spontaneously, while with an increase in the acidity of the medium, absolute values of Gibbs energies of these processes increased. The introduction of nitric acid had a positive effect on the solubilising ability of ABSA aqueous solutions in relation to the oleophilic dye Sudan I, which can be caused by the protonation of the dye and the formation of an ion associate of the solubilisate with the ABSA anion.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

1. Rusanov A. I. *Micellization in surfactant solutions*. Leningrad: Khimiya Publ.; 1992. 280 p. (In Russ.)
2. Nagarajan R. Molecular Packing Parameter and Surfactant Self-Assembly: The Neglected Role of the Surfactant Tail. *Langmuir*. 2002;18: 31–38. <https://doi.org/10.1021/la010831y>
3. Hoffmann H. Viscoelastic surfactant solutions. In: *Structure and flow in surfactant solutions*. Washington: ACS; 1994. pp. 2–31. <https://doi.org/10.1021/bk-1994-0578.ch001>
4. Ismagilov I. F., Kuryashov D. A., Vagapov B. R., Bashkirtseva N. Yu. Effect of electrolyte on micellization and rheological properties of aqueous solutions of sodium oleyl methyl taurate. *Bulletin of the Technological University Vestnik*. 2014;17(18): 46–50. (In Russ.). Available at: <https://www.elibrary.ru/item.asp?id=22480138>
5. Radushev A. V., Koltashev D. V., Nasrtdinova T. Yu., Shcherban M. G., Chekanova L. G., Plotnikova M. D. Physical and chemical properties of N-(2-Hydroxyethyl) alkylamines. *Journal of Applied Chemistry*. 2010;83(8): 1475–1479. <https://doi.org/10.1134/S107042721008029X>
6. Zabolotnykh S. A., Shcherban M. G., Solovyev A. D. Effect of the hydrochloric acid concentration on the surface-active and functional characteristics of linear alkylbenzenesulfonic acid. *Bulletin of the Karaganda University. CHEMISTRY series*. 2020;99(3): 72–79. <https://doi.org/10.31489/2020Ch3/72-79>
7. Emello G. G., Bondarenko Zh. V., Grukhalova Ye. V., Firsova L. D. Colloidal-chemical properties of technical preparations of surfactants used in the cosmetic industry. *Proceedings of BSTU*. 2012;151(4): 20–24. (In Russ.). Available at: <https://www.elibrary.ru/item.asp?id=44192982>
8. Aivazov B. V. *Workshop on the chemistry of surface phenomena and adsorption*. Moscow: Vysshaya Shkola Publ.; 1973. 206 p. (In Russ.)
9. Ravdel A. A., Ponomareva A. M. *Brief reference book of physical and chemical quantities*. Leningrad: Khimiya Publ.; 1983. 232 p. (In Russ.)
10. Demyantseva E. Yu., Kopnina R. A. *Solubilization in solutions of surfactants: educational and methodical manual*. StPb.: SPbGTURP Publ.; 2015. 31 p. (In Russ.)
11. Vasilieva E. A., Valeeva F. G., Yeliseeva O. E., Lukashenko S. S., Saifutdinova M. N., Zakharov V. M., Gavrilova E. L., Zakharova L. Ya. Supramolecular nanocontainers based on hydrophobized calix[4]resorcinol: Modification by gemini surfactants and polyelectrolyte. *Macroheterocycles*. 2017;10(2): 182–189. <https://doi.org/10.6060/mhc170509v>
12. Stas I. E., Shipunov B. P., Repeykova L. Yu., Mikhaylova O. P. The influence of the electromagnetic field in the radio-frequency band on pigment sudan III solubilization by micelles of sodium dodecylsulfate and cetylpyridinium chloride in aqueous solutions. *The News of Altai State University*. 2012;75(3-1): 194–198. (In Russ., abstract in Eng.). Available at: <https://www.elibrary.ru/item.asp?id=17877681>
13. Holmberg K., Jonsson B., Kronberg B., Lindman B. *Surfactants and polymers in aqueous solution*. 2nd Edn. John Wiley & Sons; 2002. 562 p.
14. Zabolotnykh S. A., Zhelnina V. O., Denisova S. A., Elokhov A. M., Lesnov A. E. The water – antipyrine – alkyl benzene sulfonic acid stratifying system to extract metal ions. *Journal of the Siberian Federal University. Chemistry*. 2017;10(4): 536–544. (In Russ., abstract in Eng.). <https://doi.org/10.17516/1998-2836-0047>
15. Neudachina L. K., Petrova Yu. S. *Application of surfactants in analysis: A Study Guide*. Ekaterinburg: UrFU Publ.; 2017. 76 p. (In Russ.)
16. Smit R. A., Demiantseva E. Yu., Andranovich O. S., Filippov A. P. Features of solubilizing effect of amphiphilic compounds during pulp deresination. *Bulletin of Higher Educational Institutions. Russian Forestry Journal*. 2021;379(1): 180–191. (In Russ., abstract in Eng.). <https://doi.org/10.37482/0536-1036-2021-1-180-191>

Information about the authors

Svetlana A. Zabolotnykh, Cand. Sci. (Chem.),
Researcher, Laboratory of Organic Complexing
Reagents, Institute of Technical Chemistry Ural Branch
of RAS (Perm, Russian Federation).

<https://orcid.org/0000-0001-8307-0386>
zabolotsveta@mail.ru

Aleksandr D. Solovyev, student, Faculty of
Chemistry, Perm State National Research University
(Perm, Russian Federation).

<https://orcid.org/0000-0002-7852-3683>
solovev_s92@mail.ru

Aleksey S. Sofronov, student, Faculty of Chemistry,
Perm State National Research University (Perm,
Russian Federation).

sofronov_alexey@mail.ru

Marina G. Scherban, Cand. Sci. (Chem.), Associate
Professor, Physical Chemistry Department, Perm State
National Research University (Perm, Russian
Federation).

<https://orcid.org/0000-0002-6905-6622>
ma-sher74@mail.ru

*Received 20.01.2022; approved after reviewing
28.01.2022; accepted for publication 15.04.2022;
published online 25.06.2022.*

Translated by Valentina Mittova

Edited and proofread by Simon Cox