

Influence of Various Factors on Chemical Decomposition of Oxyethylated Isononylphenols

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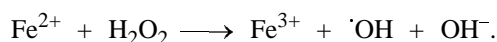
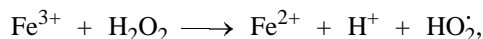
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Abstract—Oxidative decomposition of difficultly biodegradable nonionic surfactants, oxyethylated phenols with various degrees of oxyethylation (Neonols AF 9-6, 9-10, 9-12), was examined. The initial rate and extent of the oxidation depend on the degree of oxyethylation, anion of the iron salt added, and temperature.

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An important drawback of surfactants based on oxyethylated alkylphenols is that they are persistent environmental pollutants and, if getting into water reservoirs, can impair their ecological and aesthetic state [1]. The world production of such surfactants is being reduced; this is prescribed, in particular, by EU Directives. However, production of detergents in Russia is based today on only two kinds of surfactants: linear alkylbenzenesulfonates and ethoxylated *p*-isononylphenols. The prohibition of latter surfactants would make the Russian detergent industry fully dependent on the import of raw surfactants, because the domestic production of higher fatty alcohols and acids (base for the synthesis of rapidly degradable (“biologically soft”) surfactants has been lost [2].

To retain, at least temporarily, ethoxylated alkylphenols on the market of surfactants, it is necessary to develop efficient procedures of removing them from water. A powerful method for detoxication of persistent water pollutants is oxidative decomposition. Numerous oxidizing systems are known, and their range steadily expands. For example, wastewater treatment with systems $\text{H}_2\text{O}_2\text{--Fe}^{2+}$ (Fenton’s reagent) and $\text{H}_2\text{O}_2\text{--Fe}^{3+}$ (Ruff’s system), as well as the use of these systems in combination with UV irradiation became subjects of numerous studies. These oxidizing systems are essentially conjugate; it is commonly believed today that they generate highly reactive radical species [6]:



We have shown previously that oxyethylated isononylphenol with the mean degree of oxyethylation of 12 undergoes deep decomposition under the action of Ruff’s system [7]. In this study we examined decomposition of oxyethylated alkylphenols with different lengths of the oxyethyl chain, with the aim to reveal factors favoring more efficient decomposition.

In solutions of the chosen concentration, the surface activity of all the three Neonols is well pronounced; the surface tension of the starting solutions is as low as $32\text{--}36 \text{ mN m}^{-1}$. In the presence of Ruff’s system, the surface tension of the solutions increases. The increase is initially rapid, but considerably decelerates in 200–300 min (Fig. 1). The initial rate of the growth of the surface tension is different for the three Neonols and decreases with increasing length of the oxyethyl chain. Presumably, the initial linear portion of the curves primarily reflects the decomposition of the oxyethyl fragment. It is known from published data that this fragment is also more susceptible to biodegradation [8].

Within approximately 24 h, the surface tension of a solution of Neonol AF 9-6 reaches 71 mN m^{-1} , which virtually coincides with the surface tension of water and suggests deep decomposition of Neonol. The surface tension of the solutions of the other two Neonols kept for 24 h under the same conditions was still somewhat lower than that of water, suggesting that organic products of incomplete oxidation were still present in low concentrations.

It was also interesting to reveal factors affecting the rate and efficiency of degradation of Neonols. These experiments were performed with Neonol AF 9-12.

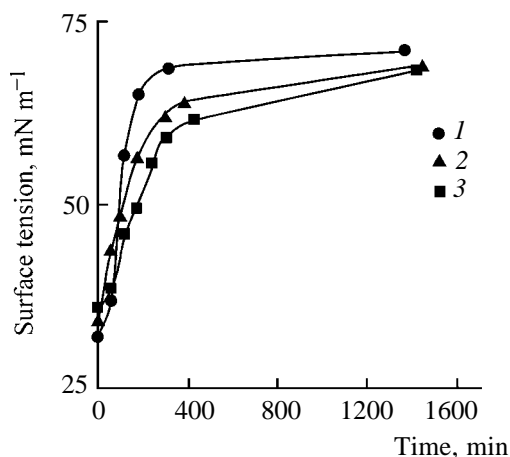


Fig. 1. Variation of the surface tension in the course of oxidation of Neonols with Ruff's system at 25°C: (1) Neonol AF 9-6, (2) Neonol AF 9-10, and (3) Neonol AF 9-12.

It is known that pH is one of decisive factors in optimization of processes performed with Ruff's system [6, 9]. Oxidation of the majority of organic compounds is the most efficient at pH 2.5–3.5, which is attributed to the effect of the solution acidity on the rate of the side process (decomposition of hydrogen peroxide with the release of oxygen) and on the state of iron ions in solution. In our experiments, pH was about 2.8, and it varied insignificantly in the course of degradation. Therefore, we did not test other pH values.

It is also known that the efficiency of oxidation of Neonols with Ruff's system is influenced by the nature of the catalyst anion [9]. We made an attempt to replace iron chloride by nitrate or sulfate in equivalent amounts.

We found that with iron nitrate the reaction is somewhat more efficient than with iron chloride (Fig. 2). With iron sulfate, the initial rate of decomposition of Neonol AF 9-12 is appreciably lower than with the other two salts, and the final result is far from the optimum: The surface tension is as low as 65 mN m⁻¹. Furthermore, in the presence of iron sulfate, a precipitate formed within a day, which was not observed with the other salts. This may be due to coagulation of iron(III) hydroxide under the action of the double-charged sulfate ion.

As expected, the rate of Neonol decomposition is strongly influenced by temperature (Fig. 3). The rate of the growth of the surface tension in the initial portions of the curves increases with temperature. However, the final surface tension after the oxidation for

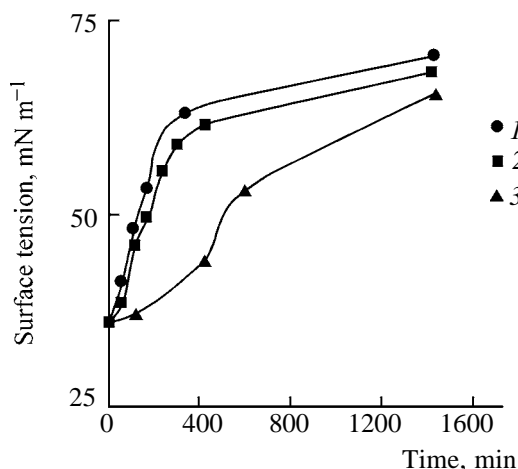


Fig. 2. Influence of anion of the iron salt on variation of the surface tension in the course of oxidation of Neonol AF 9-12: (1) Fe(NO₃)₃, (2) FeCl₃, and (3) Fe₂(SO₄)₃.

24 h is the same irrespective of the temperature. Thus, elevated temperatures are appropriate if the initial step of the decomposition should be performed rapidly.

To conclude, the rate and result of chemical decomposition of Neonols depend on the length of the oxyethylene chain, kind of the counteranion introduced with iron, and temperature. The rate and extent of the process can be controlled by varying the conditions.

EXPERIMENTAL

We used oxyethylated nonylphenols with a medium degree of oxyethylation (6, 10, and 12): Neonols AF 9-6, 9-10, and 9-12. These surfactants were pro-

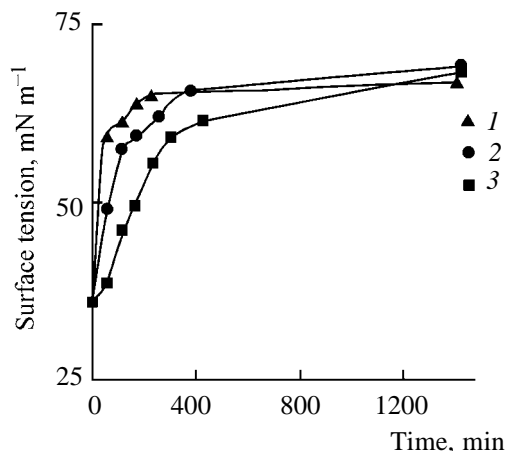


Fig. 3. Variation of the surface tension of a Neonol AF 9-12 solution in the course of decomposition with Ruff's system at (1) 45, (2) 35, and (3) 25°C.

duced by the Nizhnekamskneftekhim Limited Liability Company in accordance with TU (Technical Specification) 38.507-63-300-93.

Oxidation was performed directly in a temperature-controlled cell of a tensiometer under static conditions without stirring. The oxidant was an aqueous solution of hydrogen peroxide containing iron(III) chloride. The concentrations of hydrogen peroxide and iron salt were 56 and 1.25 mM, respectively. All the solutions were prepared in double-distilled water. The initial concentration of Neonols was 6.7×10^{-2} mM in all the cases, which is typical for wastewater treatment plants. As this concentration is lower than critical micellization concentration for all the examined Neonols, small changes in surfactant concentrations led to noticeable changes in the surface tension. This allowed the decomposition to be monitored by tensiometry.

The surface tension of solutions containing Neonols AF 9-6, 9-10, and 9-12 was measured in the course of their oxidation by the ring detachment method with a Krüss tensiometer at the required temperature.

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