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Oxidative Degradation of Polyglycols by the Ruff's System in the Aqueous Solutions

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Abstract—We have studied oxidative degradation of polypropylene glycol and polyethylene glycols of varied molecular mass induced by hydrogen peroxide in the presence of iron(III) ions. At pH 3, the process is accompanied by aggregation of iron hydroxides and occurs in the microheterogeneous system. In the cases of high-molecular substrates, the oxidation is accompanied by decrease in the polymer globulas size due to the degradation of the polymer chain.

Keywords: oxidative degradation, polyethylene glycol, polypropylene glycol, ferric salt, hydrogen peroxide, aggregation

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Alkylphenol (poly)ethoxylates, the only type of nonionic surfactants produced in Russia [1, 2], are among biologically stable compounds, and development of their degradation procedure is a topical task of modern chemistry. Such compounds are known to be degraded by ultraviolet irradiation or by oxidants as well as to undergo the electrochemical degradation [3, 4]. The Fenton's reagent [hydrogen peroxide in the presence of iron(II) salt] and the Ruff's system [hydrogen peroxide in the presence of iron(III) salt] are promising oxidative systems for degradation of nonionic surfactants [4–6]. It has been suggested that the degradation with these reagents proceeds via the chain radical process involving Fe(II) and Fe(III) species. For most substrates the efficient degradation is reached at pH 2.7–3.5; the $Fe(OH)^+$ and $Fe(OH)^{2+}$ ions as well as polymeric iron hydroxo complexes are formed under these conditions [7]. Hence, the oxidation with hydrogen peroxide in the presence of iron compounds can be accompanied with aggregation and formation of mixed iron hydroxides colloid particles, affected by the presence of surfactants [6].

The mechanism of degradation of alkylphenol polyethoxylates by the Ruff's system in the presence of iron(III) has not been elucidated so far. It has been suggested that the first stage of the process consists in the degradation of the poly(ethylene oxide) chain [8]. In this work we studied the degradation of polyethylene glycols PEGs and polypropylene glycol PPG under the above-described conditions. The substrates served as models of the nonionic surfactants free of the hydrophobic fragment. We previously demonstrated that monitoring the solution surface tension could be used as an express method to follow the surfactants degradation [6, 8].

The effect of the oxidant concentration was studied using 5 mmol/L PEG-200 aqueous solution as a representative example. Such initial concentration of PEG was chosen due to the sufficiently low surface tension (55.5 mN/m). The increase in PEG-200 degradation degree was accompanied by the reaction mixture surface tension approaching that of pure water (72.5 mN/m). Water was used as reference because under the experimental conditions the substrates were converted into water and carbon dioxide rather than depolymerized to form ethylene glycol.

At the reagents ratio of [PEG-200] : $[Fe^{3+}]$: $[H_2O_2]$ = 5 : 1 : 16, the oxidation proceeded relatively slowly, to be complete within 4 days. With the oxidant concentration increased to the ratio of 4 : 1 : 16, the PEG degradation was significant after 1 day (however, it was not complete; the surface tension of the initial solution was 55.5 mN/m, that of the reaction mixture after 1 day was 66.0 mN/m, and that of water was 72.5 mN/m). The evolution of the surface tension in the course of oxidation in the said mixture is shown in Fig. 1 (curve *1*). The curve contained a section of the slower change of the surface tension; that was likely due to the accumulation of the degradation intermediates.

Deeper degradation of PEG-200 was achieved at even higher concentrations of the oxidants. In particular, the surface tension corresponded to the complete degradation of PEG-200 after 2.5 h at the reagents ratio of 2 : 1 : 16 (Fig. 1, curve *2*); and the time to reach complete conversion was 1.5 h at the reagents ratio of 1 : 1 : 16 (Fig. 1, curve *3*). Hence, the ratio of 1 : 1 : 16 was optimal in view of the rate of PEG-200 degradation.

No scattering aggregates were found in the initial 5 mmol/L solution of PEG-200 coinciding with the data on low-molecular PEGs published elsewhere [9]. In the course of the studied oxidative degradation scattering particles of 20 to 500 nm in diameter appeared in the solution. The particles remained in the mixture even after 1 day, when the polymer degradation was complete. Evidently, the colloid particles were formed by the mixed iron hydroxide, as confirmed by the measured electrokinetic potential (+20 to +36 mV). The size of the particles and their polydispersity index depended on the oxidants concentration in the reaction mixture. The decrease in the total concentration of the oxidant led to the formation of larger and more uniform particles; that was apparently caused by the adsorption of the unreacted PEG at the iron hydroxide aggregates to stabilize the latter. The formation of colloid particles containing iron hydroxides was discussed in detail in [6] describing the oxidation of isononylphenol polyethoxylate.

Further, we studied the oxidative degradation of longer PEG-400 at the [PEG-400] : [Fe^{3+}] : [H_2O_2] ratio of 1 : 1 : 16 ([PEG-400] 5 mmol/L). The time to reach complete degradation of PEG-400 was of four hours, approximately twice longer than the degradation time in the case of PEG-200 under the same conditions. The oxidation of PEG-400 was accompanied with formation of iron hydroxide aggregates with the average hydrodynamic diameter 250 nm.

The change in the surface tension in the course of oxidation of PEG-20000 5 mmol/L solution was too slow, and therefore its measurement was subject to large errors. Hence, kinetics of PEG-20000 degradation was studied at 2.5 mmol/L of the polymer. The oxidant concentration found optimal in the case of PEG-200 (see above) was not sufficient for the complete degradation of PEG-20000. The surface tension of the reaction mixture somewhat decreased from 55.5 to 52 mN/m during the first four hours of the process, and then reached 54.5 mN/m after 24 h. In this case we likely indirectly observed the initial degradation of PEG macromolecules into the smaller fragments, decreasing the mixture surface tension. With the tenfold increase of the oxidants concentration (to the reagents ratio of 1 : 10 : 160) PEG-20000 degradation either was not efficient (it did not result in the complete conversion into inorganic compounds, rather stopping at the stage of partial fragmentation).

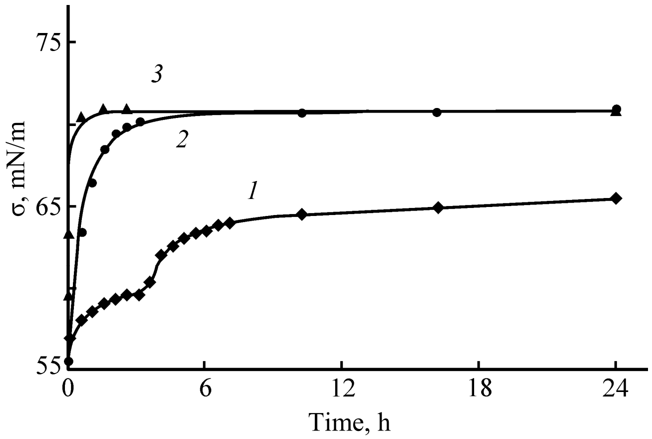

Fig. 1. Change in the surface tension in the course of PEG-200 degradation in the aqueous solution at the initial polymer concentration of 5 mmol/L. The [PEG-200] : [Fe^{3+}] : [H_2O_2] ratio: (*1*) 4 : 1 : 16, (*2*) 2 : 1 : 16, (*3*) 1 : 1 : 16.

The particles with average hydrodynamic diameter of 4.2 nm were found in PEG-20000 solution before addition of the oxidants; those particles were seemingly macromolecular globulas. In the course of the oxidation the particles diameter was decreased to 2.5 nm (the reagents ratio of 1 : 1 : 16) or to 1.6 nm (1 : 10 : 160) after 1 day reflecting the poly(ethylene oxide) chains degradation by the oxidants. Iron hydroxide aggregates were not found in the reaction mixtures probably due to high residual content of PEGs.

It was of interest to compare the features of oxidative degradation of PEGs and the more hydrophobic substrate, PPG-1025. The degradation of PPG-1025 with hydrogen peroxide in the presence of iron(III) at the reagents ratios equal to those used in the experiments with PEGs was not efficient due to higher hydrophobicity of PPG leading to the lower accessibility of the polymer chains for the low-molecular

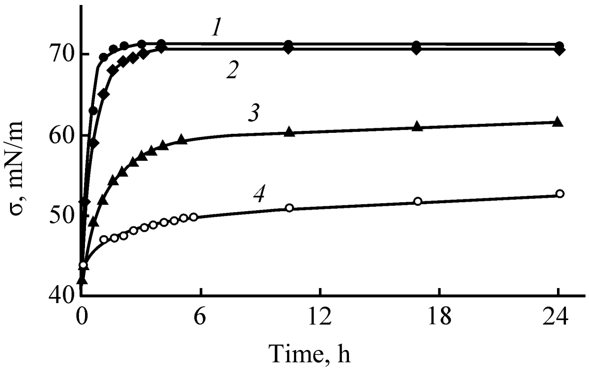

Fig. 2. Change in the surface tension in the course of PPG-1025 degradation in the aqueous solution at the initial polymer concentration of 5 mmol/L. The [PPG-1025] : [Fe^{3+}] : [H_2O_2] ratio: (*1*) 1 : 10 : 160, (*2*) 1 : 5 : 80, (*3*) 1 : 2 : 32, and (*4*) 1 : 1 : 16.

oxidants. Increasing the oxidants concentration (the PPG concentration being the same) accelerated the degradation and increased the final conversion. The highest rate of the process was observed at the components ratio 1 : 5 : 80 or at higher concentration of the oxidants (Fig. 2). The complete degradation of PPG-1025 occurred within four hours under those conditions, and the surface tension of the reaction mixture after 24 h was 70.5 mN/m.

The scattering particles with average hydrodynamic diameter of 1.7 nm were observed in the initial solution of PPG-1025. At the optimal concentration of the oxidants, those particles disappeared within several minutes after the oxidation start, and large aggregates of iron hydroxide appeared in the mixture (the size of the latter reached 160 nm after 24 h, Fig. 3). Noteworthily, the electrokinetic potential of the particles was positive and decreased from +18 to +10 mV with growing concentration of the oxidants.

To conclude, similarly to the case of nonionic surfactants, oxidative degradation of PPG and PEGs with hydrogen peroxide in the presence of iron(III) at pH 3 occurred in the microheterogeneous systems, accompanied with the formation of iron hydroxide particles. In the case of the high-molecular substrates, the initially present scattering macromolecular globulas disappeared in the course of the degradation.

EXPERIMENTAL

In this work we used polyethylene glycol samples with the average molecular mass of 200, 400, and 20000 Da (referred to as PEG-200, PEG-400, and PEG-20000, respectively), and polypropylene glycol with the average molecular mass of 1025 Da (PPG-1025). The polymers concentration was expressed as the number of the macromolecules per unit volume (mmol/L).

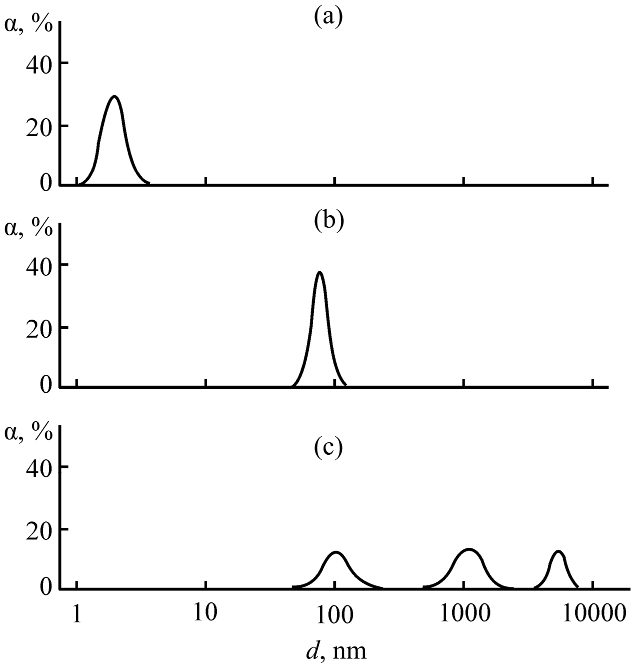

Fig. 3. Size distribution of the scattering particles in the course of PPG-1025 degradation in the aqueous solution. Initial polymer concentration 5 mmol/L; the [PPG-1025] : [Fe^{3+}] : [H_2O_2] ratio of 1 : 5 : 80; the oxidation time: (a) zero (initial solution without the oxidant), (b) 5 min, and (c) 1 day.

The oxidation of the polymers was performed with hydrogen peroxide in the presence of iron(III) nitrate at pH 3 and 25°C. To do so, the calculated volumes of iron(III) nitrate (0.25 mol/L) and hydrogen peroxide (0.4 mol/L) solutions were added to 25 mL of the polymeric substrate solution. The pH was adjusted with nitric acid solution (0.5 mol/L). The reaction mixture composition was expressed as the ratio of the reagents concentrations: [substrate] : [Fe^{3+}] : [H_2O_2] (for example, 5 : 1 : 16), the substrate standing for PPG or PEG. Addition of the polymers decreased the pure water surface tension (72.5 mN/m) down to 45–50 mN/m, depending on the nature and concentration of the substrate. The initial concentration of the substrate was chosen so that the solution surface tension was the lowest; that allowed for accurate monitoring of the degradation kinetics following the surface tension changes [6].

The surface tension was measured by the ring method on a Krüss tensiometer. The measurement accuracy was 0.5 mN/m. The polymer solutions were maintained in the measuring cell during at least one day till the equilibration prior to the experiment.

The size of the particles present in the reaction mixture was measured by means of dynamic light scattering (Zetasizer Nano-ZS, Malvern Instruments, UK), following the size distribution and the average hydrodynamic diameter of the scattering objects. For each specimen, five measurements were run in order to increase the accuracy, their duration being adjusted automatically to account for polydispersity and concentration of the particles. In order to further improve the accuracy, the quartz cell was rinsed with freshly distilled acetone three times prior to the measurement, and the specimens were filtered through the 0.45 μm filter.

The electrokinetic potential of the aggregates observed in the reaction mixture was measured with the Zetasizer Nano-ZS as well.

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