

Oxypropylation of Polyacrylic Acid

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ABSTRACT

Water soluble polymers are widely used in various industrial areas. Surface activity is also important for some applications in industry. In this study, a surface-active substance was synthesized by interaction of polyacrylic acid (PAA) with propylene oxide (PO). Polyacrylic acid was synthesized by radical polymerization of acrylic acid (AA) in toluene and under atmosphere of nitrogen. Oxypropylation reaction of PAA was carried out repeatedly for various initial reactant concentration and temperature values in order to investigate the kinetics of the oxypropylation reaction. The probable mechanism of "cooperative" character of oxypropylation reaction of PAA carboxylic groups was proposed on the basis of the obtained experimental data. The obtained compound from the reaction was characterized by a number of physico-chemical methods.

Key Words:

surface-active polymers;
oxypropylation;
polyacrylic acid;
propyleneoxide;
reaction kinetics.

INTRODUCTION

Water-soluble polymers play an important role in various branches of economy, in spite of the fact that they constitute a small part of high-molecular compounds. Having a lot of valuable properties, they are widely used in oil and gas, chemical

and petrochemical, mining, paper and textile industries, agriculture, medicine, and etc. [1-5]. Most water-soluble polymers used in these areas must be surface-active. From this standpoint, the investigation of polyacrylic acid (PAA) oxypropylation

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reaction is a matter of interest, as this reaction leads to the formation of non-ionogenic oxypropyl groups necessary for high surface activity and stability of the reagent against the action of media mineralization, microorganisms, shear stress and others [6-8].

The purpose of this work is to obtain a new water soluble surfactant by the reaction of polyacrylic acid (PAA) with propylene oxide (PO) and to investigate the kinetics of addition reaction of propylene oxide to polyacrylic acid.

EXPERIMENTAL

Acrylic acid (AA) used in this work was a product of Shostka Factory of Chemical Products (Ukraine). It had a purity of 99.5% and was vacuum distilled before the experiments. The fraction with boiling point of 309-311 K/20-21 mm Hg was selected. PO was used as an industrial product of the factory Organic Synthesis (Sumgait, Azerbaijan). It had a purity of 99.97%.

Toluene and isopropyl alcohol used were products of Shostka Factory of Chemical Products (Ukraine) with a purity not less than 99.4-99.6%.

Water was purified by double distillation before the experiments. PAA was synthesized by radical polymerization of AA in toluene and under atmosphere of nitrogen. The initial concentration of AA was 2.44 mol/L. The concentration of the initiator (azodiisobutyronitrile) (AIBN) was equal to 0.2% of the AA mass. Isopropyl alcohol (5% of the AA volume) was introduced into the system to prevent cross-linking of macromolecules. The temperature was 343 K. The polymerization was continued for 6 h. PAA was isolated by removal of liquid components on a rotary evaporator in vacuum.

The intrinsic viscosity $[\eta]$ of PAA, measured by using an Ubbelohde viscosimeter at 303 K, in 1,4-dioxane was found to be 0.378 dL/g. The molecular weight (\overline{M}_v) of the obtained PAA was calculated according to the equation:

$$[\mu] = 8.5 \times 10^{-4} \overline{M}_v^{0.5} \quad (1)$$

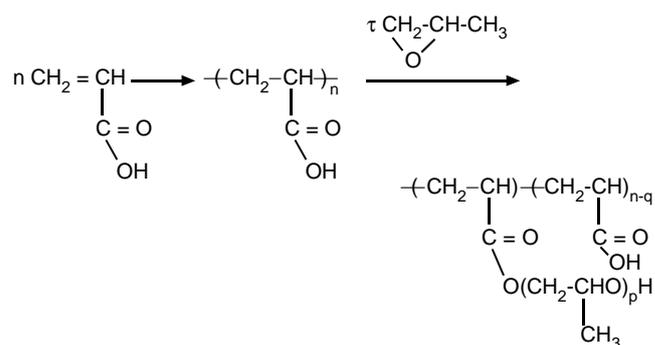
and turned out to be 200,000 [9].

Oxypropylated polyacrylic acid (OPAA) was synthesized in a 500 mL hermetic glass reactor fitted with a mixer at 150 rpm and 298 K. The solvent was water.

The reaction was also carried out repeatedly for various initial concentration (between 0.114 and 0.534 mol/L) and temperature (between 278 and 303 K) values in order to determine the order of reaction, activation energy (E_a) and pre-exponential factor (K_0) (Arrhenius constant) values, and the rate constants at the relevant temperatures. The kinetics of PAA oxypropylation reaction was studied by the gravimetric method by taking samples in the duration of 2 h reaction time. The reaction products were isolated and dried up to the constant mass on a rotary evaporator UP-1 M2 in vacuum (1-2 mm Hg). Elemental analysis was carried out at the analyzer Perkin Elmer. ^1H NMR and IR-spectra were recorded by the spectrometers Tesla BS-487C and UR-20, respectively; where $\tau = \text{qxp}$.

RESULTS AND DISCUSSION

The Scheme I of PAA synthesis and its subsequent oxypropylation may be described as in Scheme I.



Scheme I

As a result of oxypropylation reaction of PAA, the acidic number of the polymer decreases from 657 down to the range 490-540 mg KOH/g. The comparison of IR-spectra of PAA and OPAA shows clear distinctions in the range 2800-3600 cm^{-1} . The formation of hydroxyl group leads to an appearance of the corresponding large band of the valence oscillations.

^1H NMR Spectra of PAA and OPAA recorded in D2O also differ. An addition of PO to PAA causes an appearance of resonance signals of CH_3 (a doublet at 1.25-1.50 ppm) and CH_2 protons (a doublet at 3.70-3.95 ppm), CH proton (a multiplet at 4.40-4.70 ppm) and OH proton (a singlet at 4.45 ppm).

Oxypropylation of PAA also somewhat changes the

quantitative elemental composition of the polymer. PAA has the elemental composition (in mass percentage) C 50.00%; H 5.60%; and O 44.40%; (calculated values are 49.99%, 5.61% and 44.40%, respectively), but after oxypropylation the contents of these elements are equal to C 52.34, H 8.92 and O 33.74. The character of potentiometric titration curves for PAA and OPAA recorded by the ionomer EB-74 also differs.

The pKa of PAA equals 7.150 and that of OPAA is 7.275.

Using the stalagmometric method, the surface tension (σ) values of the 0.2 % (by mass) aqueous solutions of PAA and OPAA were measured at the interface with kerosene (at 293 K). They were found as:

$$\sigma_{\text{PAA}} = 28.4 \times 10^{-3} \text{ N/m}; \text{ and } \sigma_{\text{OPAA}} = 22.3 \times 10^{-3} \text{ N/m} \quad (2)$$

Taking into account that the surface tension of water itself under these conditions is $46.5 \times 10^{-3} \text{ N/m}$, a conclusion may be drawn about a significant surface activity of PAA oxypropylation product. The kinetic curves of PAA oxypropylation at 293 K and at the constant concentration of the polyacid, but at various mole ratios PO:PAA, are shown in Figure 1. As it is seen from this Figure, the rate of oxypropylation rises with increasing PO concentration. The transformation of the kinetic curves in the logarithmic scales allows us to determine the order of the reaction rate with regard to PO concentration ($n \approx 1$).

The kinetics of PAA oxypropylation was also studied at the constant concentration of PO, but at various concentrations of the polyacid (at 293 K). It was established that a variation of PAA concentration in the interval of 0.2-0.7 mol/L influences the reaction rate negligibly. On this basis, it may be stated that the order of the reaction rate with respect to PAA concentration is close to zero ($m \approx 0$).

The overall rate (v) of PAA oxypropylation is described by the equation:

$$v = -d[\text{PO}]/d\tau = k[\text{PO}]^n[\text{PAA}]^m \quad (3)$$

where, $[\text{PO}]$ and $[\text{PAA}]$ are concentrations of PO and PAA, respectively; k is the rate constant, and τ is the time of the reaction.

Taking into consideration the determined values of the rate orders with respect to reagents ($n \approx 1$; $m \approx 0$), this

equation is integrated to obtain the following relationship:

$$[\text{PO}] = [\text{PO}]_0 e^{-k\tau} \quad (4)$$

In order to find the activation energy (E_a), the temperature dependency of the PAA oxypropylation course was studied in the interval of 278-303 K (Figure 2). The extraordinary character of this dependency was established from these studies. The maximum values of the initial reaction rate and of the final PO conversion are observed at 293 K.

To determine the rate constants, the kinetic curves of PAA oxypropylation were transformed in the coordinates of the linearized form of the deduced equation ($\ln([\text{PO}]_0/[\text{PO}]) - \tau$) at 278-293 K. The rate constants at the relevant temperatures were found according to the slopes of the obtained straight lines:

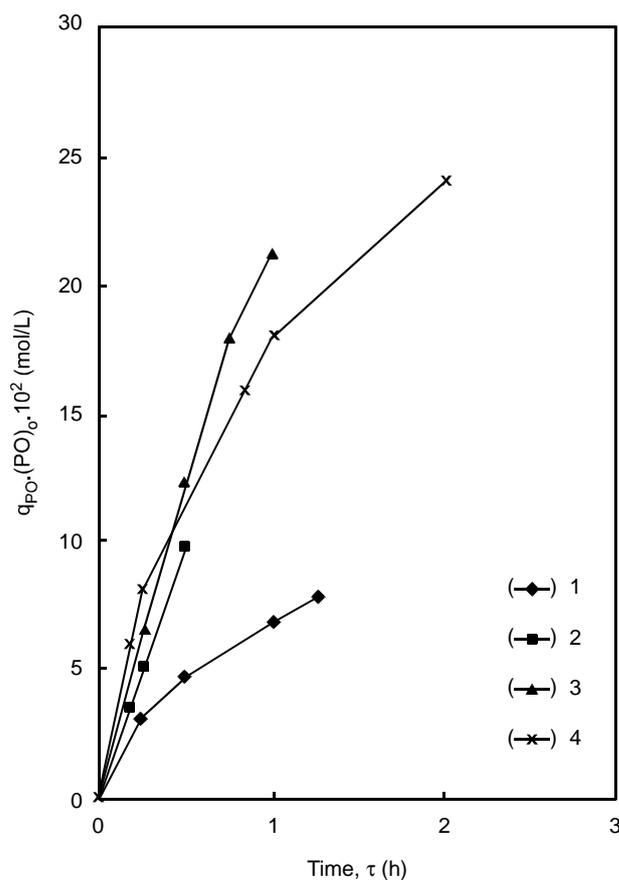


Figure 1. The kinetic curves of PAA oxypropylation at various concentrations of PO. $[\text{PAA}] = 0.267 \text{ mol/L}$; $T = 293 \text{ K}$; solvent is water; q_{PO} is PO conversion; Concentration of PO, mol/L: (1)-0.114; (2)-0.2; (3)-0.267; (4)-0.534.

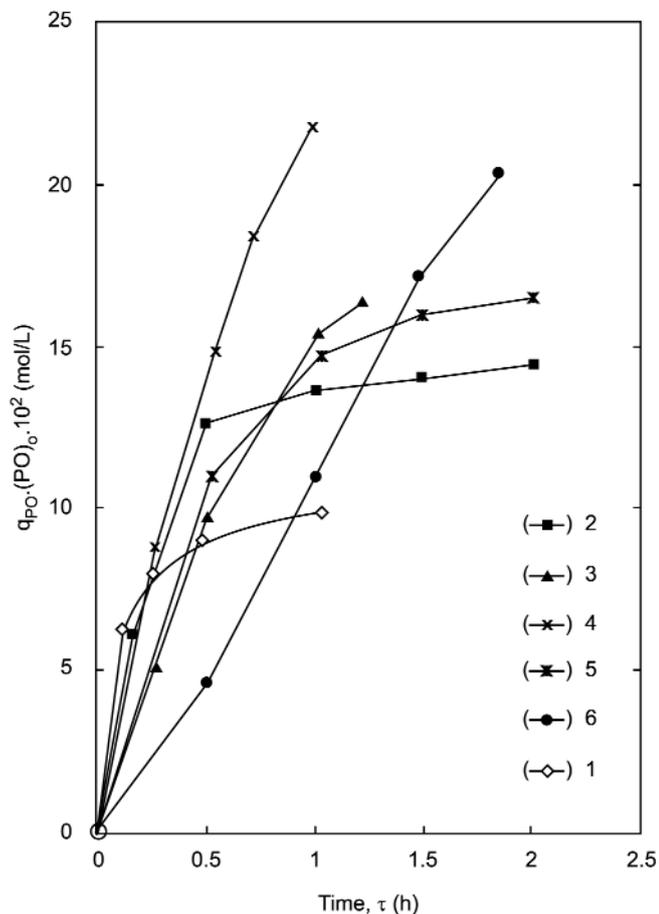


Figure 2. The kinetic curves of PAA oxypropylation at various temperatures. [PAA] = 0.267 mol/L; [PO] = 0.267 mol/L; solvent is water; q_{PO} is PO conversion; temperature, K: (1)- 278, (2)- 283, (3)- 288, (4)- 293, (5)- 298, (6)- 303.

$$k_{278} = 1.625 \times 10^{-4} \text{ s}^{-1}; k_{283} = 2.347 \times 10^{-4} \text{ s}^{-1}; k_{293} = 4.417 \times 10^{-4} \text{ s}^{-1} \quad (5)$$

Using these values of the rate constant, the average values of activation energy and the average values of pre-exponential factor (K_0), it was found that, for the interval of 278-293 K, $E_a = 44.871$ kJ/mol and $K_0 = 45752.42$ according to the logarithmic form of Arrhenius equation (Figure 3):

$$k = K_0 \cdot e^{-E_a/R\tau}; \ln k = \ln k_0 - (E_a/R)(1/\tau) \quad (6)$$

Using the calculated values of E_a and K_0 , Arrhenius equation for the given reaction is written in the following concrete form:

$$k = 45752.42 \exp [-5406.2/\tau], \text{ within } 278\text{-}293 \text{ K} \quad (7)$$

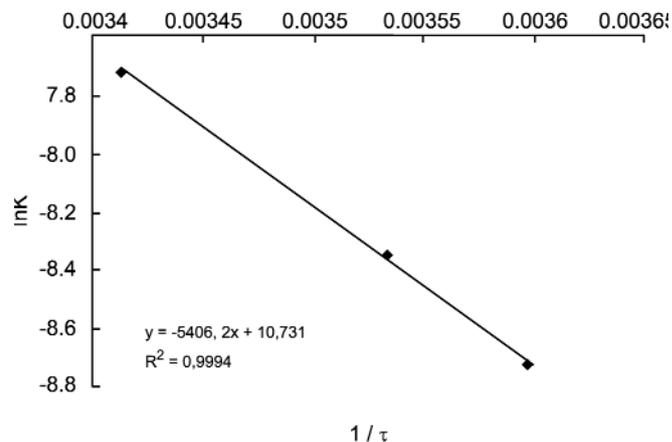


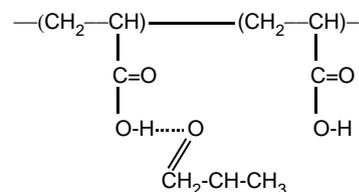
Figure 3. The kinetic curves of PAA oxypropylation for the average values of activation energy and the average values of pre-exponential factor (K_0) were calculated according to the logarithmic form of Arrhenius eqn.

Enthalpy of reaction was calculated as $\Delta H = 13374$ kJ/mol according to the following equation [10]:

$$E = \Delta H - R\tau \quad (8)$$

The investigation of the influence of medium acidity on PAA oxypropylation revealed that with a decrease in pH (due to an introduction of HCl), the reaction rate and the final conversion of PO are lowered. Substitution of water by such solvents as ethanol and 1,4-dioxane also decelerates the reaction markedly.

On the basis of the obtained results, the probable mechanism for the reaction of PO addition to PAA may be outlined. Apparently, this reaction is trimolecular. The first stage of the oxypropylation process is an addition of a PO molecule to AA units. Preliminarily, the hydrogen bonding between the PO molecule and COOH group is formed as in Scheme II.

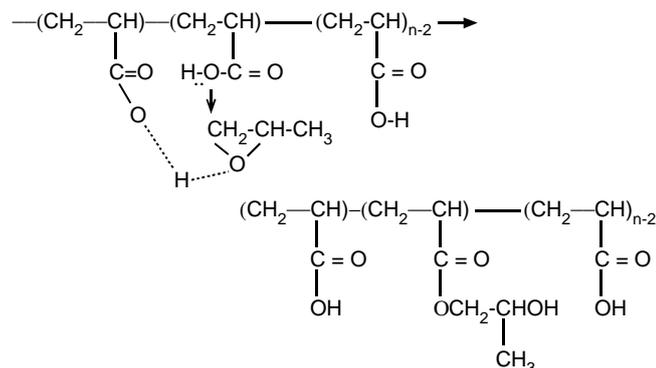


Scheme II

Upon complexation in such a manner, the oxygen atom of PO exhibits electron donating properties, while carboxylic group (more exactly, its hydrogen atom) shows

an electron accepting ability. The hydrogen bond formation contributes to significant weakening of the C O bond of the heterocycle. This circumstance mainly pre-determines subsequent opening of the epoxy ring. Oxypropylation takes place directly after a nucleophilic attack on the CH₂ group of PO by one of the adjacent carboxylic groups (more concretely, by its hydroxylic oxygen atom):

Therefore, a cooperative mechanism is realized upon



Scheme III

oxypropylation of PAA carboxylic groups. Next molecules of PO can be added in a similar way to other carboxylic groups or, with much less probability, to the OH group of the formed oxypropyl fragment, leading to the final product according to the Scheme III [2].

The derived relationships are well explained from the standpoint of the proposed mechanism. PAA macromolecules are known [11] to have a globular conformation in solutions due to hydrogen bonding between COOH groups of the same chain. Upon rising temperature to 293 K, the tendency for transition to a fibrillar conformation is enhanced, and this leads to a more intense diffusion of PO molecules to the carboxylic groups.

Further elevation of temperature must negatively influence the stability of the intermediate complex between the epoxy compound and COOH group owing to weakening of hydrogen bonding, which is expressed in lowering of the reaction rate and of final PO conversion.

A decrease of oxypropylation rate and of final PO conversion with an increase of the medium acidity may be explained by lowering of the dissociation degree of PAA carboxylic groups. A deceleration in the reaction was observed with substitution of water by ethanol or

especially 1,4-dioxane. This is most probably elicited by the formation of hydrogen bonding between their molecules and the reagents (the carboxylic groups of PO molecules). Indeed the hydrogen bonding may be even more significant in the case of using water, but because the others are larger structures, they cause significant steric hindrance for the reaction.

As it is seen, oxypropylation of PAA leads, in fact, to a copolymer. This way of obtaining the copolymer has an essential advantage over the classic one [12] consisting in omission of a preliminary and relatively complex synthesis of oxypropyl derivative of AA.

PAA Oxypropylation provides an opportunity to produce a polymeric surfactant containing both non-ionogenic and weakly-ionogenic groups. These reactive groups make possible, if necessary, to realize further chemical transformations.

CONCLUSION

A new polymeric water soluble surface-active material was produced by the oxypropylation reaction of polyacrylic acid (PAA) with propylene oxide(PO). The obtained product was found to be useful as a polymeric surfactant and the proposed method to obtain a copolymer have some advantages over the previously known method. The kinetic parameters such as the order of reaction, the activation energy and the rate constants were determined. Further chemical modifications are possible from the reactive groups that can be added by oxypropylation method.

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