

The Kinetics of Oxidation of Oxyethylated Isononylphenols under the Action of Hydrogen Peroxide in the Presence of Inorganic Salts

Yu. N. Kozyreva, I. N. Zazdravnykh, N. A. Glukhareva, and O. E. Lebedeva

Belgorod State University, Belgorod, Russia

e-mail: KozyrevaJulia@bsu.edu.ru

Abstract—The influence of some inorganic salts on the oxidative destruction of oxyethylated isononylphenols under the action of hydrogen peroxide in the presence of iron(III) ions was studied. It was shown that nitrate anions did not decrease the effectiveness of the oxidation of oxyethylated isononylphenols, chloride ions could completely inhibit the reaction, probably, because of the occurrence of a competing redox process, whereas the presence of sulfate ions transformed the system into a multiphase mixture, which negatively influenced oxidation.

INTRODUCTION

Currently, two types of homemade surface-active substances are used in the production of synthetic detergents, linear alkylbenzenesulfonates and isononylphenol ethoxylates. The former have the ecological characteristics that satisfy the EC requirements, whereas the latter cannot undergo fast biodegradation and are forbidden in EC countries [1]. The end of the use of alkylphenol ethoxylates in Russia means the dependence of the production of synthetic detergents on the import of surfactant raw materials [2]. On the other hand, uncontrolled continuation of the disposal of waste waters containing alkylphenyl ethoxylates can cause serious damage to the environment.

This problem can be solved by the development of a process for the chemical oxidation of alkylphenol ethoxylates and its inclusion into the system for purifying waste waters. The selection of a suitable oxidizer for this purpose is of fundamental importance.

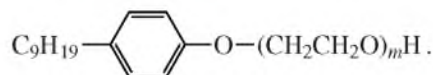
We showed in [3–5] that isononylphenol ethoxylates decompose under the action of hydrogen peroxide in the presence of iron(III) salts. Hydrogen peroxide in combination with iron ions forms fairly effective oxidative systems, which act according to the radical mechanism [6]. If iron(II) ions are used, the oxidizer is called Fenton's reagent, whereas hydrogen peroxide in combination with iron(III) ions is known as the Ruff system [6]. The oxidation of various organic substrates with these reagents was described in many works (e.g., see [7–11]). Most of the experiments were, however, performed in model solutions free of inorganic admixtures typical of natural and waste waters. The influence of inorganic salts on the Fenton process was only studied in several works, and salt concentrations used in these works were low [10, 11]. In our previous studies, we

varied salt concentrations over wide ranges. It was found that some anions can unfavorably influence the oxidation of dinitrophenols with Fenton's reagent [12].

The purpose of this work was to study the influence of inorganic salts on the oxidative destruction of oxyethylated isononylphenols with the Ruff reagent.

EXPERIMENTAL

We used Neonol oxyethylated isononylphenols produced at OOO "Nizhnekamskneftekhim." The general formula of Neonol is



The samples had different oxyethylation degrees, $m = 6$ and $m = 12$ (Neonol AF 9-6 and AF 9-12).

The oxidation of Neonols was performed with an aqueous solution of hydrogen peroxide in the presence of iron(III) chloride and various inorganic salts. The initial concentration of Neonols was 6.7×10^{-5} mol/l. The concentrations of the oxidizing reagents were 56 and 1.25 mmol/l, and the concentrations of salts were varied. All solutions were prepared using doubly distilled water. Oxidation was monitored by solution surface tension measurements. The surface tension was determined by the anchor ring method using a Krüss tensiometer at the required temperature.

RESULTS AND DISCUSSION

The surface tension (σ) of solutions of Neonols AF 9-6 and 9-12 in doubly distilled water at the initial concentration is 36 and 32 mN/m, respectively. The addi-

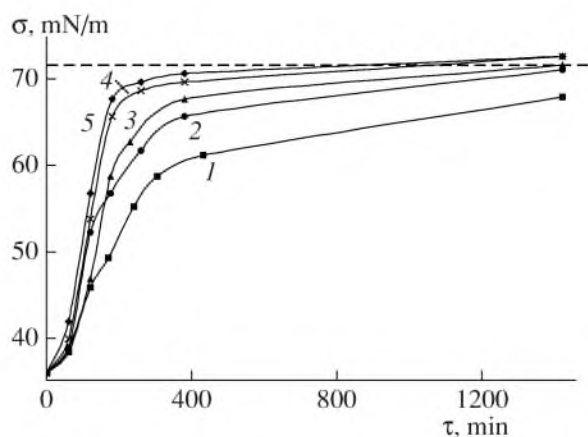


Fig. 1. Surface tension changes during the oxidation of Neonol AF 9-12 with the Ruff system in solutions of NaNO_3 of various concentrations; salt concentrations: (1) 0, (2) 0.1, (3) 0.5, (4) 1.0, and (5) 1.5 M.

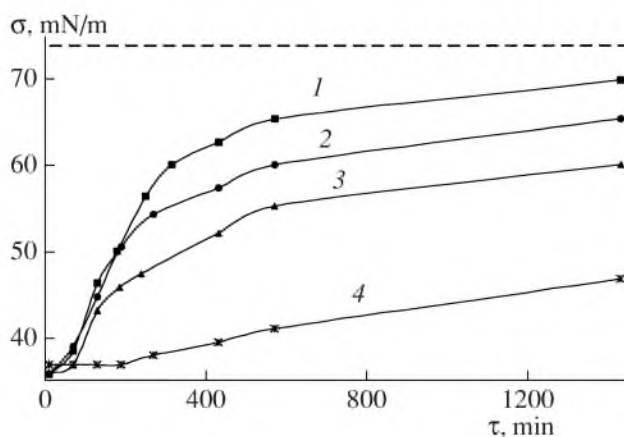


Fig. 2. Surface tension changes during the oxidation of Neonol AF 9-12 with the Ruff system in solutions of NaCl of various concentrations; (1–4) see Fig. 1.

tion to these solutions of surfactants of hydrogen peroxide or iron chloride (separately) can change σ by 1–2 mN/m. Substantial changes in solutions of Neonols only occur when both Ruff reagent components are introduced. It was shown in [4, 5] that these changes were caused by the deep oxidation of Neonols. As a result, the surface tension of solutions gradually approached the σ value for water (72.5 mN/m) at 298 K. In a day, the surface tension of solutions of Neonols AF 9-12 and AF 9-6 subjected to oxidation was 68 and 71 mN/m, respectively.

Note that the σ values recorded as the process develops are determined by the presence in solution not only of initial Neonol but also of intermediate oxidation products, which also possess surface activity. For this reason, there is no direct relation between the concentration of Neonol and surface tension, and kinetic parameters of the process cannot be determined. Conclusions can only be drawn about the rate of surface tension growth related to the occurrence of a complex reaction.

In subsequent experiments, the oxidation of Neonols was performed in solutions of salts of various concentrations. The influence of each salt on the surface tension of a solution of Neonol was studied. Inorganic salts are surface inactive substances, and, in certain instances, we observed the expected increase in surface tension of initial solutions of the surfactants by 1–4 mN/m.

Changes in σ during the oxidation of Neonols are as a rule much larger than small changes caused by the

Initial rate of surface tension growth ($W_0 \times 10^2$, mN/(m min)) during the oxidation of Neonol 9-12 by the Ruff reagent in solutions of sodium nitrate and chloride of various concentrations (c , M)

Salt	$c = 0$	$c = 0.1$	$c = 0.5$	$c = 1$	$c = 1.5$
NaNO_3	8.3	13.9	14.3	19.2	21.7
NaCl	8.1	7.8	5.8	1.5	–

introduction of salts into the system. For instance, changes in σ during the oxidation of Neonol AF 9-12 in solutions of sodium nitrate with different concentrations are shown in Fig. 1. We see that the surface tension increases by two and more times in 150–200 min of measurements. Interestingly, the initial oxidation rate increases as the concentration of sodium nitrate in solution grows (table). The final result is, however, the same for all salt concentrations studied. The last measurement taken in 1400 min gives surface tension values that closely agree with each other for all solutions. The deep oxidation of Neonol AF 9-12 was attained irrespective of the presence of sodium and nitrate ions in the system. The results for Neonol AF 9-6 completely repeated all the main trends observed for Neonol AF 9-12. The behavior of ammonium nitrate in the systems studied was on the whole similar to the behavior of sodium nitrate.

A different situation arises when chloride ions are introduced into solutions of Neonols. As follows from Fig. 2, the initial rate of the oxidation of Neonol AF 9-12 consistently decreases as the concentration of sodium chloride in solution increases (table). The effectiveness of oxidation also decreases considerably according to the σ value at the end of measurements. In a solution containing 1 mol/l sodium chloride, the final σ value is higher than the initial value by only several units. A similar picture is observed in the oxidation of Neonol 9-6.

It is likely that a process competing with the oxidation of Neonols occurs in the systems in the presence (and with the participation) of chloride ions. It can, for instance, be suggested that chloride ions are also oxidized by the Ruff system. This side process results in the almost complete inhibition of the oxidation of Neonols at high chloride ion concentrations. This suggestion is substantiated by the results obtained in the oxidation of solutions of Neonols containing another metal chloride, calcium chloride. The oxidation of Neonols then stops at lower concentrations than with sodium chloride. This

effect is easy to explain taking into account that, at equimolar concentrations of the two metal chlorides, a solution of calcium chloride contains two times more chloride ions than a solution of sodium chloride.

Thus far, the data on the influence of extraneous anions on the oxidation of Neonols were in agreement with the results of our previous studies performed for other substrates, dinitrophenols [12]. The effect of sulfate salts on the oxidative destruction of Neonols is different. In experiments with dinitrophenols, the presence of sulfates insignificantly influenced oxidation, whereas with Neonols, the introduction of sulfate ions even in low concentrations caused the complete inhibition of oxidation. Note that the result was independent on salt cations, and the data obtained for sodium sulfate were the same as for ammonium sulfate.

The following observations are of importance: in the presence of any concentration of sulfates, we visually observed solution turbidity already in 1 h from the beginning of oxidation. Simultaneously, a loose orange precipitate formed. Such a behavior of solutions can be caused by the simultaneous occurrence of the following processes. It is likely that the precipitate is an iron compound. The introduction of sulfate can favor coagulation of, for instance, iron hydroxide sol. Solution turbidity is indicative of possible transformations of oxyethylated alkylphenols. The solubility of these compounds in water is limited, solution turbidity is indicative of the formation of a new phase enriched in surfactants. Electrolytes influence the temperature interval of the existence of the single-phase system and can decrease the turbidity temperature [13]. It is likely that this is the effect caused by the introduction of sulfates into our systems; that is, the system becomes multiphase, and its components disperse over different phases. As a result, the oxidative destruction of Neonols in such a multiphase system becomes impossible.

Compared with the effects caused by various anions, the influence of cations on the oxidative destruction of Neonols is less unambiguous. Data on the influence of nitrates containing cations in different valence states on the process under consideration are given in Fig. 3. The influence of inorganic cations on the initial rate of surface tension growth ($W_0 \times 10^2$, mN/(m min)) was as follows:

No salt	NaNO ₃	Ba(NO ₃) ₂	Al(NO ₃) ₃
8.1	13.9	4.9	1.8

We see that the initial rate of oxidation of Neonol AF 9-12 decreases as the valence of cations increases. Simultaneously, the result of oxidation becomes worse, and the final surface tension value in the presence of aluminum nitrate is lower. The same trend was observed for Neonol AF 9-6 (Fig. 3). The changes observed can be a consequence of a change in the charge of the cation, although the nature of this effect is unclear.

To summarize, the oxidation of oxyethylated alkylphenols with the Ruff reagent should be performed tak-

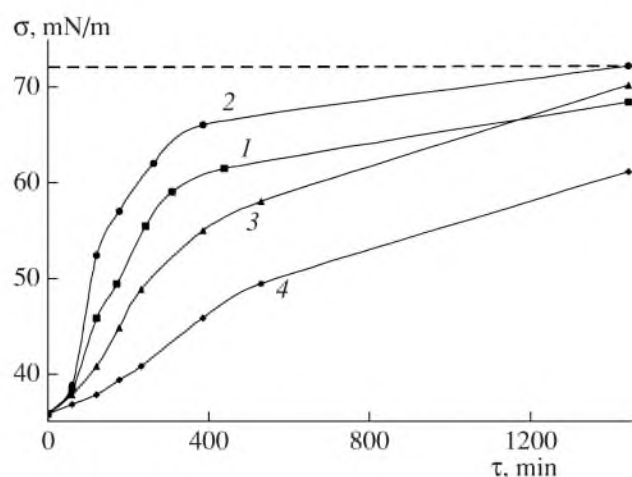


Fig. 3. Surface tension changes during the oxidation of Neonol AF 9-12 (1) in the absence of a salt and in solutions of (2) sodium nitrate, (3) barium nitrate, and (4) aluminum nitrate, concentration 0.1 mol/l.

ing into account possible influence of extraneous salts on the oxidizing system and the state of the surfactant itself. The influence of cations can be ignored, but the presence of chloride and sulfate anions, which unfavorably influence the oxidation of Neonols, should be taken into account.

REFERENCES

1. S.-D. Hager, *Bytovaya Khim.*, No. 12, 32 (2003).
2. V. V. Bocharov, *Bytovaya Khim.*, No. 8, 4 (2002).
3. O. E. Lebedeva, N. A. Glukhareva, N. E. Zheltyakova, et al., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **47** (8), 14 (2004).
4. Yu. N. Kozyreva, E. N. Kolesnikova, N. A. Glukhareva, and O. E. Lebedeva, *Zh. Prikl. Khim.* **78** (12), 2056 (2005) [*Russ. J. Appl. Chem.* **78** (12), 2024 (2005)].
5. Yu. N. Kozyreva, N. Yu. Aleinik, N. A. Glukhareva, et al., *Zh. Obshch. Khim.* **77** (7), 1131 (2007) [*Russ. J. Gen. Chem.* **77** (7), 1215 (2007)].
6. B. A. Dolgoplosk and E. I. Tinyakova, *Generation of Free Radicals and Their Reactions* (Nauka, Moscow, 1982) [in Russian].
7. E. G. Solozhenko, N. N. Soboleva, and V. V. Goncharuk, *Khim. Tekhnol. Vody* **26** (3), 219 (2004).
8. B. W. Tyre, R. J. Watts, and G. C. Miller, *J Environ. Qual.* **20** (4), 832 (1991).
9. M. Fukushima and K. Tatsumi, *Environ. Sci. Technol.* **35** (9), 1771 (2001).
10. E. M. Siedlecka and P. Stepnowski, *Pol. J. Environ. Stud.* **14** (16), 823 (2005).
11. U. Bali and E. C. Catalkaya, *J. Environ. Sci. Health* **38** (10), 2259 (2003).
12. A. A. Solov'ev, M. A. Pashina, and O. E. Lebedeva, *Zh. Prikl. Khim.* **80** (2), 276 (2007) [*Russ. J. Appl. Chem.* **80** (2), 275 (2007)].
13. N. Schönfeld, *Grenzflächenaktive Äthylenoxidaddukte* (Wissenschaftliche Verlagsgesellschaft, Stuttgart, 1976; Khimiya, Moscow, 1982).