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**STUDY OF POLYMERIZATION OF METHACRYLATE
GROUPS CONTAINING BY THE DONOR-ACCEPTOR
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ABSTRACT

The article deals with the synthesis reaction to produce and interact with dialkylaminoalkyl halogen-containing substances, their composition and structure was studied by elemental, IR, PMR-spectroscopic analyzes. Electrocapillary studied curves, the electric charge density, the concentration of adsorbed molecules, the dependence of the differential capacitance of the synthesized substances. The results of the studies showed that the synthesized crystalline quaternary ammonium salt with dialkylaminoalkyl methacrylate-based materials have the properties of halogen-containing surfactant, cation type.

**ИССЛЕДОВАНИЕ ПОЛИМЕРИЗАЦИИ МЕТАКРИЛАТСОДЕРЖАЩИХ
ГРУПП ДОНОРНО-АКЦЕПТОРНЫМ МЕТОДОМ****И.Н. Хайдаров**

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диалкиламиноалкилметакрилат,
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соль, синтез, поверхностное
натяжение,
электрокапиллярные кривые,
адсорбция.

ABSTRACT

В статье рассматривается синтез реакции получения и взаимодействия диалкиламиноалкилметакрилатов с галоидсодержащими веществами, изучен их состав и структура путем элементных, ИК-, ПМР-спектроскопических анализов. Изучены электрокапиллярные кривые, плотность электрического заряда, концентрации адсорбированных молекул, зависимость дифференциальной ёмкости синтезированных веществ. По результатам проведенных исследований показано, что синтезированная кристаллическая четвертичная аммониевая соль на основе диалкиламиноалкилметакрилатов с галоидсодержащими веществами обладают



*свойствами поверхностно-активного
вещества, катионного типа.*

Introduction. In order to obtain some thermodynamic parameters characterizing the final product of the interaction of monomeric surfactants with potassium persulfate, using the example of β -methacryloylethyl-N,N-dimethylallylammonium bromide and potassium persulfate in water, the equilibrium constant (K_p) of the complexation reaction and the molar extinction coefficient (ϵ) of the complex were determined by graphical solution of the Benesi-Hildebrand equation [4-5]:

$$\frac{[C_1]l}{D} = \frac{1}{K_p \epsilon} \cdot \frac{1}{[C_2]} - \frac{1}{\epsilon}$$

where: D is the optical density at the maximum absorption of the complex ($\lambda_{\max}=328$ nm); l – cuvette thickness (0,1 sm); C_1 – potassium persulfate concentration, mol/l; C_2 – concentrations β -methacryloylethyl-N,N-

dimethylallylammonium bromide, mol/l [6-9].

Optical density measurements were carried out for a series of solutions with different concentrations β -methacryloylethyl-N,N-dimethylallylammonium bromide (3,0-6,0 mol/l) and a constant content of potassium persulfate (0.075 mol/l), at 283, 288 and 293K. Values $\frac{[C_1]l}{D}$ were represented as a function of $\frac{1}{[C_2]}$, in this case, the tangent of the angle of inclination of the line gave the value $\frac{1}{K_p \epsilon}$, and the segment cut off on the ordinate axis, $-\frac{1}{\epsilon}$. Values found K_p and ϵ are presented in Table 1.

Table 1.

Graphical solution of the Benesi-Hildebrand equation

Temperature, K	Molar extinction coefficient, L/mol.cm	Equilibrium constant of the complexation reaction, l/mol
283	829	0,04
288	834	0,09
293	830	0,15

As can be seen, the molar extinction coefficient (ϵ) of the complex is practically independent of temperature, and the equilibrium constant of the complex formation reaction (K_p) even in a narrow temperature range (283-293K) increases with increasing temperature [10-12].

To determine the reaction constants for the complex-radical

polymerization of monomeric cationic surfactants with a minimum number of experiments and to increase the reliability of the obtained data, a computer-aided mathematical design of experiments was used. The kinetic parameters of the cationic surfactant β -methacryloylethyl-N,N-dimethylallylammonium bromide at low temperatures were determined using the



least-squares method of mathematical design of experiments.

The kinetic equation for the rate of polymerization of the quaternary monomer salt β -methacryloylethyl-N,N-dimethylallylammonium bromide can be written as follows: $V = K/PB^n/MEDAAB^m$ (1). Considering that for Arrhenius systems $K = Ae^{-E/RT}$

(2)

Where: A- pre-exponential factor; E- activation energy; R- gas constant; T- temperature, equation (1) has the form:

$$V = A / PB^n / MEDAAB / m e^{-E/RT}$$

(3)

In the studies, the concentration of benzoyl peroxide varied within the range 0,01-0,04 mol/l, β -methacryloylethyl-N,N- dimethylallylammonium bromide- 0,25-1,0 mol/l, and the temperature varied between 298 to 313K. By taking the logarithm of equation (3) we can obtain:

$$\lg V = \lg A + n \lg /PB/ + m \lg /MEDAAB/ - E/RT \lg e \quad (4)$$

or in general, a first-order polynomial will have the following form:

$$\hat{Y} = a_0 + a_1 Z_1 + a_2 Z_2 + a_3 Z_3 \quad (5), \text{ где:}$$

$$\hat{Y} = \lg V; a_0 = \lg A; a_1 = n; a_2 = m;$$

$$a_3 = -E/R \lg e; Z_1 = \lg /PB/; Z_2 = \lg /MEDAAB/; Z_3 = 1/T$$

To determine the coefficients of the equation (5) a linear orthogonal plan-PFE was drawn up (table. 2).

The regression equation in a dimensionless system has the form;

$$U = v_0 + v_1 X_1 + v_2 X_2 + v_3 X_3 \quad (6)$$

In this case, linear formation was used:

$$v_0 = -5,1567; v_1 = 0,2093; v_2 = 0,3692; v_3 = 0,2329$$

In accordance with (5) and (6) taking into account (7)

$$n = 0,60; m = 1,56; A = 0,610^3; E = 65,4 \text{ kJ/mol.}$$

The kinetic equation for the radical polymerization of the quaternary salt of β -methacryloylethyl-N,N-dimethylallylammonium bromide at moderate temperatures in the presence of benzoyl peroxide takes the following form: $V = 0,610^3 /PB^{0,60} /MEDAAB^{1,56} e^{-65,4/PT}$ (8)

Table 2.

Matrix for planning the polymerization of β -methacryloylethyl-N,N-dimethylallylammonium bromide in the presence of benzoyl peroxide

N ^o п/п	PB mol/l	MEDAAB mol/l	T, K	V10 ^{5*} mol/l s	X ₀	X ₁	X ₂	X ₃
1	0.04	0.25	298	0.11	+	+	-	-
2	0.01	0.25	298	0.05	+	-	-	-
3	0.04	0.25	313	0.19	+	+	-	+
4	0.01	0.25	313	0.09	+	-	-	+
5	0.04	1.0	298	0.41	+	+	+	-
6	0.01	1.0	298	0.13	+	-	+	-
7	0.04	1.0	313	2.0	+	+	+	+
8	0.01	1.0	313	0.70	+	-	+	+



* - the average value of V was obtained from three parallel experiments.

The obtained results further confirm the donor-acceptor mechanism of complex-radical polymerization of cationic surfactants.

The structure and composition of the synthesized monomer and polymer

Name of the substance	Elemental composition							
	calculated, %				found, %			
	C	H	N	Br	C	H	N	Br
NM CPAV	47,48	7,19	5,03	28,77	47,29	6,95	5,06	28,48
VM KPAV	47,48	7,19	5,03	28,77	46,81	7,38	5,10	28,62

Spectroscopic data showed that the unit of the resulting polymer corresponds in composition and structure to a monomeric quaternary salt. The allyl bond in the polymers is preserved. Stretching vibrations were observed in the IR spectra. -CH₂-CH=CH- groups in both the monomer and polymer salt in the region 1620 cm⁻¹. Polymerization took place, apparently, due to the opening of the double bond of the methacrylate groups, since the absorption bands C=C- groups at 1640 cm⁻¹ absent.

In the investigated range, preliminary experiments established the absence of a "dark" reaction.

It should be noted that in the presence of a stable TMPO inhibitor the reaction does not occur, which indicates the radical nature of the process.

Similar results were obtained during the polymerization of a monomeric cationic surfactant based on β-methacryloylethyl-N,N-

salts were confirmed by IR spectroscopy and elemental analysis (Table 3).

Table 3.

Elemental composition of low-molecular and high-molecular-weight surfactants based on β - methacryloylethyl-N,N-dimethylammonium bromide

dimethylmethylenecarboxyammonium iodide. The effect of monomer and initiator concentrations on polymerization kinetics was studied over a wide range of values. It is evident that the reaction rate increases consistently with increasing concentrations of both monomer and initiator. The polymerization reaction orders found from logarithmic dependences were 0.5 for the initiator and 1.6 for the monomer. The polymerization of MEDMAI in dimethyl sulfoxide at low conversions can be described using the classical equation: $V=K[M]^{1.6} \cdot [I]^{0.5}$.

The slightly overestimated value of the order for the monomer, in contrast to the theoretical value of 1.0, indicates the formation of a molecular complex compound during the interaction of β-methacryloylethyl-N,N-dimethylmethylenecarboxyammonium iodide with dinitrile azobisisobutyric acid.

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