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M.I. Abdukakhkharova
Tashkent State Technical University

A.I. Ismailov
Tashkent State Technical University

U.M. Mirzaev
Tashkent State Technical University

R.I. Ismailov
Tashkent State Technical University

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OBTAINING SOME THERMODYNAMIC PARAMETERS CONTAINING METACRYLATE AND ALLYL GROUPS CONTAINING IN COMPOSITION

M.I. Abdukakhkharova¹, A.I. Ismailov¹, U.M. Mirzaev¹, R.I. Ismailov¹

¹Tashkent State Technical University

Abstract

The article discusses the preparation of some thermodynamic parameters characterizing the final product of complex radical polymerization of amino alkyl acrylate derivatives containing both methacrylate and alkyl groups of low molecular weight compounds with electron acceptors - polymerization initiators at temperatures that exclude thermal decomposition of the initiators themselves. The equilibrium constant of the complication reaction and the molar extinction coefficient of the complex were determined by graphically solving the Beneshe-Hildebrand equation, the heats of complex formation, entropy, Gibbs energy were found, and the elemental composition of low molecular weight and high molecular weight substances was determined. As can be seen from the studies, the molar extinction coefficient of the complex practically does not depend on temperature, and the equilibrium constant of the complexation reaction even in a narrow temperature range (283–293 K) increases with increasing temperature. The structure and composition of the synthesized monomeric and polymer salt were also considered in the work, and confirmed by IR-spectroscopy and analysis of elemental composition, the obtained spectroscopic data showed that the unit of the formed polymer corresponds in composition and structure to the monomeric quaternary salt, and the allyl bond in the polymers is preserved. It can be seen from the studies that, with an increase in the concentration of both the monomer and the initiator, the reaction rate naturally increases.

Key words: *thermodynamic parameters, complex radical polymerization, aminoalkyl acrylate and halogen-containing substances, methacrylate and allyl groups, potassium persulfate, benzoyl peroxide (BP), dinitrile azobisisobutyric acid.*

Nucleophilic substitution of the halogen by amino groups occurs, in the interaction of reactive halogenated monomers with amino compounds, which is accompanied by spontaneous polymerization and the formation of ammonium polymers. Kinetic studies have shown that the initial stage of the process is the reaction of nucleophilic substitution of halogenated monomers with amino compounds and the formation of quaternized groups that contribute to the polarization of the double bonds of the monomers. This, along with the formation of associates of monomer units, is responsible for the course of spontaneous polymerization [1-10].

A study of the structure of the formed ammonium polymers showed that when using an excess of halogenated monomers, non-quaternized halogenated monomers are involved in the spontaneous polymerization reaction along with quaternized monomer molecules. It was shown that the process of spontaneous polymerization also occurs during the interaction of polymer-monomer systems capable of forming an ammonium group. The relatively high reaction rates of spontaneous polymerization are due to the adsorption of activated monomers on the macromolecules of the polymers and the formation of ion pairs. The process of the formation of ammonium polymers during the interaction of reactive halogen derivatives of polymers with

polymer amino compounds, as well as the interaction of reactive dihalo derivatives with polyfunctional amino compounds, was studied [11-17].

In order to obtain some thermodynamic parameters characterizing the final product of complex radical polymerization of aminoalkyl acrylate derivatives containing both methacrylate and allyl groups in water, the equilibrium constant (K_p) of the complexation reaction and the molar extinction coefficient (ϵ) of the complex were determined by graphically solving the Benesi-Hildebrand equation :

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

where D is the optical density at the maximum absorption of the complex ($\lambda_{\max} = 328 \text{ nm}$);

l is the thickness of the cell (0.1 cm);

C_1 is the concentration of potassium persulfate, mol/l;

C_2 is the concentration of the monomeric salt of methacryloethyl-N, N-dimethylallyl ammonium iodide (MEDMAI), mol/l.

The optical density was measured for a series of solutions with different monomer concentrations (3.0-6.0 mol/l) and a constant content of potassium persulfate (0.075 mol/l) in them, at 283, 288, and 293K. The values were presented as a function of, while the tangent of the slope of the line yielded a value, and the segment cut off on the ordinate. The found values of K_p and ϵ are presented in table. one.

Table.1.

Graphical solution of the Benesi-Hildebrand equation

| Temperature, K | Molar coefficient extinction, ϵ , l/mol | Equilibrium constant complexation reactions, 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 complexation reaction (C_r) even in a narrow temperature range (283–293 K) increases with increasing temperature.

From the temperature dependence of the equilibrium constant of the complex formation reaction, the thermodynamic parameters of the complex formation process were determined - the heat of complex formation (ΔH), the magnitude of the Gibbs energy change (ΔG) and entropy (ΔS), the values of which are presented in Table 2, indicate a high stability of the complex.

Table.2.

Thermodynamic characteristics of the complex monomer - potassium persulfate in water

| Warmth of education complex, $-\Delta H$, kJ/mol | Entropy, $-\Delta S$, J/mol | Entropy, $-\Delta S$, J/mol |
|---|------------------------------|------------------------------|
| 9,02 | 30,7 | 0,14 |

To determine the reaction constants of the complex radical polymerization of a monomer substance with a minimum amount of experiment and increase the reliability of the information obtained, the method of mathematical planning of the experiment using a computer was used.

The kinetic parameters of the monomer salt at low temperatures were determined by the least squares method of mathematical planning of the experiment.

The kinetic equation for the polymerization rate of the quaternary monomeric salt can be written as follows:

$$V = K (BP)^n (MEDMAI)^m, (1)$$

Given that for Arrhenius systems

$$K = Ae^{-E/RT}, (2)$$

where A is the preexponential factor;

E- is the activation energy;

R- is the gas constant;

K- constant, equation (1) has the form:

$$V = A (BP)^n (MEDMAI)^m e^{-E/RT}, (3)$$

In studies, the concentration of benzoyl peroxide varied in the range of 0.01-0.04 mol/l, the monomeric salt - 0.25-1.0 mol/l, and the temperature ranged from 298 to 313K. Logarithm of equation (3), we can obtain:

Table.3.

Monomer salt polymerization planning matrix in the presence of benzoyl peroxide

| N ₀ | BP, mol/l | MEDMAI, 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.

$$\lg V = \lg A + n \lg / BP / + m \lg / MEDMAI / - E / RT \lg e (4)$$

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

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

where $\hat{Y} = \lg V$; $a_0 = \lg A$; $A_1 = n$; $a_2 = m$;

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

To determine the coefficients of equation (5), a linear orthogonal plan-PFE was compiled (Table 3)

The regression equation in a dimensionless system has the form;

$$Y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 (6)$$

In this case, linear education is used:

$$b_0 = -5.1567; b_1 = 0.2093; b_2 = 0.3692; b_3 = 0.2329 (7)$$

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

$$n = 0.60; m = 1.56; A = 0.6103; E = 65.4 \text{ kJ / mol.}$$

The kinetic equation for the radical polymerization of a quaternary salt at moderate temperatures in the presence of benzoyl peroxide takes the following form:

$$V = 0.6103 (PB)^{0.60} (MEDMAI)^{1.56} e^{-65.4 / RT} (8)$$

The coordinates of the center of the plan and the intervals of variation are given in table 4.

The obtained results additionally confirm the donor-acceptor mechanism of complex radical polymerization.

Table. 4.**Coordinates of the center of the plan and intervals of variation**

| Factor | $\lg(\text{BP}), Z_1$ | $\lg(\text{MEDMAI}), Z_2$ | Temperature, K^{-1}, Z_3 |
|-------------------------------------|-----------------------|---------------------------|-----------------------------------|
| Variation Intervals ΔZ_i | 0,3013 | 0,3013 | 0,000008 |
| Plan Center Coordinates, Z_j^0 | -1,700 | -0,3013 | 0,00327 |

The structure and composition of the synthesized monomeric and polymer salts are confirmed by IR spectroscopy and analysis of the elemental composition shown in table 5.

The data of spectroscopic studies showed that the link of the resulting polymer in composition and structure corresponds to the monomeric quaternary salt. The allyl bond in the polymers is retained. In the IR spectra, stretching vibrations of $-\text{CH}_2-\text{CH}=\text{CH}-$ groups were observed in both the monomeric and polymer salts in the region of 1620 cm^{-1} . The polymerization apparently took place due to the opening of the double bond of methacrylate groups, since there are no absorption bands of the $\text{C}=\text{C}$ group at 1640 cm^{-1} .

Table. 5.**The elemental composition of low molecular weight and high molecular weight substances based on monomeric salts**

| Name of substance | Elemental composition | | | | | | | |
|----------------------------------|-----------------------|------|------|-------|----------|------|------|-------|
| | calculated, % | | | | found, % | | | |
| | C | H | N | Br | C | H | N | Br |
| low molecular weight substances | 47,48 | 7,19 | 5,03 | 28,77 | 47,29 | 6,95 | 5,06 | 28,48 |
| high molecular weight substances | 47,48 | 7,19 | 5,03 | 28,77 | 46,81 | 7,38 | 5,10 | 28,62 |

In the studied interval, preliminary experiments established the absence of a "dark" reaction.

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

Similar results were obtained during the polymerization of a monomer salt based on MEDMAI. The effect of the concentration of monomer and initiator on the kinetics of polymerization was studied in a wide range of their values. It can be seen that with an increase in the concentration of both the monomer and the initiator, the reaction rate naturally increases. The orders of the polymerization reaction found from the logarithmic dependences turned out to be 0.5 at the initiator, 1.6 at the monomer. The polymerisation of MEDMAI in dimethyl sulfoxide in the low-conversion region can be described in terms of the classical equation: $V=K [M]^{1.6} [I]^{0.5}$.

Thus, it was found that a slightly overestimated order value in terms of monomer, in contrast to the theoretical value of 1.0, indicates the formation of a molecular complex

compound in the interaction of MEDMAI with dinitrilazobisisobutyric acid.

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