

Oxidative Degradation of Neonol AF 9-12

Yu. N. Kozyreva, E. N. Kolesnikova, N.A. Glukhareva, and O.E. Lebedeva

Belgorod State University, Belgorod, Russia

Abstract—The oxidative degradation of a difficultly degradable surfactant, oxyethylated isononylphenol (Neonol AF 9-12), with aqueous hydrogen peroxide containing iron(III) chloride was studied tensimetrically.

The wide application of surfactants, primarily, household chemicals, leads to wastewater pollution with these agents. As a rule, surfactant-containing municipal wastes of large cities are treated at wastewater treatment plants in combination with some industrial wastes. However, biodegradation of some surfactants is not sufficiently fast to decrease their content in decontaminated wastewater to the level of the maximum permissible concentration (MPC). Oxyethylated alkylphenols, the only type of nonionic surfactants produced in Russia, belong to extremely slowly degradable “biologically hard” surfactants. To remove these surfactants from wastewater, local treatment facilities and specific physicochemical technique are required [1].

Published methods for water treatment to remove oxyethylated alkylphenols are few. The degradation of Igepal CA 520 commercial product mainly consisting of oxyethylated octylphenol with varied degree of oxyethylation was studied in [2]. It was found that UV light (365 nm) decomposes this surfactant in the presence of iron(III).

The oxidative degradation of oxyethylated alkylphenols shows much promise in view of the fact that this procedure has been successfully used for degradation of other chemically resistant xenobiotics. The Fenton reagent [mixture of hydrogen peroxide with iron(II) or iron(III) salts] is one of the most efficient oxidants [3]. The iron cations present in this reagent induce the hydrogen peroxide decay by a radical mechanism.

The oxidative degradation of oxyethylated isononylphenol with hydrogen peroxide in the presence of iron(III) was studied in [4]. It was found that this surfactant is effectively decomposed by hydrogen peroxide. In this study, with Neonol AF-9-12 as an example, we attempted to evaluate the extent of its oxidative degradation under the action hydrogen peroxide and to find the optimal conditions of this process.

EXPERIMENTAL

In our experiments, we used oxyethylated isononylphenol with an average degree of oxyethylation of 12 (Neonol AF 9-12, Neonol) produced by Nizhnekamskneftekhim Limited Liability Company in accordance with TU (Technical Specifications) 38.507-63-300-93.

Neonol was subjected to oxidative degradation by its treatment with aqueous hydrogen peroxide in the presence of iron(III) at varied concentrations of these reagents. The oxidant solutions were prepared in twice-distilled water.

The Neonol oxidation was monitored by surface tension measured by the ring detachment technique on a Kruss tensimeter at room temperature (23°C).

In all the experiments, the Neonol concentration was 6.7×10^{-5} M. This value is lower than the critical micelle concentration (CMC) of Neonol. Therefore, even minor variations in the Neonol concentration give rise to noticeable changes in the surface tension. In contrast, at the surfactant concentration exceeding CMC, the surface tension is insensitive to the surfactant concentration.

The surface tension at the initial Neonol concentration was 38 mN m^{-1} . On adding hydrogen peroxide to aqueous Neonol, the surface tension did not change significantly: the surface tension was 37.5 mN m^{-1} in 1 h, and 34 mN m^{-1} after 1 day. On keeping aqueous Neonol without adding hydrogen peroxide for 1 day, the surface tension decreases to a similar extent owing to attainment of the equilibrium sorption of Neonol at the interface between the aqueous surfactant and air.

A different pattern is observed after adding H_2O_2 in combination with a Fe(III) salt to aqueous Neonol. In this mixture, the surface tension noticeably increases after 15 min (see Fig. 1a), and this increase

reaches a maximum after approximately 1 h. We believe that this increase in the surface tension is caused by a decrease in Neonol concentration due to its oxidative degradation.

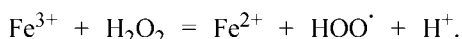
In the initial experiments, the iron(III) chloride concentration was kept constant (10 mM), while the hydrogen peroxide concentration was varied. Figure 1a shows that the maximum surface tension substantially depends on the H₂O₂ concentration. At a H₂O₂ concentration of 16.5 mM, Neonol degrades only partially. At a H₂O₂ concentration 66.0 mM, the surface tension reaches 67–68 mN m⁻¹, suggesting a high degree of Neonol degradation.

Further studies showed that the degree of Neonol degradation is also influenced by the Fe(III) concentration. Figure 1b demonstrates how the surface tension changes in the system with a constant H₂O₂ concentration (56 mM) and variable Fe(III) content.

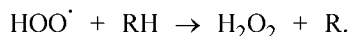
We found that the initial rate of Neonol oxidation increases with the iron(III) content. After the completion of the experiment, the surface tension of the final solution was 71 mN m⁻¹. Comparison of this value with the surface tension of twice-distilled water (72.5 mN m⁻¹) shows that, in our experiments, the Neonol degradation was virtually complete, because, otherwise, the surface tension would decrease.

With increasing iron(III) concentration, the initial rate of Neonol oxidation grows but the surface tension of the solution decreases after the completion of the experiment (see Fig. 1b). It is possible that the Neonol oxidation was incomplete under these conditions.

It is known that, in oxidation of Neonol with H₂O₂ in the presence of Fe(III), radicals are generated by the reaction



In accordance with the stoichiometry of this reaction, the most efficient oxidation of Neonol should be reached at an approximately equimolar ratio of H₂O₂ and Fe(III) in the reaction mixture. In the first step of Neonol oxidation, the HOO· radical ruptures one of bonds in the Neonol molecule by the scheme



To reach complete oxidation of oxyethylated nonylphenol, a large amount of these radicals is required.

CONCLUSIONS

(1) The oxidative degradation of Neonol with hydrogen peroxide in the presence of Fe(III) allows efficient removal of this surfactant from wastewater.

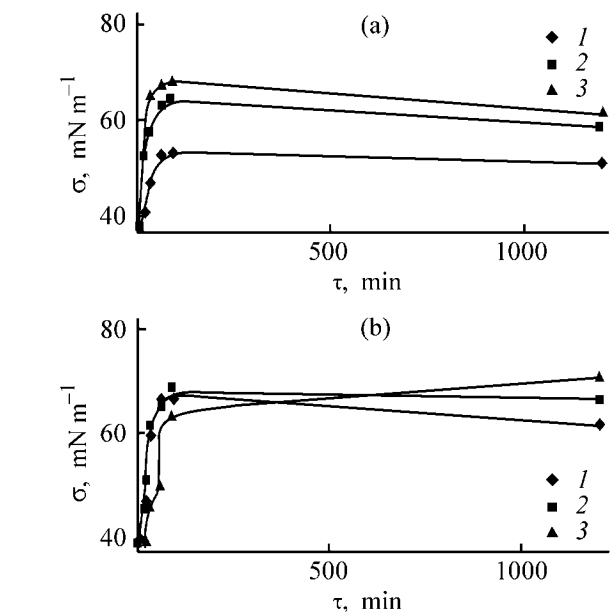


Fig. 1. Variation of surface tension σ with time τ in the course of oxidative degradation of Neonol. (a) FeCl₃ concentration 10 mM; H₂O₂ concentration, mM: (1) 16.5, (2) 33, and (3) 66. (b) H₂O₂ concentration 56 mM; FeCl₃ concentration, mM: (1) 10, (2) 2.5, and (3) 1.25.

(2) The rate and completeness of surfactant oxidation can be controlled by varying the oxidant content. At optimal ratio of hydrogen peroxide and iron(III) chloride, the surface tension of solution contaminated with the surfactant becomes approximately equal to that of twice-distilled water, which indicates that the surfactant degradation is virtually complete.

(3) Oxidative degradation of surfactants can be used instead of biodegradation technique or in combination with it to rupture the strongest bonds in the surfactant molecules. The development of an efficient technique for water treatment to remove Neonol can prolong the commercial use of surfactants of this kind until new softer nonionic surfactants is developed.

REFERENCES

1. Bocharov, V.V., *Byt. Khim.*, 2002, no. 8, pp. 4–8.
2. Brand, N., Mailhot, G., and Bolte, M., *Environ. Sci. Technol.*, 1998, vol. 32, no. 18, pp. 2715–2720.
3. Rudakov, E.S., *Reaktsii alkanov s okislitelnyami, metallokompleksami i radikalami v rastvorakh* (Reactions of Alkanes with Oxidants, Metal Complexes and Radicals in Solutions), Kiev: Naukova Dumka, 1985.
4. Lebedeva, O.E., Glukhareva, N.A., Zheltyakova, N.E., et al., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 2004, vol. 47, no. 8, pp. 14–17.