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**SYNTHESIS, PROPERTIES OF METHACRYLOILETHYL-N, N -
DIMETHYLALLYLAMMONIUMBROMIDE AND METHACRYLOILETHYL-N, N -
DIMETHYLMETHYLENECARBOXYIAMMONIUMIODIDE**

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ABSTRACT

The possibility of realization of adjustable in a complex-radical polymerizationsynthesized monomer is shown on the basis of methacryloilethyl-N, N -dimethylallylammoniumbromide (MEDAAB) and methacryloilethyl-N, N -dimethylmethylenecarboxyammoniumiodide (MEDMAI) at presence initiator persulfat calyx (PC) at moderate temperatures (283-293K). Synthesized polymeric in the water environment possess strongly pronounced surface-active properties, essentially reducing a superficial tension of water, show bactericidal abilities and define energy of adhesion and cohesion of the modifier on a surface of natural fibres, improve wettability of a fibre, critical concentration micelleformation.

Keywords: Cationic surface-active substances, critical concentration micelle formation (CCM), adsorption, wettability, energy of adhesion and cohesion, a superficial tension, sensitivity to microorganisms, hydrophilic and hydrophobic balance (HLB).

INTRODUCTION

Despite presence research¹⁻³, devoted to questions of synthesis of polymer methods of the spontaneous, usually-radical and photoinitiatedpolymerization, based on high-volume processes, a question on a finding of more accessible methods of their synthesis, allowing to carry out reactions at rather low temperatures, to prevent course of undesirable collateral processes, is an actual problem in modern colloid chemistry.

However, in the literature results of researches and the mechanism of reaction of synthesis and polymerisationmonomeasuredquaternaryammonium the bases are discussed, reactions of spontaneous polymerization are studied and established the zwitter-ionic mechanism of polymerisationquaternaryammoniumsalts on the basis of interaction reaction haloidcontainingmonomers with amino compounds, and researches on the in a complex-radical polymerization based on the donor-acceptorinitiation of aliphatic and aromatic tertiaryaminewith

haloidalkyl at moderate temperatures, were not spent till now.

EXPERIMENTAL

Crystal salts of monomer synthesised interaction reaction of metacryloilethyl-N, N -dialkilamin with haloidalkyl (allilbromideor monoiodoaceticacid) as follows: in a conic flask placed 1 moldimethylaminoethylmethacrylate (DMAEMA), 30 ml of absolute acetone and added on drops 1 molhaloidcontaining connections, white crystals of salt dropped out in 3-4 hours. A flask with the received salts placed in a refrigerator for 2-3 days for brimfulldeposition crystal salts. The received salts blastic from a solution of absolute acetone and ethanol in the ratio 9:1. The synthesised crystal salts, are dissolved in water and organic solvents.

As a result of interaction reaction, for example, metacryloilethyl-N, N -dimethylamine with 3-bromopropen-1crystal salt methacryloilethyl-N, N -di-

methylallylammoniumbromide is formed, methacrylolethyl-N, N -diethylamine with α -iodoacetic acid forms crystal salt of methacrylolethyl-N, N -dimethylmethylenecarboxyammoniumiodide.

In the IR-spectr of crystal salt of methacrylolethyl-N, N -dimethylmethylenecarboxyammoniumiodide the intensive wide strip in the field of 3200-3600 cm^{-1} , characteristic to valency fluctuation associated hydroxyl to group $\text{O} \geq \text{C}-\text{OH}$, valency fluctuations

$>\text{C}=\text{O}$ the groups connected with double communication at 3100 cm^{-1} , an absorption strip $^+\text{N}-\text{CH}_2-$ groups in the field of 2800-2900 cm^{-1} , valency fluctuations $\geq \text{C}=\text{O}$ carbonyl groups of carboxyl is observed at 1720 cm^{-1} , valency fluctuations of carbonyl groups having interface to double communication in area of 1630 cm^{-1} , valency fluctuations $\geq \text{C}-\text{O}-\text{C} \leq$ communications at 1150 cm^{-1} deformation fluctuations dimethyl groups - $\text{N}(\text{CH}_3)_2$ at 1380 cm^{-1} (fig. 1).

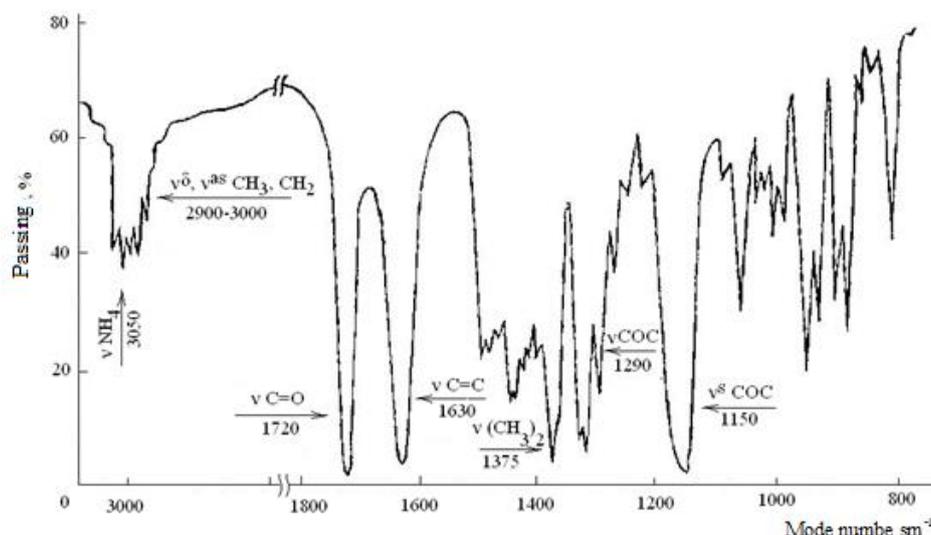


Fig. 1. IR-spectr crystal quaternary salts on the basis of methacrylolethyl-N, N - dimethylmethylenecarboxyammoniumiodide.

The structure of crystal salt of PMR-spectris also confirmed. In the PMR-spectrin the field of 5,76-6,30 m.p. Are observed two signals corresponding to nonequivalent protons $=\text{CH}_2$, connected with double communication. In the field of 4,6-is observed the signal of protons $-\text{O}-\text{CH}_2-$ groups; at 4,0 m.p. it is shown triplet a signal concerning to $-\text{N}^+-\text{CH}_2-$ group; signal $-\text{N}(\text{CH}_3)_2$

groupy, is observed in the field of 3,4 m.p.; the protons of group connected with carboxyl by an ion through methylen of group in the field of 3,0 m.p.; methyl the protons connected with carbon because of equivalent character are observed in a kind, singlet at 2,0 m.p. (Fig. 2).

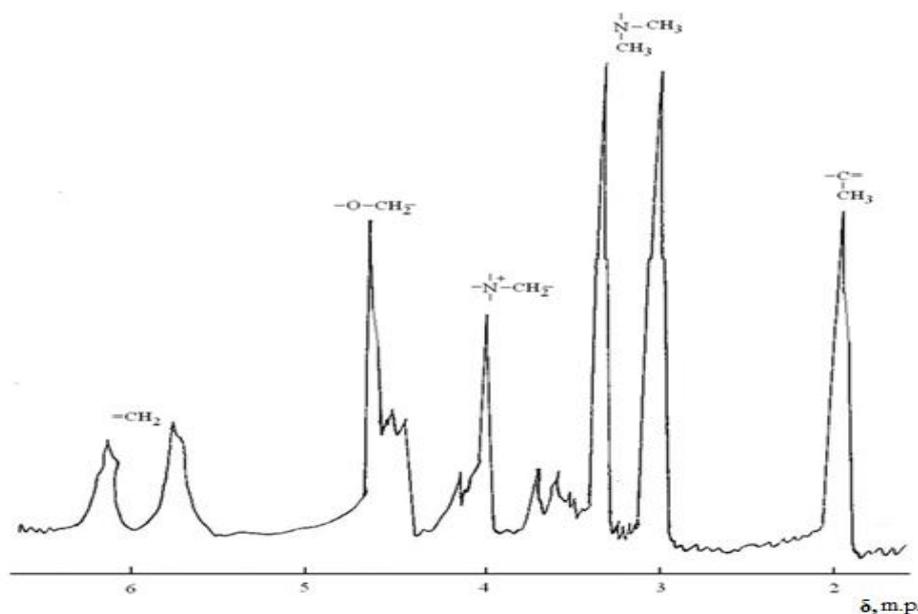


Fig. 2. PMR-spectr crystal quaternary salts on the basis of methacrylolethyl - N, N-dimethylmethylenecarboxyammoniumiodide

Kinetic of polymerizations by a was investigated dilatometric method. A superficial tension was investigated by the control over a blanket condition on border a solution - air by measurement of a superficial tension of a solution in static conditions. Definition of critical concentration micelle formation was carried out on isotherms of a superficial tension.

Measurements of a superficial tension allow to estimate superficial activity of monomer and to calculate according to the thermodynamic equation of Gibbs superficial surplus of the dissolved substance (adsorption) and the area occupied in sated adsorption a layer. Bactericidal action of monomer estimated on diameter of suppression of growth of various fungi and bacteria. A method for determination of wettability based on definition of a regional corner wetting of the drop put on the moistened surface.

RESULTS AND DISCUSSION

In work for the first time have experimentally established that synthesised low-molecular monomer - methacryloylethyl-N, N-dimethylallylammoniumbromide and methacryloylethyl - N, N - dimethylmethylenecarboxyammoniumiodide in the water environment in the presence of the initiator of the personal computer, and also in the environment of organic solvents in the presence of initiators peroxidebenzoyl and dinitrilazobisisooil acids at temperatures 283-293K, initiators excluding thermal disintegration, polymerization with formation high-molecular polymer.⁴⁻⁷

Have experimentally established that low-molecular monomer on the basis of methacryloylethyl-N, N-dimethylallylammoniumbromide polymerization in the presence of the initiator - persulfat calyx in the water environment. Defined a reaction order on a monomeasure (0,5-2,0 mol/l) and to the initiator (1,10-3 \div 5 \cdot 10⁻³ mol/l) which has appeared, accordingly, equal 1,48 and 0,5. The overestimated value of an order of reaction on a monomeasure, in comparison with theoretical which is equal 1,0, specifies in its participation not only in reaction of growth of a chain, but also in reaction of formation of the molecular complex which disintegration produces initiating centres. Speed of polymerization grows with temperature and its dependence on return value of temperature (in an interval 283-298K) submits to the equation of Arrenius, energy of activation makes 53,7 kDj/mol.

For the purpose of reception of some thermodynamic parametres characterising an end-product on an example of interaction methacryloylethyl-N, N-dimethylallylammoniumbromide with persulfat calyx in water the balance constant (K_r) reactions complexformation and factor of molar extinction of (ϵ) a complex by the graphic decision of the equation of Beneshi-Hildebranda (tab. 1) has been defined.

Apparently from given tab. 1, the factor of molar extinction a complex practically does not depend on temperature, and the constant of balance of reaction complexformation even (283-293K) grows in a narrow temperature interval with rise in temperature.

Tab. 1. Value of factor molyrecstins(ϵ) and balance constants (K_r) at different temperatures

T, K	ϵ , L/mol·sm	K_r , L/mol
283	829	0,04
288	834	0,09
293	830	0,15

From temperature dependence of a constant of balance of reaction of formation of a complex thermodynamic parametres of process complexcreating- warmth

of formation of a complex (ΔH), sizes of change of energy of Gibbs (ΔG) and entropy (ΔS) (tab. 2) have been defined. Values of thermodynamic parameters testify to stability of a complex.

Tab. 2.

Thermodynamic characteristics process of formation in a complex of methacryloylethyl-N, N-dimethylallylammoniumbromide with persulfat calyx in the water environment

$-\Delta H$, kDj/mol	$-\Delta S$, Dj/mol	$-\Delta G$, kDj/mol
9,02	30,7	0,14

Similar results have been received for process of polymerization monomeasured of monomer -methacryloylethyl-N, N-dimethylmethylenecarboxyammoniumiodide, methacryloylethyl-N, N-dimethylpropylammoniumbromide.

In work results of research of physical and chemical properties synthesised cationic SAS, colloid-chemical properties of their solutions, in particular are resulted: the superficial tension, moistening, sensitivity to some microorganisms, critical concentration micelle

formation, influences on process of adhesion and cohesion, are calculated value gidrofilno-lipofilno balans.⁸⁻¹⁵

Processing of natural fibres by solutions of monomer on the basis of methacryloylethyl-N, N-dimethylpropylammoniumbromide considerably reduces a corner of their wetting by water, i.e. improves wettability of their surface water.¹⁴ Regional corners of wetting of the modified natural fibres depending on concentration of solutions modifying monomer are resulted on fig. 3.

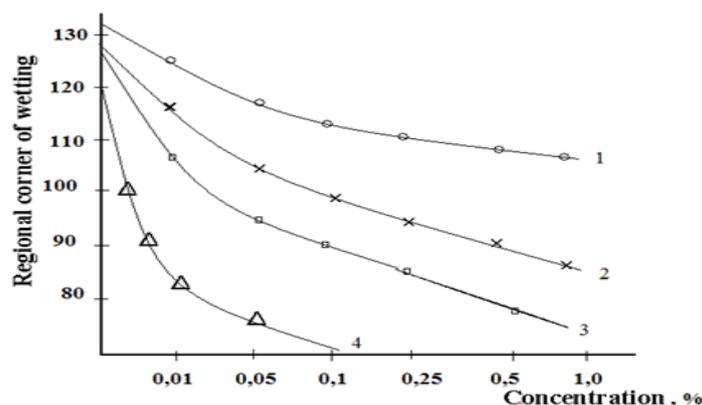


Fig. 3. Dependence of a regional corner of wetting by water of albuminous of fibres from concentration of solutions of modifying monomer: methacryloilethyl – N, N - dimethylallylammoniumbromide (1), cetylpyridinechloride (2), dupanol (3), oxyethylizedalkulphenol.

Efficiency of action of solutions synthesised high-molecular polymer on the basis of MEDAAB on wettability of a fibre was compared by water to similar effect of action of solutions of low-molecular monomer: cationic-cetylpyridinechloride (CPC), anion- dupanol (DP) and nonionic-oxyethylizedalkylphenol.

Monomer methacryloilethyl-N, N - dimethylallylammoniumbromide and cetylpyridinechloride possess the big superficial activity in comparison with dupanol and oxyethylized polystyrene and considerably influence on intermolecular of cohesion liquid interaction. With the growth of concentration of the monomer, having small superficial activity, energy of its adhesion increases. Extreme dependence of energy of adhesion weed - methacryloilethyl-N, N dimethylallylammoniumbromide from concentration of the second it is possible to explain saturation of a surface of fibres with molecules of monomer.

Dependence of a superficial tension of water solutions of the synthesized substances on their concentration by a method of the greatest pressure of vials on Re-binder (fig. 4) is defined. The facts show that investi-

gating substances possess considerable superficial activity. However, higher superficial activity is observed at synthesized cationic surface-active substance on the basis of methacryloilethyl-N, N - dimethylallylammoniumbromide in comparison with other superficially - active substances, such, as cetylpyridinechloride, dupanol and oxyethylizedalkylphenol. This results from the fact that at synthesized cationic surface-active substance on the basis of methacryloilethyl-N, N - dimethylallylammoniumbromide the double communications which presence promotes increase of an index of polarity contain. Sites of excesses at an exit of isotherms on a plateau correspond to critical concentration mycellocreating. It is visible that rather strong superficial activity of polymer on the basis of methacryloilethyl-N, N - dimethylallylammoniumbromide in comparison with cetylpyridinechloride, dupanol, oxyethylizedalkylphenol (fig. 4) possesses. On the basis of experimental data of a superficial tension of solutions of the considered of monomer measured at their various concentration, have been calculated energy of cohesion molecules in solvent and adhesion of monomer on albuminousfibres.

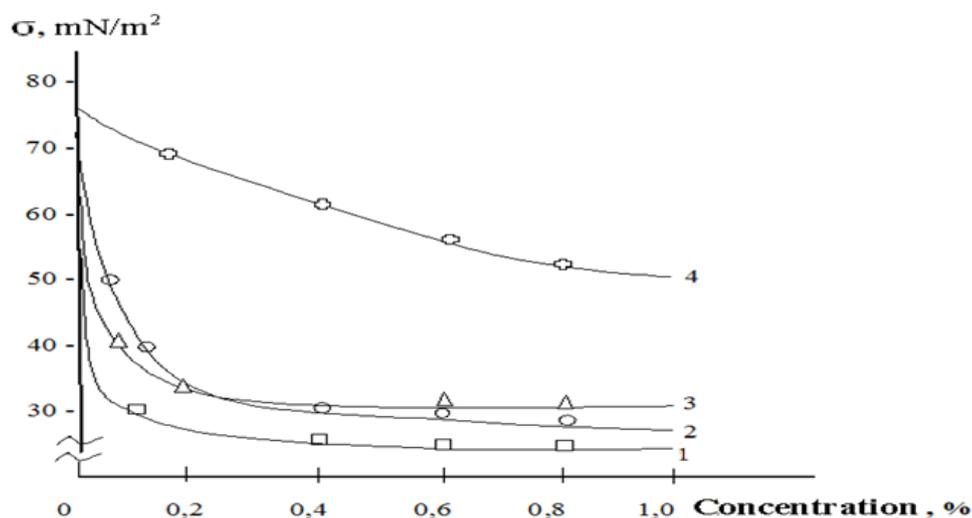


Fig. 4. Dependence of superficial on-tension of solutions of monomer from concentration: 1-methacryloilethyl-N, N-dimethylallylammoniumbromide, 2- cetylpyridinechloride, 3-dupanol, 4-oxyethylized alkylphenol.

Settlement values of energy of cohesion (W_k) and adhesions (W_a) are resulted in tab. 3. Under the resulted fact law is accurately traced that cetylpyridinechloride possesses rather smaller superficial activity, than polymerMEDAAB and influences on cohesive inter-

molecular interaction of a liquid owing to what its presence at a solution not strongly reduces energy of cohesion of solvent molecules. The greatest most strongly influences energy of cohesion of polymer on the basis of methacrylolethyl-N, N-dimethylallylammoniumbromide, possessing superficial activity.

Tab. 3.

Dependence of values of energy of cohesion (W_k) and adhesions (W_a) solutions surface-active substances from their concentration

Concentration of monomer, %	Polymer MEDAAB		SPC		DP		OP	
	W_k	W_a	W_k	W_a	W_k	W_a	W_k	W_a
0,01	140,6	26,0	120,8	25,0	111,8	31,4	111,1	30,7
0,025	140,0	31,8	94,8	26,6	101,8	31,8	87,1	38,3
0,05	138,0	43,2	79,4	27,4	89,8	37,9	80,7	42,1
0,10	129,0	50,0	69,6	31,8	82,2	43,9	79,4	44,6
0,50	114,6	55,3	66,8	35,7	74,2	43,5	74,6	43,9

The greatest most strongly influences energy of cohesion of polymer on the basis of methacrylolethyl-N, N-dimethylallylammoniumbromide, possessing superficial activity.

Application of chemical compounds with various degree of biological activity can lead to balance infringement in the surrounding nature, to occurrence of sharp and chronic poisonings of live organisms, their change immunobiological reaction, increase of level of the general disease and working capacity decrease.¹⁶ A particular interest among chemical compounds represent monomeasured and polymeric of monomer. It is necessary to notice that at laboratory diagnostics of data on a poisoning with chemical reactants, especially sensitivity of some microorganisms to the last are extremely limited and inconsistent. Considering the given circumstance, sensitivity of some microorganisms to low - and high-molecular cationic to surface-active substances on the basis of methacrylolethyl-N, N - dimethylmethylenecarboxyammoniumiodide and methacrylolethyl-N, N - dimethylallylammonium has been studied.

Results of the spent researches have shown that cultures staphylococcus, an intestinal stick, proteus and salmonellas are sensitive to all examinees of monomer and polymer. At the same time, it is interesting to notice that cultures yeast-like sort of mushrooms candidate have appeared tolerant to action of all considered monomer and polymer.

Repeated researches have convincingly shown that among the studied systems the greatest bacteriostatic and bacteriacidic effect possess monomer and polymer on the basis of methacrylolethyl-N, N - dimethylmethylenecarboxyammoniumiodide. Thanks to iodine and bromine presence in the synthesized monomer and polymer at processing of textile fibres by them and materials on their basis, the last get antimicrobial properties.

Efficiency of surface-active substances characterise special number - hidrofилно-lipofilny balance (HLB). The important characteristic of molecules colloidal the monomer, having crucial importance for their superficial and volume properties so, and for their ap-

plication, the parity of two opposite groups of a molecule - hydrophilic and waterproof (lipophilic) is, so-called gidrofilno-lipofilny balance.^{17,18}

It is necessary to notice that HLB is the important quantitative characteristic colloidal the monomer, connected with their various application.

On the basis of given values HLB hydrophilic groups and lipophilic groups under Griffin's offered formula values HLB synthesized monomer are calculated. Calculated value of HLB for monomer methacrylolethyl-N, N - dimethylmethylenecarboxyammoniumiodide makes: $HLB = 9,2 \cdot 3,8 + 7 = 12,4$; and for methacrylolethyl-N, N - dimethylallylammoniumbromide - $HLB = 16,2 \cdot 4,75 + 7 = 18,45$, numbers HLB are linearly connected by superficial activity. This parameter underlies characteristics of properties of monomer and in practice till now usually quality of monomer estimate on numbers HLB. Received values HLB correspond to process accompanied solubilization water solutions, from this it follows that superficial activity of monomer defines their ability to lower a superficial tension, to cause foaming, wetting etc. Calculated values of HLB testify to use monomer as surface-active modifiers for improvement of properties of textile fibres.

CONCLUSION

For reception cationic polymer with the set properties are improved known and new ways of complex-radical polymerization activated donor- acceptor by interaction cationic monomer with acceptors electrons - initiators of polymerization are developed at the temperatures excluding thermal disintegration of initiators.

Synthesized polymer in the water environment possess strongly pronounced surface-active properties, essentially reducing a superficial tension of water, show bactericidal abilities and define energy of adhesion and cohesion the modifier on a surface of natural fibres, improve wettability of a fibre, water solutions are characterised inherent in them electroconductivity of, viscosity, critical concentration mycellocreating.

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OBTAINING DETERGENTS FOR TECHNICAL PURPOSES BASED ON «SUPER-ALKALI» AND ACTIVE ADDITIVES

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Abstract

The optimal formulations of technical cleaners are determined. Experimental data of the article allow us to conclude that alkaline solutions containing surfactants contribute to the removal of oily stains, since under their action fats are «saponified».

Keywords: super-alkali, surfactant, sodium metasilicate, ammonium polyphosphate, ammonium monophosphate, detergents and cleaning products, alkaline.

Today in the world, the use of modern technologies in acceleration of the development of industry, the solution of environmental problems, the production of competitive and environmentally friendly substances is becoming an actual problem. In recent years, on the basis of new developments, innovative approaches, there has been an increase in the production of products necessary for industry.

One of the main directions of economic development of Uzbekistan is the development of natural resources, their integrated use and the creation of competitive import-substituting products based on local raw materials. The chemical industry is the base industry, which is in close relationship with all sectors of the economy. Therefore, the development of the chemical industry is a priority task for the modern development

of the economy of the Republic of Uzbekistan. One of the chemical products is powdered detergents (PD), the need for which is steadily increasing due to the development of industries of the national economy that consume detergents. The market for detergents and cleaning products includes the following segments of the market of household chemical goods: synthetic detergents (SD), bleaches and products that complement the action of laundry detergent, as well as cleaning products.

The effectiveness of a detergent and the quality of cleaning a metal surface largely depends on the properties of the treated surface - its roughness, sensitivity to the corrosive effect of the detergent, the presence of oxides on the surface, its homogeneity [1].