Colloid-Chemical Effects in the Oxidative Destruction of Isononylphenol Ethoxylate

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Abstract—The possibility of the oxidative destruction of isononylphenol ethoxylates in micellar solutions with critical micellization concentrations of up to 3.5 by the Ruff system (hydrogen peroxide in the presence of Fe^{3+} ions) is established in principle. It is shown that iron hydroxocomplex polymerization, which leads to the formation of large colloid particles but does not lower the efficiency of a surfactant oxidation, can proceed in a solution at pH 3–5. It is established that the concentration of micelles in a Neonol solution falls sharply during oxidation at the optimum ratio of surfactant and oxidative reagents, and they virtually disappear at the initial stage of oxidation. In contrast, oxidation results in growth of the sizes of micelles upon a lack of oxidative reagents.

Keywords: oxidative destruction, polymerization, surfactant, iron hydroxocomplexes, micellar solutions, isononylphenol ethoxylate.

INTRODUCTION

The popular alkylphenol ethoxylate domestic surfactants have a major drawback: the compounds biodegrade slowly. The alkylphenol ethoxylates can remain on the market if an alternative scheme for their mineralization is developed. There are few known works dealing with the destruction of alkylphenols and oxyethylated alkylphenols. The destruction of the commercial product Igepal CA 520, consisting of octylphenol oxyethylates with different degrees of oxyethylation, was studied in [1], and the surfactant was shown to decompose under the action of UV radiation in the presence of iron(III). It is also known that the destruction of nonylphenol ethoxylate can proceed during ozonation or combined treatment with ozone and UV radiation [2].

We showed earlier that the Ruff system (hydrogen peroxide in combination with iron(III) ions) is able to oxidize alkylphenol ethoxylates in solutions with concentrations below the critical micellization concentration (CMC), and we studied the kinetics of the oxidative destruction on the basis of colorimetric and tensometric data [3–6]. However, the question of the intermediate stages of this process remains open. Considering the ability of compounds with a diphilic structure to aggregate in solutions, and the tendency of Fe^{3+} hydroxocomplexes toward polymerization, it is of interest to establish the presence of these effects in the process under different conditions (surfactant concentration, pH, temperature). Such an opportunity is offered by dynamic light scattering.

EXPERIMENTAL

Neonol—oxyethylated isononylphenol $C_9H_{19}C_6H_4(OCH_2CH_2)_nOH$ (OOO Nizhnekamsk-neftekhim, Russia) with an average oxyethylation degree of $n = 10$ (Neonol AF 9–10) was used in this work.

The Neonol was oxidized in an aqueous solution of hydrogen peroxide in the presence of iron(III) chloride. The initial concentration of Neonol was equal to its CMC or higher, and the concentrations of the oxidative reagents were chosen in dependence on this value. All of the solutions were prepared with the use of twice distilled water. The oxidation of Neonol was performed as follows: specified volumes of a 0.25-M iron(III) chloride solution and a 0.40-M hydrogen peroxide solution were added to an aqueous Neonol solution (0.25 ml) of a certain concentration.

The progress of the oxidation was traced by the change in the solution surface tension, which was determined by the ring method on a Krüss tensimeter at a specified temperature (25°C), as described in [6].

At the same time, the process was controlled by means of dynamic light scattering. Measurements were performed on a Zetasizer Nano ZS device (Malvern Instruments), which allowed us to establish the distribution according to size and to determine the average hydrodynamic size of scattering particles in the solution, including surfactant micelles. Since the presence of dust microparticles in solutions complicates estimates of the size of micelles, solutions of the surfactant and oxidative reagents were filtered through

a microfilter with 0.2-μm pores. The measuring cell was repeatedly washed with freshly distilled acetone immediately before analysis. According to the light scattering data, the average diameter of Neonol AF 9–10 micelles was 7.8 nm at concentrations of less than 4.0 CMC (Fig. 1a), and was thus in agreement with the scanty data available in the literature for other oxyethylated surfactants, e.g., Triton X-100 [7].

In addition, the electrokinetic potential of the particles in solution was measured on a Zetasizer Nano ZS device after destruction of the surfactant was terminated.

RESULTS AND DISCUSSION

We showed earlier that true solutions of alkylphenol ethoxylates with concentrations lower than the CMC relatively easily undergo oxidative destruction by the Ruff system, and this is accompanied by an increase in the surface tension of solutions [3–6]. In this work, oxidation was performed in solutions whose concentration was equal to or higher than the Neonol AF 9–10 CMC.

At the first stage of experiments, the Neonol AF 9–10 concentration was equal to its CMC of 8×10^{-5} mol/l, and the initial concentrations of the oxidative reagents (hydrogen peroxide and Fe^{3+} ions) were 16.0 and 1.0 mmol/l, respectively.

Oxidation was performed at three values of pH. Since alkylphenol ethoxylates are nonionic surfactants, the change in pH does not influence their behavior in a solution. The only expected effect might be a change in the clouding point of the surfactant at the high electrolyte concentrations used to regulate pH. The pH value is assumed to have a much greater influence on the state of iron ions in a solution (more specifically, on their hydrolysis). According to existing concepts [8], the working pH range for the Ruff system nearly coincides with the range of the existence of iron hydroxyl $FeOH^{2+}$ and dihydroxyl $Fe(OH)_2^+$ cations (pH 2.7–3.5), and the radical decomposition of hydrogen peroxide proceeds more intensively under the action of these iron forms. We selected pH values both within and outside the above range.

At pH 5, an increase in the surface tension from 33.0 mN/m immediately after the reagents were mixed to 72.5 mN/m one day later indicated the termination of oxidation and the nearly complete decomposition of the surfactant. It should be noted that micelles were barely detected in the initial solution of Neonol with a concentration equal to its CMC. However, ~40.0 nm scattering particles, which were quite large in comparison with micelles and grew to ~90.0 nm over time, appeared immediately after the oxidant was added. A day later, when the destruction of the surfactant was already terminated as indicated by tensometric data, ~50-nm colloid particles (presumably of iron hydroxide) still remained in the solution and did not disap-
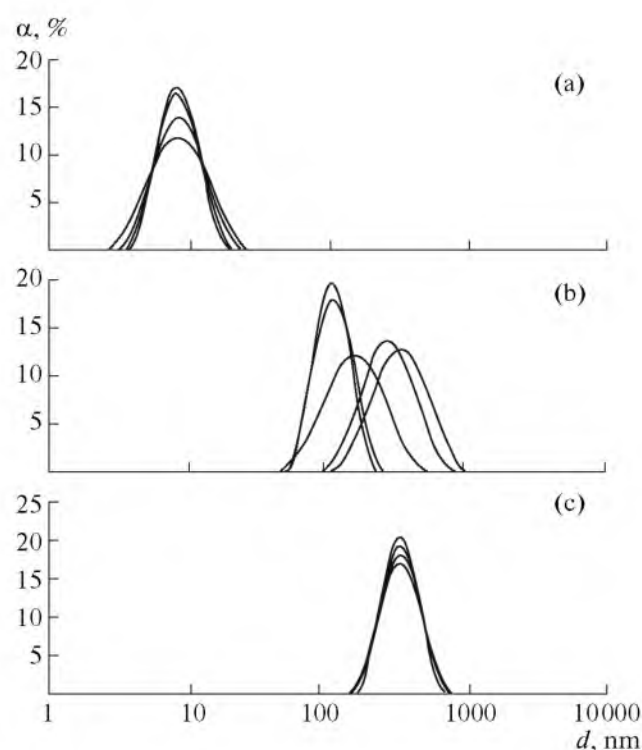

Fig. 1. Size distribution of scattering particles for (a) a Neonol AF 9–10 solution with a concentration of 2.6×10^{-4} mol/l, (b) the same solution in 20 min after an oxidative system was introduced, and (c) the same solution after oxidation was terminated. α is the fraction of particles, and d is the diameter.

pear later. Just a slight change in their size was observed. The formation of scattering particles agreed with the tendency of Fe^{3+} hydroxocomplexes toward polymerization at pH 3.5–7.0 [8]. However, the polymerization rate is most likely comparable with the oxidative destruction rate: prior to conversion into inactive polymer forms, iron hydroxocations have time to generate a considerable amount of active radical particles, which in turn oxidize the surfactant.

When the oxidation of Neonol AF 9–10 was carried out at pH 3 (all other factors remaining the same), the growth rate of the surface tension remained virtually unchanged in the initial process stage. One day later, the surface tension was 70.5 mN/m, and particles of colloid sizes were present in the solution after oxidation. We may conclude that the propensity of hydroxocomplexes toward polymerization is extremely pronounced at pH 3.

The assumption that scattering particles in solutions are formed by iron hydroxide after oxidation is confirmed first of all by the measured value of their electrokinetic potential (+55.0 mV); i.e., they are charged positively. Second, we also registered the formation of colloid particles in the control experiment, in which we mixed iron salt with hydrogen peroxide in
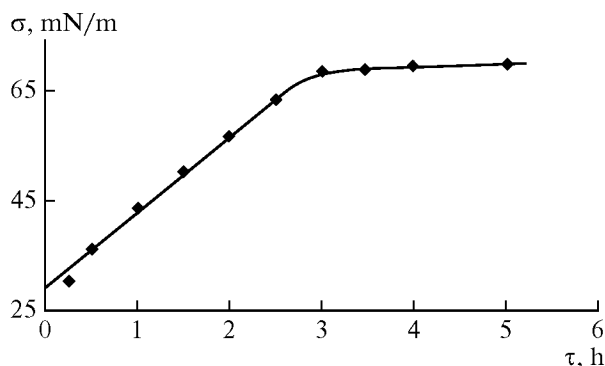
σ, mN/m

Fig. 2. Change in surface tension σ during the oxidative destruction of a Neonol AF 9–10 micellar solution.

the above concentrations in the absence of the surfactant.

As a result of these observations, it was of interest to perform the oxidation of Neonol in a strongly acidic medium. At pH 1, the oxidative destruction was very slow: the surface tension did not change at all for the first three hours (33.0 mN/m), and the destruction of the surfactant was terminated only after 12 days, when the surface tension reached 70.5 mN/m. It is important that such an acidic solution did not include colloid particles, i.e., there was no aggregation of iron-containing particles. The obtained results conform completely to the concepts in [9], according to which nonhydrolyzed iron cations exhibit low activity in the radical destruction of hydrogen peroxide.

To study the oxidative destruction of Neonol in a micellar solution, we selected the following concentrations of reagents: 2.6×10^{-4} mol/l (3.25 CMC) of Neonol, 68.2 mmol/l of hydrogen peroxide, and 4.1 mmol/l of Fe^{3+} ions. At the specified molar ratio of the components in a reaction mixture of 1 : 262 : 16, a temperature of 25°C, and a pH of 5, the decomposition of the surfactant was almost terminated in 5 h. The change in the surface tension due to the reduction of the surfactant concentration during oxidation is shown in Fig. 2.

Surfactant micelles, which were easily detected at the chosen concentration in the initial solution, were not registered 15–20 min after the oxidant was added, and large particles appeared whose size at the initial stage varied within a rather wide interval (Fig. 1b). In all likelihood, the obtained data reflect the dynamic character of the process, during which the destruction of micelles, the increase in their size, and the formation of hydroxoiron complexes occur simultaneously. The influence of oxygen microbubbles on the measurement results cannot be excluded either, as the concentration of hydrogen peroxide was quite high at the initial stage of the reaction. However, only colloid iron-containing particles remained in the solution

immediately after the process was terminated and for the next several days (Fig. 1c).

It is likely that the oxyethyl chain of Neonol undergoes destruction at the initial stage of the oxidant's action on micelles and gradually becomes shorter, thus leading to a reduction in Neonol solubility and the coalescence of small surfactant micelles into larger micelles near the cloud point. When performing oxidation in a micellar solution with the same concentrations of reagents but at a lower temperature of 15°C, we managed to observe a micelle size increase caused by the shortening of the surfactant oxyethyl chain. In the first two hours of the process, the average diameter of the scattering particles grew gradually from 7.8 to 12.7 nm. Three hours later, there were no micelles, and the process proceeded as described above.

The growth of micelles at the initial stage of destruction was also observed upon a lack of oxidant. At a Neonol : hydrogen peroxide : iron(III) salt molar ratio of 1.0 : 51.6 : 3.2 and a pH of 1.5, micelles grew gradually to 16 nm for the first four hours, and the solution clouding typical of surfactants with a short oxyethyl chain was observed in 6 h; i.e., the size of the aggregates fell outside the limits of measurements, exceeding 6.0 μm. Oxidation continued slowly, however, accompanied by a slight rise in the surface tension to 43.0 mN/m over the next 20 days and a slow reduction in the sizes of the scattering particles. The addition of a fourfold excess of oxidant relative to its initial amount in the clouded reaction mixture led to the rapid disappearance of light scattering and a rise in surface tension to 70.5 mN/m in 1 h, indicating that the destruction of the surfactant was terminated.

CONCLUSIONS

Our results allow us to assert that the concentration of micelles in a Neonol solution falls sharply during oxidation at the optimum ratio of surfactants and oxidative reagents, and they virtually disappear at the initial oxidation stage. Oxidation proceeds with a gradual increase in the surface tension of the solution, in compliance with the regularities established earlier for nonmicellar solutions [4–6]. In contrast, oxidation leads to the growth of the sizes of micelles upon a lack of oxidative reagents.

Hence, the possibility of the oxidative destruction of nonylphenol ethoxylates in micellar solutions with a concentration up to 3.5 CMC by the Ruff system was established in principle, based on the our analysis of the colloid-chemical effects of the process.

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REFERENCES

1. N. Brand, G. Mailhot, and M. Bolte, Environ. Sci. Technol **32**, 2715 (1998).

2. V. V. Goncharuk, V. F. Vakulenko, Yu. O. Shvadchina, A. N. Sova, A. V. Nevinnaya, and Yu. V. Sidorenko, Khim. Tekhnol. Vody **26**, 329 (2004).

3. O. E. Lebedeva, N. A. Glukhareva, E. N. Kolesnikova, N. E. Zheltyakova, and Yu. N. Kozyreva, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol. **47** (8), 14 (2004).

4. Yu. N. Kozyreva, N. Yu. Aleinik, N. A. Glukhareva, E. N. Kolesnikova, and O. E. Lebedeva, Zh. Obshch. Khim. **77**, 1131 (2007) [Russ. J. Gen. Chem. **77**, 1215 (2007)].

5. Yu. N. Kozyreva, E. N. Kolesnikova, N. A. Glukhareva, and O. E. Lebedeva, Zh. Prikl. Khim. **78**, 2056 (2005) [Russ. J. Appl. Chem. **78**, 2024 (2005)].

6. Yu. N. Kozyreva, I. N. Zazdravnykh, N. A. Glukhareva, and O. E. Lebedeva, Zh. Fiz. Khim. **83**, 843 (2009) [Russ. J. Phys. Chem. A **83**, 729 (2009)].

7. G. D. J. Phillies and J. E. Yambert, Langmuir **12**, 3431 (1996).

8. E. G. Solozhenko, N. M. Soboleva, and V. V. Goncharuk, Khim. Tekhnol. Vody **26**, 219 (2004).

9. M. L. Kremer, J. Phys. Chem. **107**, 1734 (2003).