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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

SYNTHESIS OF NEW SURFACTANTS BASED ON PROPYLENE OXIDE AND EPICHLOROHYDRIN COOLIGOMERS

Speciality:	2304.01– Macromolecular chemistry 2314.01 – Petrochemistry
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GENERAL DESCRIPTION OF THE WORK

The current state of the problem and its relevance. It is known that surfactants have several unique properties and these properties vary depending on their structure. Thus, colloidal-chemical indices of surfactants depend on the nature of their polar (hydrophilic) and non-polar (hydrophobic) groups. Their colloidal-chemical indices differ depending on the length of the alkyl chain in the hydrophobic part, the structure of the hydrophilic part, and the number of polar groups.

It's known from the literature that oligomeric propoxy derivatives obtained by catalytic interaction of a number of members of higher aliphatic monoatomic alcohols, polyatomic aliphatic alcohols and higher carboxylic acids with propylene oxide (PO), heterochain oligomeric compounds containing chloropropoxy units and obtained by the interaction of these derivatives with epichlorohydrin (ECH) in the presence of a catalyst possess both surface activity and valuable, practically useful properties[1].

Synthesis of surface-active cooligomers containing units of PO and ECH in a heterochain and their detailed study is of a special interest. These surfactants make possible formation of new ionic groups in a heterochain as a result of quaternization reaction (using ethanolamines) in the presence of CH_2Cl groups of epichlorohydrin units. As a result, it's possible to regulate the nature of changes in physicochemical properties as well as applicable properties of the surfactants due to the sequence of chlorooxypropylene and oxypropylene units of surface-active cooligomers and effect of ethanolamine.

Recently, a significant attention is paid to the study of obtaining process and properties of the products formed by the interaction of a special class of polymer-surfactant complexes – polyelectrolites with oppositely charged surfactants. Study of polyelectrolyte-surfactant

[1] Asadov Z.G. Synthesis, physicochemical characteristics and properties of oligomeric surfactants based on pentaerythritol and propylene oxide / Z.G.Asadov, R.A.Ragimov, G.A.Akhmedova // Russian Journal of Applied Chemistry, 2011. Vol. 84. №.7, - p. 1188−1194.

complexation depending on the nature of cationic surfactants headgroup and polyelectrolyte chain, effect of these factors on colloidal-chemical properties of the obtained complexes as well as definition of the application areas is of great interest. Investigation of these issues, obtainment of polymer - surfactant complexes and studying of development of methods for managing their properties is relevant both from a scientific and practical point of view and has a practical value.

In the light of the above, the dissertation deals with a relevant topic – obtaining non-ionic surface-active cooligomers based on higher monocarboxylic acids and epoxides, transformation of them into ionic surfactants with ethanolamines, obtaining polyelectrolite-surfactant complexes by stirring cationic surfactants with polyelectrolytes, study and application of the useful properties of the obtained products.

The object and the subject of the research. The object of the research is synthesis of cooligomer surfactants based on acids and two epoxy compounds (PO and ECH) at the same time, the complexes of meth(acrylate) polyelectrolytes with catonic surfactants obtained by the interaction with ethanolamines. The subject of the research is studying of petroleum-collecting, petroleum-dispersing, petroleum-squeezing properties of non-ionic and cationic surfactants of oligomeric nature, as well as polyelectrolyte-surfactant complexes by changing the sequence of chloroxypropylene and oxypropylene units in a heterochain.

The purpose and objectives of the research. Synthesis of new ionic and non-ionic surfactants based on higher monocarboxylic acids (C_{12}, C_{14}), PO, ECH and alkanolamines, obtaining complexes based on them and meth(acrylate) polyelectrolytes, determination of physicochemical properties and colloidal-chemical parameters of the products, determination of the products properties for collecting petroleum films from water basins surfaces having different range of mineralization as well as squeezing more petroleum out of layers by studying structure-dependent properties via changing the structure of obtained surfactants.

The following researches were carried out in the dissertation to achieve the goal:

- obtainment of non-ionic surfactants based on the interaction of lauric (LA), myristic (MA) acids with PO and ECH, transformation of them into ionic surfactants with ethanolamines, study of the obtained products;
- obtainment and study of cationic surfactants by the interaction of aminoalcohols (obtained by the reaction of alkylamines with PO) with ethylenechlorohydrin (ECH);
- obtainment and study of polyelectrolyte-surfactant complexes of the synthesized ionic surfactants with neutralized and oxypropylated polyacrylic (PAA) and polymetacrylic (PMAA) acids;
- identification of the synthesized surfactants by various physical and chemical research methods, as well as study of petroleum-collecting, petroleum-dispersing, petroleum-squeezing, antimicrobial properties.

Investigation methods. Contemporary physical and chemical methods (IR, UV and NMR spectroscopy, derivatography, dynamic light scattering, elemental analysis, conductometry, tensiometry, pH-metry, differential scanning calorymetry, viscometry etc.) were used for identification of the products obtained by the researches and determination of their properties.

The main provisions submitted to the defence:

- cationic surfactants were obtained by the reaction of oligomeric non-ionic surfactants containing units of chloroxypropylene and oxypropylene based on higher monocarboxylic acids with ethanolamines, changing nature of surfactants properties was determined by the effect of sequence of chloroxypropylene and oxypropylene units and ethanolamines;
- colloidal-chemical properties of new surfactants containing hydroxyethyl and hydroxypropyl groups based on alkylamines, PO and ECH were determined, thermodynamic parameters of micelle formation and adsorption processes were calculated;
- polyelectrolyte-surfactant complexation was studied depending on the nature of headgroup of cationic surfactants and polyelectrolyte chain and the effect these factors on colloidal-chemical properties of the obtained complexes were studied;

- ability of the obtained surfactants to localize thin petroleum films spread over water surface was studied, useful application properties (petroleum-squeezing and antimicrobial) was defined.

Scientific novelty of the investigation. For the first time:

- corresponding non-ionic surface-active cooligomers (by changing sequence of chloroxypropylene and oxypropylene units) were synthesized on the basis of higher monocarboxylic acids (C_{12} or C_{14}), PO and ECH;
- oligomers synthesized on the basis of higher monocarboxylic acids (C_{12} or C_{14}) and C_3-epoxides were transferred to ammonium salt and resulted in transformation of non-ionic surfactants into cationic surfactants;
- the complexes were developed on the basis of cationic surfactants obtained on the basis of higher monocarboxylic acids (C_{12} or C_{14}), ECH, PO (at a mole ratio of 1:1:2, respectively) and ethanolamines [diethanolamine (DEA) and triethanolamine (TEA)] with (meth)acrylate polyelectrolytes;
- aminoalcohols synthesized by interaction of alkylamines (C_8H_{17},C_9H_{19},$C_{12}H_{25}$,$C_{16}H_{33}$) with PO (1:1 and 1:2 mole ratio) were transformed into corresponding ammonium salts by ECH;
- the complexes were developed based on alkylamine ($C_{12}H_{25}$) with PO at a mole ratio of 1:1 and 1:2 and ECH-based cationic surfactants with (meth)acrylate polyelectrolytes;
- surface tension of aqueous solutions of synthesized non-ionic, ionic surfactants and polymer-surfactant complexes at the air border was determined and colloidal-chemical parameters were determined;
- effect of various factors on petroleum-collecting, petroleum-dispersing, petroleum-squeezing, antimicrobial properties of the synthesized surfactants and polymer-surfactant complexes was studied.

Theoretical and practical value of the work. Synthesized surfactants with high surface activity may be applied in different areas of industry, including to increase oil recovery factor in oil reservoirs as a petroleum-squeezing agent, as well as a localizing agent collecting environmentally hazardous thin petroleum films from water basins surface.

Personal participation of the author. The author outlines the main goals and tasks to achieve them. Problem statement, experiments and tests, systematization and generalization of the results were performed by the participation of the author.

Publications. 30 scientific works were published on the topic of the dissertation, including 12 articles, 18 abstracts in international and republican conferences.

Approbation. The results of the dissertation work were presented and discussed in the following conferences: the III Republican conference "Modern Problems of Monomer and Polymer Chemistry" (Sumgayit, 2015); scientific conference dedicated to the 80th anniversary of M.Naghiyev Institute of Catalysis and Inorganic Chemistry of ANAS (Baku, 2016); the IX Baku International Mammadaliyev Conference on Petrochemistry (IPCP of ANAS, Baku, 2016); International scientific-technical conference "Petrochemical Synthesis and Catalysis in Complex Condensed Systems", dedicated to academician B.K.Zeynalov's 100th anniversary (IPCP of ANAS, Baku, 2017); international scientific conference "Actual Problems of Modern Natural Sciences" dedicated to National Leader H.Aliyev's 94th anniversary (Ganja, 2017); XI All-Russian School-conference of Young Scientists "Theoretical and Experimental Chemistry of Liquid-Phase Systems" (Krestov Discussions, Ivanovo, Russia, 2017); scientific conference "Actual Problems of Ecology and Soil Science in the XXI century" dedicated to National Leader H.Aliyev's 94th anniversary (Baku, 2018); the XII international scientific conference "Actual Problems of Chemistry" for doctoral students, masters and young researchers dedicated to the National Leader H.Aliyev's 95th anniversary (Baku State University, 2018); "Actual Problems of Modern Natural and Economic Sciences" dedicated to the National Leader H.Aliyev's 95th anniversary (Ganja, 2018); scientific-practical conference "Oil Processing and Innovative Prospects for the Development of Oil and Chemistry" dedicated to academician V.S.Aliyev's 110th anniversary (IPCP of ANAS, Baku, 2018); international scientific-practical conference and school of young researchers "Chemistry, Chemical Technology and Ecology: Science, Production, Education"

(Dagestan State University, Russia, Makhachkala, 2018); the III international scientific conference “Young Researchers” dedicated to the National Leader H.Aliyev’s 96th anniversary (Baku Engineering University, 2019); scientific-practical conference “Role of Engineering in Innovative Development of Azerbaijan: “Aims and Perspectives” (Baku Engineering University, 2019); international scientific conference “Actual Problems of Modern Natural Sciences” dedicated to the National Leader H.Aliyev’s 97th anniversary (Ganja, 2020); the II international scientific conference of young scientists and specialists "Multidisciplinary approaches to solving modern problems of fundamental and applied sciences (Natural Sciences)" (Baku, 2020); “The IV International Scientific Conference of Young Researchers” dedicated to the National Leader Haydar Aliyev’s 97th anniversary (Baku Engineering University, 2020); republican scientific-practical conference on “The Challenges of Modern Chemistry and its Development Trends” (Western Caspian University, Baku, 2020); republican scientific conference titled “Modern Problems of Chemistry” (Sumgayit State University, 2021).

The dissertation work was performed in the laboratory “Surface-active reagents and preparations” of Y.H.Mammadaliyev Institute of Petrochemical Processes of ANAS on the research work plan (State registration No.0113Az2035).

The scope of the work. The dissertation work consists of 188 pages, including introduction, 5 chapters, conclusions, 237 references. The dissertation includes 37 tables and 110 figures. The dissertation structure includes contents (6004 characters), introduction (13647 characters), the first chapter (39958 characters), the second chapter (12323 characters), the third chapter (54125 characters), the fourth chapter (29208 characters), the fifth chapter (37977 characters), conclusions (3062 characters), list of abbreviations (1108 characters). The dissertation totally includes 190300 characters (with the exception of tables, figures, list of a cited scientific literature).

Introduction explains and justifies actuality of the topic, the goals and objectives, scientific novelty and practical value of the

work.

The first chapter is devoted to the discussion of literature materials and justification of the issue on the synthesis and properties of ionic cooligomers and polymers based on oligomeric and polymeric surfactants collecting thin petroleum films from water surface, two types of epoxide-based non-ionic cooligomers and polymers, two different epoxy compounds.

The second chapter describes the primary substances, their purification degrees and the methods for purification, synthesis techniques for non-ionic and ionic surfactants, surface activity of surfactants, electrical conductivity, the properties of petroleum-collecting, petroleum-dispersing and petroleum-squeezing out of stratal waters.

The third chapter is devoted to conversion of non-ionic surfactants obtained by interaction of higher monocarboxylic acids (C_{12},C_{14}) with PO and ECH to ionic surfactants by the reaction in the presence of ethanolamines as well as synthesis of oligomers based on LA, polyethylenepolyamine (PEPA) and C_3 epoxides, determination of colloidal-chemical parameters of obtained ionic and non-ionic surfactants, study of their petroleum-collecting, petroleum-dispersing, petroleum-squeezing properties.

The fourth chapter describes synthesis, study of surfactants on the basis of alkylamines (C_8,C_9,C_{12},C_{16}), PO and ECH, including determination of colloidal-chemical parameters, research results on petroleum-collecting and petroleum-dispersing properties.

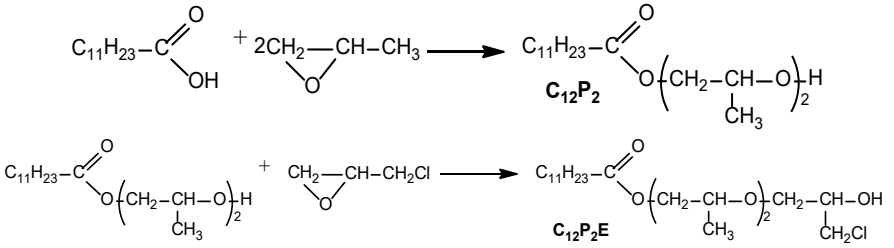
The fifth chapter includes materials on obtaining polyelectrolyte-surfactant complexes of produced ionic surfactants by (meth)acrylate-based polymers, studying by physicochemical methods, determining of their colloidal-chemical parameters and also on the petroleum-collecting and petroleum-dispersing properties.

The dissertation ends with the conclusions of the scientific work and a list of references.

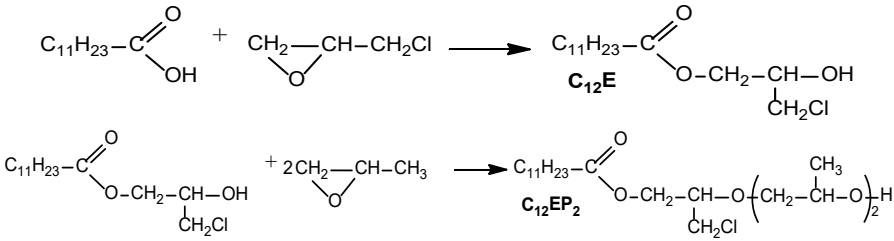
THE MAIN CONTENT OF THE WORK

Synthesis and Properties of Non-Ionic Surfactants Based on Lauric Acid, Propylene Oxide and Epichlorohydrin

Non-ionic surfactants were synthesized by interaction of LA with PO and ECH. The reaction was conducted in two directions. In the first way, initially, ester of LA with PO was synthesized, then, ECH was added to it. The reaction schemes may be described as follows:



In the second direction, at first, ester of LA with ECH was obtained, then, PO was added. The reactions of both types were carried out at 150-160°C in the presence of triethylamine catalyst. The reaction schemes may be described as follows:



High surface activity of these substances was determined using tensiometer at water-air interface and surface tensions isotherms were constructed (Fig.1).

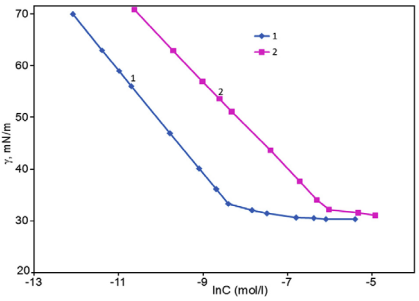


Fig. 1. Dependence graphs of surface tension on natural logarithmic concentration at the water-air interface for non-ionic surfactants $C_{12}P_2E$ (1) and $C_{12}EP_2$ (2)

Colloidal-chemical parameters of surfactants were determined as a result of the investigations (Table 1). As is evident, CMC of the composition obtained by binding of LA to PO was much lower in comparison with the composition obtained by binding of ECH to PO. Comparison of γ_{CMC} and pC_{20} values of the samples revealed that these indicators were higher, but π_{CMC} was lower for $C_{12}P_2E$.

Table 1.

Colloidal-chemical parameters of the synthesized non-ionic surfactants (25°C)

Surfactant	$\Gamma_{max.}\times10^{10}$, mol·cm^{-2}	$A_{min}\times10^{2}$, nm^2	$CMC\times10^{5}$, mol·dm^{-3}	pC_{20}	γ_{CMC} mN·m^{-1}	π_{CMC}, mN·m^{-1}	ΔG_{mis}, kJ·mol^{-1}	ΔG_{ad}, kJ·mol^{-1}
$C_{12}P_2E$	1.71	97.1	2.3	4.47	30.3	41.7	-20.6	-23.19
$C_{12}EP_2$	2.01	82.6	24.0	3.66	32.0	40.0	-14.95	-16.94

Note: CMC – critical micelle concentration; γ_{CMC} – surface tension value at CMC; Γ_{max} – maximum adsorption; A_{min}– minimal surface area on cross-section of polar group; π_{CMC} – surface pressure; pC_{20} – adsorption efficiency of surfactant; ΔG_{mic} – Gibbs free energy of micellization; ΔG_{ad} –Gibbs energy of adsorption process.

Γ_{max} value for $C_{12}P_2E$ is lower than $C_{12}EP_2$, but A_{min} is higher, vice versa. ΔG_{mic} and ΔG_{ad} values have been measured for these surfactants. Gibbs free energy values of adsorption and micellization processes are negative, therefore both processes occur spontaneously.

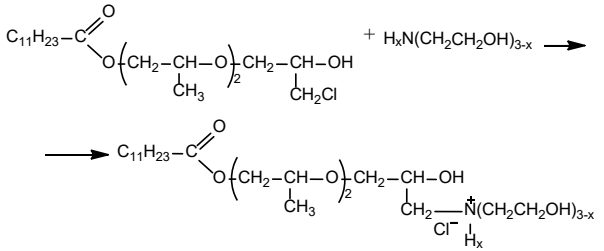
Petroleum-collecting and petroleum-dispersing capacities of the synthesized surfactants were studied under laboratory conditions in the form of undiluted product and 5 wt. % aqueous dispersion in 3 types of water - sea, fresh and distilled water, on Pirallahy petroleum film of 0.17 mm thickness.

Reagent efficiency is estimated by petroleum-collecting coefficient (K) indicating reduction of petroleum layer surface area, K_D (%) – indicating purification degree of water surface from petroleum under reagent effect and shelf life – τ. Undiluted form of $C_{12}EP_2$-containing surfactants show the highest petroleum-collecting

efficiency in all 3 types of water (seawater, fresh and distilled waters), K_{max}=76.0, 101.3 and 86.8; τ=144 h, respectively. But $C_{12}P_2E$ in 5wt. % aqueous dispersion - K_{max}=76.0, 76.0 and 60.8; τ=168 h, respectively.

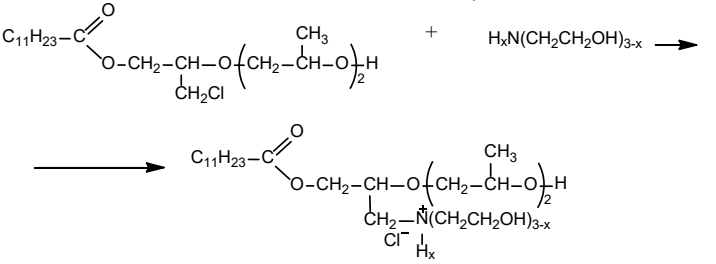
Synthesis and Properties of Cationic Oligomeric Surfactants Based on Lauric Acid, Propylene Oxide, Epichlorohydrin and Ethanolamines

Quaternization reaction of chloroxypropyl derivative of the obtained esters by chloromethylene group was conducted with ethanolamines and cationic surfactants were produced.Mono- (MEA), di- (DEA) and triethanolamine (TEA) were used as ethanolamines. The reaction occured according to the following scheme:



where x=0 ($C_{12}P_2ET$ - $C_{12}P_2E$ salt with TEA), 1 ($C_{12}P_2ED$ -$C_{12}P_2E$ salt with DEA) or 2 ($C_{12}P_2EM$ - $C_{12}P_2E$ salt with MEA).

As noted above, new cationic surfactants were produced through quaternization reaction of the chloroxypropyl derivative (obtained by oxypropylation of chloroxypropyl ester produced through interaction of LA and ECH with PO) with ethanolamines:



where x=0 ($C_{12}EP_2T$), 1 ($C_{12}EP_2D$) or 2 ($C_{12}EP_2M$).

Surface activity as well as specific electroconductivity of the

produced surfactants were determined at the water-air interface (Fig. 2, 3) and colloidal-chemical parameters were determined (Table 2).

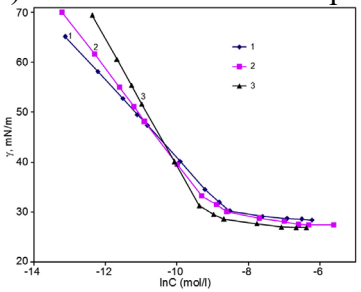


Fig. 2. Dependence graphs of surface tension on natural logarithmic concentration at the interface with air for $C_{12}P_2EM$ (1), $C_{12}P_2ED$ (2) and $C_{12}P_2ET$ (3) aqueous solutions

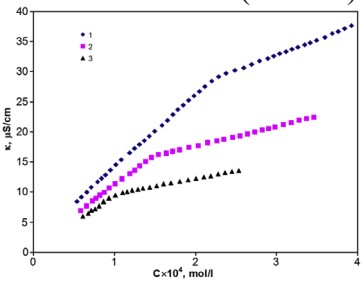


Fig. 3. Dependence graphs of $C_{12}P_2EM$ (1), $C_{12}P_2ED$ (2) and $C_{12}P_2ET$ (3) aqueous solutions electrical conductivity on concentration

It was determined that the CMC is lower in the surfactants with oxypropylene unit at the beginning of the chain. As the number of ethylol groups rises in hydrophilic part of both two classes of cationic surfactants, CMC, A_{min}, γ_{CMC} and pC_{20} values diminish, but degree of counterion binding - β, Γ_{max} and π_{CMC} increases.

The synthesized surfactants - diluted $C_{12}P_2EM$, $C_{12}EP_2M$ and $C_{12}EP_2T$ show higher results (K_{max}=121.5, τ>6 days in seawater) due to petroleum-collecting capacity and also shelf life of collected petroleum.

Table 2.

Colloidal-chemical parameters of synthesized oligomeric surfactants

SAS	CMC×10⁴, mol·dm⁻³		B	$\Gamma_{max}\times10^{10}$, mol·cm⁻²	$A_{min}\times10^{2}$, nm²	pC_{20}	γ_{CMC}, mN·m⁻¹	π_{CMC}, mN·m⁻¹	ΔG_{mic}, kJ·mol⁻¹	ΔG_{ad}, kJ·mol⁻¹
$C_{12}P_2EM$	1.9[a]	2.0[b]	0.56	1.58	105.2	4.96	28.5	43.5	-33.14	-35.87
$C_{12}P_2ED$	1.5	1.5	0.67	1.91	86.9	4.91	27.4	44.6	-36.43	-38.77
$C_{12}P_2ET$	1.3	1.2	0.73	2.57	64.6	4.79	27.0	45.0	-38.35	-40.10
$C_{12}EP_2M$	6.1	6.2	0.65	1.97	84.2	4.31	27.6	44.4	-30.26	-32.51
$C_{12}EP_2D$	2.8	2.9	0.69	2.20	75.5	4.56	27.3	44.7	-34.25	-36.29
$C_{12}EP_2T$	2.4	2.5	0.81	3.50	47.4	4.26	27.2	44.8	-37.38	-38.66

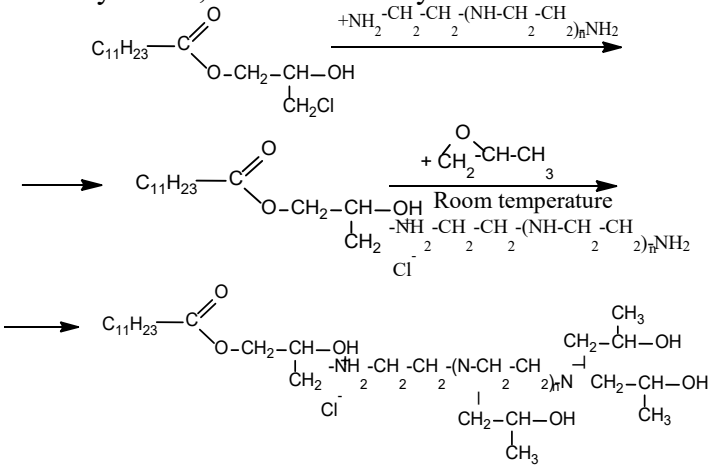
[a]CMC values determined by tensiometric method

[b]CMC values determined by conductometric method

Synthesis and Study of Oligomeric Surfactants Based on Lauric Acid, Epichlorohydrin, Polyethyleneamine and Propylene Oxide

The ester synthesized through interaction of LA and ECH was

first effected by PEPA, then followed by PO.



The obtained oligomeric surfactants were studied under laboratory conditions as petroleum-squeezing reagent for increasing oil recovery factor in oil wells and were proven to be highly effective (Table 3).

Table 3.

Petroleum-squeezing capacity of oligomeric surfactant based on LA chloroxypropyl ester, PEPA and PO (0.05 wt.% aqueous solution)

Reagent	Water	p_a , %	S,%	$\eta_{nonaqueous}$,%	$\eta_{fin.}$, %	$V_{sol.}$	WPF
Reagent-free	Fresh	42.50	80.80	37.82	58.96	11.21	23.52
Reagent-free	Seawater	32.25	100.00	38.60	78.60	20.50	19.65
With surfactant	Fresh	30.34	108.86	29.55	94.00	12.51	12.22
With surfactant	Seawater	30.34	106.30	16.50	99.00	10.11	9.60

Note: φ_a – absolute porosity; S – petroleum saturation coefficient; $\eta_{nonaqueous}$ – petroleum-squeezing in dry season; $\eta_{fin.}$ – final petroleum-squeezing; WPF- water-petroleum factor; $V_{sol.}$ – solution consumption.

Thus, petroleum-squeezing coefficient of solution in dry season was 29.55% and final petroleum-squeezing coefficient was 94% in fresh water, but in seawater 16.50% and 99.00% respectively.

Synthesis and Properties of Non-ionic Oligomeric Surfactants Based on Myristic Acid, Propylene Oxide and Epichlorohydrin

Oligomeric surfactants based on MA, PO and ECH were obtained by 2 different ways on the above reaction schemes (oxypropylene-chloroxypropylene – C_{14}PE and chloroxypropylene-oxypropylene – C_{14}EP). Colloidal-chemical parameters of the synthesized surfactants were determined. CMC value of the surfactant firstly bonded to MA by ECH was higher (Table 4), but γ_{CMC} values were lower in comparison with C_{14}PE. π_{CMC} values for C_{14}EP were higher than C_{14}PE, pC_{20} values of C_{14}PE was higher than C_{14}EP. Γ_{max} value of C_{14}EP was higher than corresponding value of C_{14}PE, but A_{min} was lower, vice versa.

Table 4.

Colloidal-chemical parameters of non-ionic surfactants synthesized on the basis of MA, PO and ECH (25°C)

SAS	$\Gamma_{max}\times10^{10}$, mol·cm^{-2}	$A_{min}\times10^{2}$, nm^2	CMC$\times10^{5}$, mol·dm^{-3}	pC_{20}	γ_{CMC}	π_{CMC}, mN·m^{-1}	ΔG_{mic}, kJ·mol^{-1}	ΔG_{ad}, kJ·mol^{-1}
C_{14}EP	1.87	88.7	21.1	4.88	26.6	45.4	-20.97	-23.39
C_{14}PE	1.53	108.3	10.5	5.56	29.0	43.0	-22.70	-25.50

Among 5 wt.% aqueous non-ionic surfactants in dispersed form synthesized on the basis of MA, ECH and PO, C_{14}EP represented maximal petroleum-collecting capacity in distilled and fresh waters (in both waters K_{max}=40.5, τ=144 h), but C_{14}PE in seawater (K_{max}=30.4, τ=75 h).

Synthesis and Properties of Cationic Surfactants Based on Myristic Acid, Propylene Oxide, Epichlorohydrin And Ethanolamines

Cationic surfactants were obtained by quaternization reaction of MA chloroxypropylene-oxypropylene/oxypropylenechloroxy-propylene derivatives with ethanolamines (MEA-C_{14}EPM/C_{14}PEM, DEA-C_{14}EPD/C_{14}PED, TEA-C_{14}EPT/C_{14}PET, methylmonoethanol-amine-C_{14}EPMM/C_{14}PEMM, and methyldiethanolamine-C_{14}EPMD/C_{14}PEMD) at 1:1 mole ratio of CH_2Cl group:ethanolamine and colloidal-chemical parameters were determined (Table 5).

Table 5.

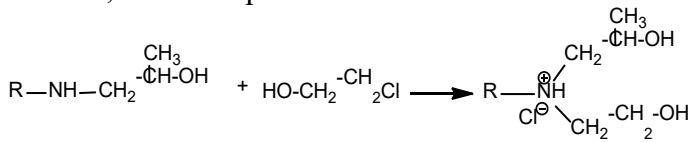
Colloidal-chemical parameters of synthesized surfactants

Surfactant	β	Γ_{max} ×10^{10}, mol·cm^{-2}	A_{min} ×10^{2}, nm^2	CMC×10^4, mol·dm^{-3}		pC_{20}	π_{CMC}, mN·m^{-1}	γ_{CMC}, mN·m^{-1}	ΔG_{mic}, kJ·mol^{-1}	ΔG_{ad}, kJ·mol^{-1}
C_{14}EPM	0.46	2.40	69.1	1.53[a]	1.57[b]	4.68	43.7	28.3	-31.78	-33.60
C_{14}EPD	0.49	2.52	65.9	1.09	1.13	4.85	44.8	27.2	-33.68	-35.46
C_{14}EPT	0.53	2.97	56.0	0.99	0.97	4.83	45.1	26.9	-34.95	-36.47
C_{14}EPMM	0.42	1.18	141.1	1.50	1.51	5.82	46.1	25.9	-30.98	-34.90
C_{14}EPMD	0.48	1.40	118.4	0.91	0.88	5.65	45.6	26.4	-34.12	-37.37
C_{14}PEM	0.33	1.92	86.7	1.40	1.46	4.94	43.0	29.0	-29.24	-31.49
C_{14}PED	0.36	2.35	70.6	0.95	0.93	4.92	43.7	28.3	-31.21	-33.06
C_{14}PET	0.41	2.65	62.7	0.62	0.62	5.11	44.7	27.3	-33.85	-35.53
C_{14}PEMM	0.30	1.66	100.2	1.36	1.33	5.21	45.4	26.6	-28.67	-31.41
C_{14}PEMD	0.35	1.98	83.7	0.91	0.88	5.02	42.0	30.0	-31.12	-33.24

It was determined that the CMC value of the surfactants with oxypropylene unit at the beginning of the chain were lower. As the number of ethylol groups in hydrophilic part rises, the values of CMC, A_{min} and γ_{CMC} diminish, but β, Γ_{max}, pC_{20} and π_{CMC} increase. As the number of CH_2CH_2OH groups rises, pC_{20}, π_{CMC} diminishes, but γ_{CMC} increases for the surfactants having a methyl group simultaneously with ethylol groups. Ammonium-type salts have higher petroleum-collecting capacity than primary ethers. C_{14}EP-based ionic surfactants represents higher petroleum-collecting properties. C_{14}EPMM represents higher petroleum-collecting capacity in all 3 waters (K_{max}=50.6, τ>6 days).

Synthesis and Study of Cationic Surfactants Based on Alkylisopropylamines and Ethylenechlorohydrin

Interaction reaction of alkylisopropylamine obtained by interaction of alkylamine with PO at a mole ratio of 1:1, with ethylenechlorohydrin (ECH) occurs on the following scheme at equimolar ratio, room temperature:



R=C_8H_{17} (C_8PEt); C_9H_{19} (C_9PEt); $C_{12}H_{25}$ (C_{12}PEt); $C_{16}H_{33}$ (C_{16}PEt).

Surface activity (Fig. 4) and electrical conductivity (Fig. 5) of the synthesized compounds at 20, 25, 30 and 35 ºC was studied and colloidal-chemical parameters were determined (Tab. 6). As is seen,

the CMC decreases by elongation of the chain in the hydrophobic part. Decrease in the hydrophilic group hydration by the increase of temperature leads to micellization.

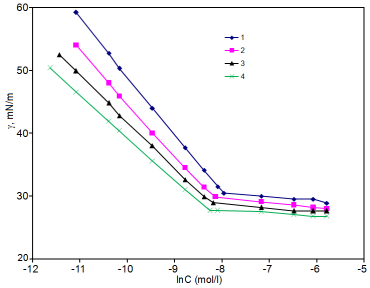


Fig. 4. Surface tension isotherms of C_{12}PEt: 1 - 20°C; 2 - 25°C; 3 - 30°C; 4 - 35 °C

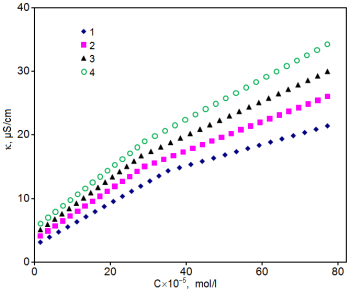


Fig. 5. Concentration dependent graphs of C_{12}PEt specific electroconductivity: 1 - 20°C; 2 - 25°C; 3 - 30°C; 4 - 35°C

Increase in temperature also causes water aggregate collapse near hydrophobic fragment that complecates micellization (CMC increases). Inclusion of CH_2OH fragment to headgroup of surfactants causes decrease in CMC values. CMC values decrease by the elongation of alkyl and alkylol chain of headgroup in surfactants.

Table 6.

Colloidal-chemical parameters of the surfactants synthesized on the basis of alkylisopropylamine and ECH

SAS	T, °C	β	$\Gamma_{max}\times10^{10}$, mol/cm^2	A_{min}, Å^2	CMC$\times10^4$, mol/L	π_{CMC}, mN/m	γ_{CMC}, mN/m	pC_{20}
C_8Pet	20	0.29	2.10	79.1	4.43	42.7	30.1	4.26
	25	0.27	1.84	90.3	4.09	43.0	29.0	4.39
	30	0.26	1.63	101.6	3.91	42.2	29.0	4.61
	35	0.24	1.54	108.2	3.47	43.0	27.4	4.68
C_9Pet	20	0.41	1.93	86.1	4.26	43.2	29.6	4.36
	25	0.37	1.78	93.4	3.63	43.5	28.5	4.56
	30	0.34	1.55	107.2	3.22	43.4	27.8	4.75
	35	0.29	1.37	121.1	2.48	43.1	27.3	4.95
C_{12}Pet	20	0.47	1.89	87.7	3.52	43.3	29.5	4.52
	25	0.42	1.69	98.5	2.94	43.8	28.2	4.71
	30	0.4	1.47	113.0	2.80	43.6	27.6	4.88
	35	0.38	1.32	126.1	2.61	43.5	26.9	5.05
C_{16}Pet	20	0.57	1.85	89.6	1.56	41.8	31.0	4.62
	25	0.55	1.65	100.6	1.52	42.0	30.0	4.86
	30	0.51	1.43	116.0	1.30	42.1	29.1	5.12
	35	0.49	1.32	126.2	1.21	43.5	26.9	5.24

Important thermodynamic parameters, such as Gibbs free

energy (ΔG), entropy (ΔS) and enthalpy change (ΔH) have been determined for synthesized cationic surfactants (Tab. 7).

Table 7.

Thermodynamic parameters of micellization and adsorption processes of the surfactants synthesized on the basis of alkylisopropylamine and ECH at 20, 25, 30 and 35°C

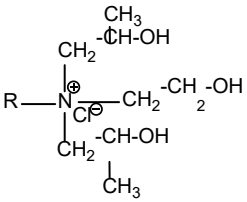
SAS	T, °C	ΔG_{mic}, kJ/mol	ΔG_{ad}, kJ/mol	ΔS_{mic}, J/mol K	ΔH_{mic}, kJ/mol	ΔS_{ad}, J/mol K	ΔH_{ad}, kJ/mol
C_8PEt	20	–24.27	–26.30				
	25	–24.55	–26.89	56.5	–7.7	117.2	8.1
	30	–24.91	–27.49	71.6	–3.2	118.6	8.4
	35	–25.29	–28.10	77.6	–1.4	123.2	9.9
C_9PEt	20	–26.66	–28.90				
	25	–26.89	–29.33	45.8	–13.2	87.2	–3.3
	30	–27.14	–29.95	51.4	–11.6	122.7	7.2
	35	–27.42	–30.57	56.2	–10.1	124.2	7.7
C_{12}PEt	20	–28.48	–30.76				
	25	–28.60	–31.21	26.9	–20.6	89.2	–4.6
	30	–28.85	–31.82	48.5	–14.2	121.9	5.1
	35	–29.16	–32.46	61.1	–10.3	128.4	7.1
C_{16}PEt	20	–33.52	–35.78				
	25	–33.76	–36.31	47.5	–19.6	105.1	–5.0
	30	–34.04	–36.98	55.1	–17.4	138.5	5.0
	35	–34.41	–37.72	75.4	–11.2	144.3	6.7

Elongation of hydrophobic chain strenghtens a tendency of these molecules toward micelle formation which results in increased negativity of the values of ΔG_{mic}. The ΔG_{ads} values are more negative than ΔG_{mic}. The ΔS_{ads} values are positive and a little larger than the ΔS_{mic} values.

This reflects a larger freedom of motion of hydrocarbon moiety at the air-water interface. ΔH_{mic} values are negative evidencing that the micelle formation process is exothermic in the studied temperature range. ΔS_{mic} is always positive, ΔH_{mic} - negative. As the temperature increases, both parameters increase.

Analysis of petroleum-collecting properties of the alkylisopropylolamine- and ECH-based surfactants reveals that the surfactant with C_{12} alkyl chain length as a solution has more effective petroleum-collecting properties (K_{max}=50.7 in seawater).

Alkyldiisopropylolamines were obtained at a mole ratio 1:2 of alkylamine and PO (converted to quaternary ammonium salts by ethylol group on quaternization reaction). The final product may be described as follows:



R=C_8H_{17} (C_8P_2Et); C_9H_{19}(C_9P_2Et); $C_{12}H_{25}$ ($C_{12}P_2Et$); $C_{16}H_{33}$ ($C_{16}P_2Et$).

Each nitrogen atom is bonded to one alkyl, one ethylol and two isopropylol groups and a chloride counterion. Colloidal-chemical parameters of the obtained surfactants were determined (Tab. 8).

Table 8.

Colloidal-chemical parameters of the surfactants synthesized on the basis of alkyldiisopropylolamie and ECH

SAS	β	CMC ×10^4, mol·dm^{-3}		Γ_{max} ×10^{10}, mol·cm^{-2}	A_{min} ×10^2, nm^2	γ_{CMC}, mN·m^{-1}	π_{CMC}, mN·m^{-1}	pC_{20}	ΔG_{mic}, kJ·mol^{-1}	ΔG_{ad}, kJ·mol^{-1}
C_8P_2Et	0.39	3.04[a]	3.07[b]	2.85	58.3	35.5	36.5	3.99	-27.86	-29.14
C_9P_2Et	0.47	2.91	2.94	2.80	59.4	32.8	39.2	4.06	-29.62	-31.02
$C_{12}P_2Et$	0.48	2.56	2.60	2.77	59.9	32.1	39.9	4.28	-30.27	-31.71
$C_{16}P_2Et$	0.58	2.18	2.20	2.52	65.8	31.9	40.1	4.59	-32.97	-34.56

Dependence of the CMC for these surfactants on number of carbon atoms in a hydrocarbon chain - n(C) is represented in Fig. 6. log CMC decreases by increase in n(C). CMC values decreases, but πCMC increases by increase in hydrophobicity as a result of the growth of hydrocarbon fragment from C_8P_2Et to $C_{16}P_2Et$. $C_{16}P_2Et$ represents the highest adsorption efficiency - pC_{20} (Fig. 7).

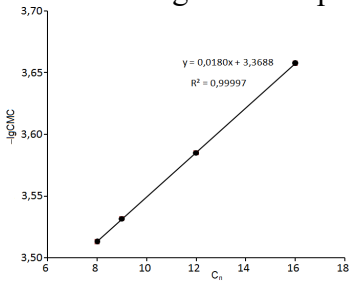


Fig. 6. Dependence of log(CMC) for C_8P_2Et, C_9P_2Et, $C_{12}P_2Et$ and $C_{16}P_2Et$ on the number of carbon atoms in alkyl chain

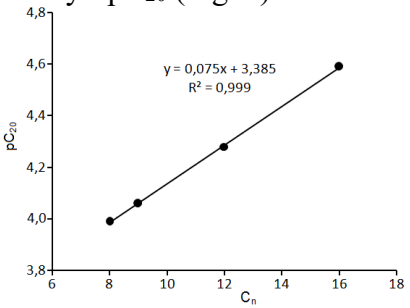


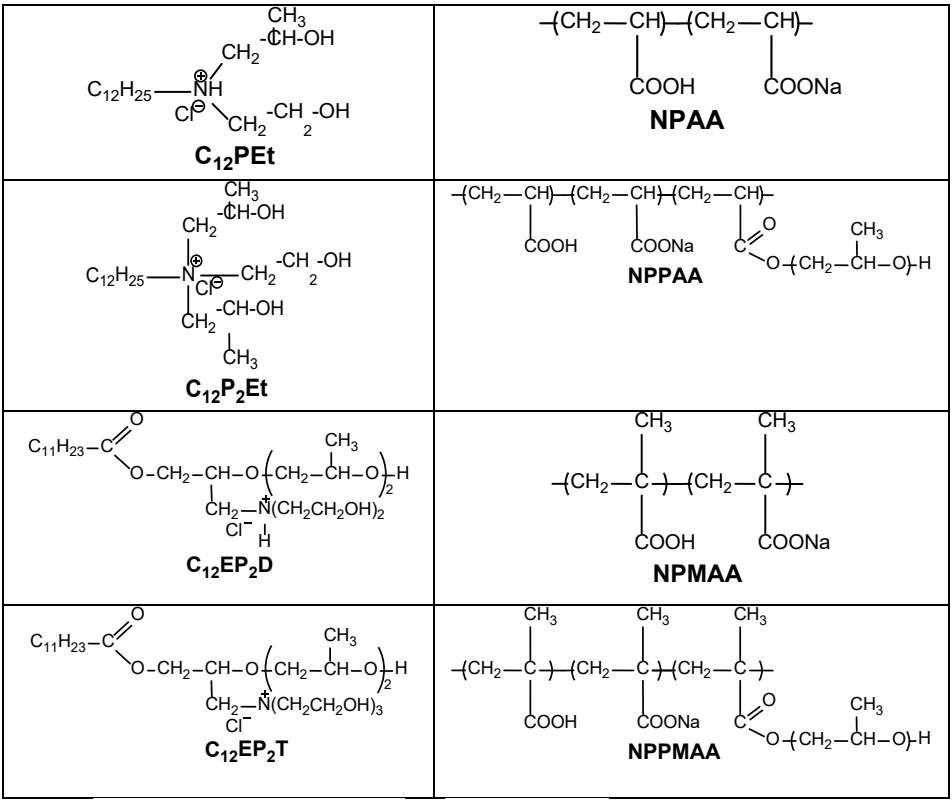
Fig. 7. Dependence of pC_{20} for C_8P_2Et, C_9P_2Et, $C_{12}P_2Et$ və $C_{16}P_2Et$ on the number of carbon atoms in alkyl chain

Petroleum-collecting capability of surfactants increases by elongation of alkyl chain to C_{12} in the synthesized surfactants. Further elongation of alkyl chain relatively weaks petroleum-

collecting capacity of the synthesized surfactants. The bactericidal efficacy of the synthesized $C_{12}P_2Et$ against sulfate-reducing bacteria has also been found.

Obtainment and Study of Polyelectrolyte - Surfactant Complexes

The complexes of PAA and PMAA as well as their oxypropylated derivatives and different hydrophilic groups-containing surfactants with C_{12}-alkyl chain were obtained for the purpose of studying effects of both surfactants and ionic groups nature of polymer in counterion surfactant-polymer systems. The formulas of the surfactants and polyelectrolytes in the complexes as follows:



Characteristic density - [η] for PAA is 20 dl/g, but for PMAA 0.16 dl/g. Average molecular weight was measured according to Mark-Houwing equation – for PAA – 69 000 and PMAA – 59 000. 50% of the both polyacids were neutralized and resulted in obtaining

NPAA and NPMAA. Addition of PO up to the proportion of free carboxylic groups to NPAA and NPMAA with α=0.5 resulted in obtaining NOPAA and NOPMAA.

Polyelectrolyte-surfactant complexes were prepared by stirring of aqueous solutions of polyacid (0.01% wt.) and surfactant 0.2% concentration solutions. Specific electroconductivity and surface activity of surfactant-polyelectrolyte complexes were measured (25°C), isotherms were constructed (Fig. 8, 9) and surface activity parameteres were determined (Tab. 9).

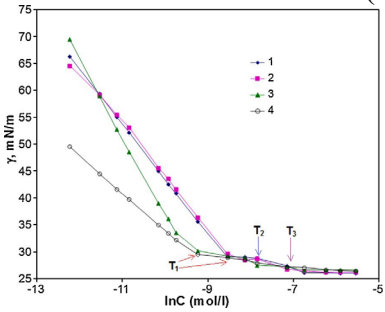


Fig. 8. Dependence graph of surface tension of $C_{12}EP_2D$-polyelectrolyte complex on the concentration of surfactant: 1-NPAA, 2-NOPAA, 3-NPMAA, 4-NOPMAA

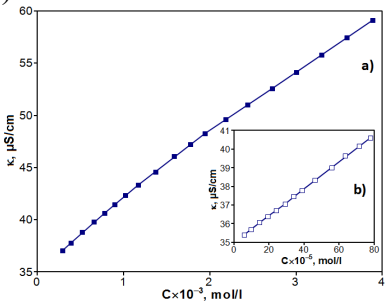


Fig. 9. Dependence graph of specific electroconductivity of $C_{12}EP_2D$-NPAA complex on the concentration of surfactant: a) (0-8·10^{-3} mol/l); b) (0–1.5·10^{-3} mol /l)

An increase in concentration of surfactant in a solution causes formation of a complex between surfactant molecules and polyelectrolyte polar groups. In this case, surface tension value decreases sharply. The concentration interval in which the surface tension is partially stabilized results in the completion of the exchange reaction between surfactant molecules and polar groups of polyelectrolyte. In this case, the surfactant counterion is substituted by polyelectrolyte ion. After completion of the process, that's to say after completely saturation of monomer units by surfactants, surfactant molecules added to the solution are used in the formation of free micelles. It results in reduction of surface tension. Formation of micelles ends after the CMC.

The value of T_3 is lower in the systems with a large number of isopropylol groups in the headgroup of surfactant in the complex.

Table 9.

Surface activity parameters of aqueous solutions of polyelectrolyte-SAS complexes (298K)

Complex	β_1	B_2	$T_1\times10^4$, mol·dm^{-3}		$T_2\times10^3$, mol·dm^{-3}	$T_3\times10^3$, mol·dm^{-3}		CAC/CMC	$\Gamma_{max}\times10^{10}$, mol·cm^{-2}	$A_{min}\times10^2$, nm^2	π_{CMC}, mN·m^{-1}
NPAA-C_{12}Pet	0.10	0.30	6.20[a]	6.17[b]	3.08	3.90[a]	4.32[b]	0.143	1.73	96.2	41.3
NOPAA- C_{12}PEt	0.14	0.31	1.55	6.17	1.23	3.09	3.08	0.200	1.52	109.2	41.7
NPMAA- C_{12}PEt	0.17	0.44	1.05	1.54	1.23	1.85	1.87	0.08	1.79	92.5	41.3
NOPMAA- C_{12}PEt	0.14	0.30	1.5	4.63	3.09	3.05	4.32	0.107	2.01	82.6	42.4
NPAA-$C_{12}P_2$Et	0.05	0.25	0.58[a]	0.52[b]	0.39	0.55[a]	0.52[b]	0.100	2.11	78.6	41.3
NOPAA- $C_{12}P_2$Et	0.29	0.36	1.55	0.52	0.26	0.39	0.40	0.130	2.80	59.3	39.6
NPMAA-$C_{12}P_2$Et	0.24	0.26	1.05	2.62	0.52	1.85	1.00	0.262	1.64	101.2	42.5
NOPMAA-$C_{12}P_2$Et	0.12	0.15	1.30	1.31	0.26	0.42	0.39	0.336	1.63	102.1	42.0
NPAA- $C_{12}EP_2$D	0.03	0.19	2.90[a]	1.95[b]	0.78	1.15[a]	1.17[b]	0.167	2.05	80.8	45.9
NOPAA- $C_{12}EP_2$D	0.29	0.30	1.90	1.95	0.39	1.08	0.78	0.250	1.95	85.1	45.6
NPMAA- $C_{12}EP_2$D	0.44	0.50	0.97	0.97	0.29	0.40	0.39	0.250	2.90	57.2	44.5
NOPMAA-$C_{12}EP_2$D	0.27	0.38	0.92	0.97	0.29	0.37	0.39	0.250	1.40	118.4	44.8
NPAT- $C_{12}EP_2$T	0.22	0.31	0.89[a]	1.80[b]	0.36	0.74[a]	0.72[b]	0.250	2.90	57.2	43.8
NOPAT- $C_{12}EP_2$T	0.32	0.39	0.54	0.89	0.27	0.39	0.36	0.247	2.62	63.4	44.4
NPMAT- $C_{12}EP_2$T	0.50	0.52	0.45	2.70	0.36	1.85	1.00	0.270	1.57	105.9	45.2
NOPMAT-$C_{12}EP_2$T	0.34	0.41	0.45	0.89	0.36	1.00	0.72	0.124	1.52	109.3	45.0

T_1–CAC-critical aggregation concentration;T_2–critical saturation concentration; T_3–CMC-critical micellization concentration, β_1-degree of a surfactant counterion binding at critical aggregation concentration, and β_2 degree of counterion binding at critical micellization concentration

The value of T_3 decreases by increase in the number of ethylol groups of surfactant headgroup in PAA-based complexes among surfactant-polyelectrolyte complexes with $C_{12}EP_2D$ and $C_{12}EP_2T$. But the value of T_3 rises by increase in the number of ethylol groups of surfactant headgroup in PMAA-based complexes.

Viscosimetric measurements of surfactant-polyelectrolyte complexes (t=25°C) reveal that (Fig. 10) relative viscosity of NPAA is higher in comparison to NPMAA. This may be due to the presence of helical NPMAA macromolecules in the aqueous solution and the fact that methyl group hinders the interaction among polar groups. Oxypropylation of polyelectrolytes causes decrease in their relative viscosity values.

Ionic groups in polymer chain are converted to non-ionic groups by oxypropylation of free carboxyl groups.Therefore the number of interacting polar groups decreases and it results in a decrease in relative viscosity.

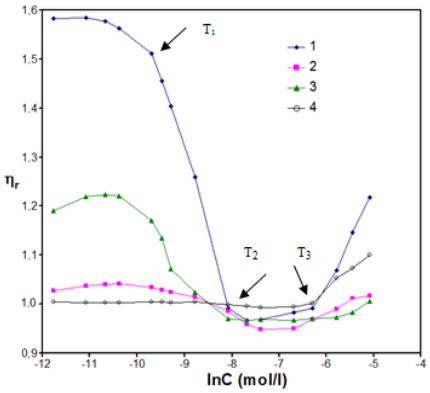


Fig. 10. Dependence graphs of relative viscosity of C_{12}Pet-polyelectrolyte complex from the concentration of surfactant: 1-NPAA, 2-NOPAA, 3-NPMAA, 4-NOPMAA

Micellization in aqueous solutions of surfactant-polyelectrolyte complexes, Gibbs free energy values of aggregation processes as well as Gibbs free energy values change (ΔG^{o}_{ps}) of interaction among surfactants were measured.

Some physicochemical interactions prevail in polyelectrolyte-surfactant complexes in comparison to electrostatic interaction forces.

This is due to the presence of complex functional fragments (ethylol and isopropylol) in the headgroup of the studied surfactants.

The complex structure of the headgroups makes difficult their approach to the functional groups in polymer. It results in formation of hydrogen bond instead of electrostatic interaction force.

As a result of the studies it was revealed that colloidal-chemical, specific electroconductivity, viscosity parameters of surfactant-polyelectrolyte complexes depend on the nature of headgroups in surfactant and polyelectrolyte.

The antibacterial properties of the synthesized polyelectrolyte-surfactant complexes were studied by disk diffusion method and it was determined that they have different effects against *B.anthracoides*, *C.albicans, S.aureus and K.pneumoniae.*

The obtained complexes possess stronger petroleum-collecting and petroleum-dispersing properties. So, that NOPMAA-$C_{12}P_2Et$ represents the highest petroleum-collecting capacity ($K_{max.}$=125.0, τ~3 days), but NPAA-C_{12}Pet –the highest petroleum-dispersing capacity (K_D=99.2%, τ>3 days) in seawater.

CONCLUSION

1. Two different non-ionic oligomeric surfactants were synthesized based on lauric acid, propylene oxide (n=2) and epichlorohydrin (m=1) and cationic surfactants were obtained through quaternization reaction using ethanolamines. The surface activity properties of the obtained cationics were comparatively investigated. It was established that, for the surfactants having oxypropylene unit at the beginning of the heterochain, the CMC value is smaller. For the cationic surfactants of both groups, with a rise in the number of ethylol groups in the hydrophilic fragment, the magnitudes of CMC, A_{min}, and γ_{CMC} decline whereas the values of β, Γ_{max}, pC_{20}, and π_{CMC} increase. 5 wt-% aqueous solutions of $C_{12}P_2EM$, $C_{12}EP_2M$ and $C_{12}EP_2T$-based cationic surfactants represent stronger petroleum-collecting properties on the water with different mineralization degrees (K_{max}=121.5, τ>6 days) [2,3,8,10,11,16,17,24].
2. Two different non-ionic surfactants were synthesized based on myristic acid, propylene oxide (n=1) and epichlohydrin (m=1) and the cationic surfactants were obtained by the interaction of these esters with ethanolamines. The surface activity properties of the obtained cationics were comparatively investigated. It was established that, for the surfactants having a propoxy unit at the beginning of the heterochain, the CMC value is smaller. For the cationic surfactants of both groups, with a rise in the number of ethylol groups in the hydrophilic fragment, the values of CMC, A_{min} and γ_{CMC} decreases but the values of β, Γ_{max}, pC_{20} və π_{CMC} increase. Among the surfactants having methyl groups along with ethylol fragments, with an increase in the number of ethylol groups, the values of pC_{20} and π_{CMC} diminish whereas the γ_{CMC} value increases. The surfactants on the basis of C14EP possess stronger petroleum-collecting properties (K_{max}=50.6, τ>6 days) in comparison to C_{14}PE-based surfactants [13,15,18,22,23].
3. An oligomeric-type product was obtained based on lauric acid chloroxypropyl ester, polyethylenepolyamine and propylene oxide, several physicochemical properties were studied and

determined that the oligomeric-type surfactant possesses the capacity of increasing oil recovery factor in oil wells (as a petroleum-squeezing reagent). The final petroleum-squeezing of 0.05 wt. % aqueous solution of this reagent (in seawater) is 99.0% (reagent-free – 78.6%) [6, 20, 26, 30].

4. Hydroxyethyl- and hydroxypropyl groups-containing ionic surfactants were synthesized by the reaction of alkylisopropylolamine and alkyldiisopropylolamine obtained by the interaction of alkylamine (C_8H_{17}, C_9H_{19}, $C_{12}H_{25}$, $C_{16}H_{33}$) and propylene oxide (at mole ratios of 1:1 and 1:2) with ethylenechlorohydrin, their important colloidal-chemical parameteres were determined. It was determined that elongation of alkyl chain up to C_{12} causes increase in petroleum-collecting capacity of surfactants (K_{max}=46.8, τ>10 days). Further elongation of the alkyl chain relatively weaks the petroleum-collecting capacity of the synthesized surfactants [4,5,7,9,12].
5. Polyelectrolyte-surfactant complexes were prepared by stirring of aqueous solutions of the modifiers (neutralized by 50 % mol K_{max}=46.8, τ>10 days of PAA or PMAA with NaOH and oxypropylated by propylene oxide) with the surfactants (four cationic surfactants with dodecyl chain). Colloidal-chemical parameters and specific electroconductivities of the polyelectrolyte-surfactant complexes and surfactants, as well as viscosity parameters of the complexes and polyelectrolyte were studied comparatively and determined that these properties depend on the nature of the surfactants headgroups and polyelectrolyte. The complexes represent higher petroleum-collecting and petroleum-dispersing properties (K_{max}=125.0, K_D=99.2%) [1,14,19,21,25,27, 28, 29].

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