Corrosion Protection of Metallic Surfaces in Peroxide – Surfactant Formulations

I E Chişan¹, D Vărăşteanu*, I Fierăscu¹, R C Fierăscu¹, I-L Calancea² and R Petre³
¹National Institute for Research and Development in Chemistry and Petrochemistry ICECHIM-Bucharest, 202 Splaiul Independentei, 060021, Bucharest, Romania
² Research Center for Navy Constanta, 4 Stefanita Voda, 900402, Romania
³Scientific Research Center for CBRN Defence and Ecology – SRCCBRNDE, 225 Oltenitei Road, 041309, Bucharest, Romania

*E-mail: dvarasteanu@yahoo.com

Abstract. Formulations containing surfactants and oxidizing agents can be used to neutralize hazardous material from different surfaces contaminated in cases of chemical aggressions. The formulations act chemically through different mechanisms on hazardous materials, transforming them into inactive agents. The surfactants are used to solubilise the slightly soluble chemical warfare agents and catalyse their decontamination. In this work we evaluated the stability of surfactants in hydrogen peroxide solutions, the surface active properties of surfactants system and also performed a study of the different types of surfactants, including amino acid-based surfactants, and corrosion inhibitors in an aqueous solution of hydrogen peroxide to identify the mixture that better protect the surfaces against corrosion. Corrosion tests were performed on cast iron and aluminum surface, evaluating the pinching, staining as well as staining color intensity of the surface at 24 hours after the solution is deposited on the surface. Based on the results obtained, formulations containing a system of three surfactants and a corrosion inhibitor in an aqueous solution of hydrogen peroxide were selected.

1. Introduction

In case of CBRN (chemical, biological, radiological or nuclear) incidents, an entire perimeter that encompasses people, land, water sources, equipment and buildings is contaminated with hazardous materials. Decontamination consists in the removal of these materials from the affected area [1]. The main priority is to carry out the decontamination actions on the people, followed by the decontamination of the entire affected area, in order to avoid the subsequent danger of contamination. Surfactants were initially used in decontamination operations that involved physical processes to remove chemical or biological warfare agents or radiological agents. During the First World War, when mustard was first used as a chemical warfare agent, water and soap were used to remove the chemical from the skin [2]. Afterwards the surfactants were included in chemical decontamination compositions. The development of decontamination systems based on surfactants [3-9] could be realized due to versatility of these compounds, in terms of structure and properties. The surfactant molecules consists in a hydrophobic portion, usually a long alkyl chain and a polar group, ionisable or non-ionisable (hydrophilic portion). In solutions the adsorption of surfactants at the interfaces creates an adsorption layer which serves as a link between phases and determines the modification of the surface properties of solutions. A more or less condensed state of this layer determines the specific
action of the surfactant (washing agent, emulsifier, foaming agent, wetting agent, dispersant, etc.). In
the formulations of CBRN decontamination agents, surfactants are used to improve the solubility of
sparsingly soluble chemical contaminants in aqueous medium, allowing better contact between the
contaminant and the reactive decontamination component. The most used classes of surfactants are
cationic surfactants (quaternary ammonium salts), anionic surfactants (alkyl sulphates, 
alkylaryl sulfonates, alpha olefin sulfonates) or nonionic surfactants (polyethoxylated derivatives, amine oxides). The neutralizing reagents (detoxification) of the contaminants are compounds with 
active oxygen or active chlorine, which pose corrosion problems on metals.

In this work we propose a ternary surfactant system including an amino acid based surfactant
(sodium lauroyl sarcosinate) that can be used in decontamination systems. It was studied the 
synergism of nonionic surfactants (polyethoxylated derivatives, amine oxides) to sodium lauroyl 
sarcosinate (NaLSar) regarding the behavior of mixed micelles and the stability of surfactants in 
hydrogen peroxide solutions. Corrosion behaviour of surfactants in hydrogen peroxide solutions with 
various corrosion inhibitors on cast iron and aluminum surface were investigated.

2. Materials and Methods

2.1. Materials

The following materials were used in the experiments:

Surfactants: Sodium lauroyl sarcosinate (NaLSar) from Merck, active matter 95%, molecular 
weight 293.40; lauryl dimethyl amine oxide (AO) from Enaspol, R = C_{12}-C_{14} (even numbered), active 
matter 30%, molecular weight 229.40; C_{12}-C_{14} alcohol ethoxylated 7EO (L7) from PCC Exol, active 
matter 90%, HLB 12.9, molecular weight 506.

Glycols: Polyethylene glycol 2000 (Merck) density 1.21 g/cm³, propylene glycol (Merck) density
1.04 g/cm³.

Oxidizing agent: H_2O_2 30% solution (Scharlau), density 1.11 g/cm³.

Corrosion inhibitors: triethanolamine (Merck) 98.5% purity; sodium silicate (Scharlau) density 1.37
g/cm³; benzo triazole (Merck) g/cm³.

Distilled water was used for the preparation of surfactant solutions and formulations.

2.2. Methods

2.2.1. Determination of critical micelle concentration. The critical micelle concentration (CMC) of
each surfactant NaLSar, AO, L7 and for ternary surfactant system (NaLSar:L7:A0 with mass ratio
1:2:3) was determined from surface tension measurements carried out on a KSV automatic 
tensiometer Sigma 700, by the Du Nouy ring technique. After preparing the physical setup, the 
experiment proceeds in stages. Precisely known amounts of stock fluid were added in a vessel filled 
with 40 mL distilled water with the help of an automatic dispenser connected to the instrument. The 
instrument stirred the solution and the surface tension values were measured after the required stability 
of the solution is accomplished. The critical micelle concentration value is determined from the graph 
of surface tension in function of logarithmic concentration from the intersection of slope and baseline.

2.2.2. Determination of surfactant stability in hydrogen peroxide. The stability of surfactants in 
hydrogen peroxide was evaluated by determining the active oxygen content of solutions every two
weeks. Active oxygen was determined by permanganometry, using potassium permanganate to titrate 
an acidified test solution. Blank solutions of hydrogen peroxide were used in order to evaluate the 
effect of surfactants on the stability of surfactant formulations.

2.2.3. Corrosion testing. The corrosion behavior of metallic surfaces when exposed to surfactant 
formulations containing oxidizing agent and corrosion inhibitors on the metallic was examined. The 
metallic plates used in experiments consisted in grey cast iron with tensile strength 200 MPa and 
aluminum plate with tensile strength 90 MPa. In case of cast iron plate, the corrosion experiment is 
done by placing 2g of steel chips (OL50 steel chips) on the clean surface of the cast iron plate. 2 mL
solution is dripped onto the chips, in order to cover the entire amount of chips. The cast iron plate was 
placed into desiccator for 24 hours, than the chips are removed and the cast iron plate examined. In the
case of aluminum plate, the corrosion experiment is performed by dripping onto the plate 2 mL solution, and after 24 hours in which the plate was held in a desiccator, the surface of aluminum plate was examined.

3. Results and discussions

3.1. Determination of critical micelle concentration

Surfactants solutions act in accordance with the laws of ideal dilute solutions up to the reach of a particular concentration named critical micelle concentration, above which the surfactant molecules are associated in spherical aggregates called micelles, having the hydrophilic regions in contact with surrounding water molecules and the lipophilic tail sequestered in the micelle centre, to have the lowest contact surface towards the aqueous phase. At the critical micelle concentration the surface tension of the solution is minimal, and although the surfactant concentration increases the surface tension no longer decreases, remaining constant. Critical micelle concentration is of great importance for the use of surfactants, since it specifies the optimal concentration for meaningful use.

For the examined surfactants the critical micelle concentration was determined. The surface tension variation with concentration for individual and ternary surfactant system is shown in Figure 1.

![Equilibrium Surface tension versus Concentration](image)

**Figure 1.** Plot of surface tension versus concentration for single surfactants and ternary surfactant system.

The works are a continuation of the studies performed for binary systems of surfactants with sarcosinated sodium lauroyl or sodium lauroyl glycinic content [10]. Besides the critical micelle concentration, the data supplied by the software of automatic tensiometer are used in the calculation of the maximum surface excess concentration at the air–liquid interface (\( \Gamma_{\text{max}} \)) and the minimum area per surfactant molecule at the air–liquid interface (\( A_{\text{min}} \)). \( \Gamma_{\text{max}} \) is evaluated with Gibbs adsorption equation:

\[
\Gamma_{\text{max}} = \frac{1}{2.303nRT} \left( \frac{dy}{d\log c} \right)
\]

Where: \( R \) is gas constant, \( dy/d\log c \) is the surface activity, \( T \) is temperature in K and \( n \) is a factor dependent on the type of surfactant (\( n=2 \) for ionic surfactants).

For the maximum surface excess concentration, the minimum area per molecule \( A_{\text{min}} \) is calculated according to relation:
N representing Avogadro’s number.

Surfactant efficiency can be calculated according to equation 3, as a reduction from the surface tension value \( \gamma_0 \) of distilled water of 71 mN/m and surface tension of aqueous surfactant solution \( \gamma \) at critical micelle concentration.

\[
\pi = \gamma_0 - \gamma
\]

In Table 1 are summarized the surface parameters of surfactant aqueous solutions.

| Sample | Surfactants and mixtures | CMC (%) | Surface tension at CMC (mN/m) | Efficiency \( \frac{d\gamma}{d\log c} \) (mN/m/decade) | \( 10^{10} \times \Gamma_{\text{max}} \) (mol/cm\(^2\)) | \( 10^2 \times A_{\text{min}} \) (nm\(^2\)) |
|--------|------------------------|---------|--------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| 1      | NaLSar                 | 2.405x10\(^{-1}\) | 27.33                          | 43.67                                         | -19.87                                         | 1.59                                          | 104                                          |
| 2      | AO                     | 1.496x10\(^{-2}\) | 25.94                          | 45.06                                         | -25.31                                         | 4.04                                          | 41                                           |
| 3      | L7                     | 1.726x10\(^{-3}\) | 27.57                          | 43.43                                         | -18.49                                         | 2.96                                          | 56                                           |
| 4      | NaLSar+L7+AO           | 3.155x10\(^{-3}\) | 25.93                          | 45.07                                         | -22.12                                         | 3.54                                          | 47                                           |

As shown in Figure 1 and Table 1, adding non-ionic surfactants to the anionic surfactant NaLSar improves the surface parameters of mixed surfactant system.

The CMC value of the mixture NaLSar:L7:AO with mass ratio 1:2:3 is lower than the CMC values for NaLSar and AO aqueous solutions. The surface tension at critical micelle concentration of the mixture NaLSar+L7+AO is decreasing to the value of 25.93 mN/m, which is more efficient than the surface tension at CMC of NaLSar and L7 solutions and practically equal with the surface tension at CMC of AO solution. The minimum area per molecule for mixture NaLSar+L7+AO also shows a decreased value, especially compared to minimum area per molecule for NaLSar solution.

The lower values for surface parameters obtained for the aqueous solution of mixture NaLSar+L7+AO compared with individual surfactants suggests a synergistic effect might occur by the interaction of surfactants.

The evaluation of the interactions between NaLSar and non-ionic surfactants can be determined from the deviation of experimental CMC values from the ideal CMC values. In ideal solutions, CMC obeys a linear behaviour consistent with micellar composition. However, many surfactant systems do not respect a linear relation toward surfactant composition.

For surfactant systems the ideal CMC, CMC\(_{\text{ideal}}\), can be calculated using Clint’s equation [11]:

\[
\frac{1}{\text{CMC}_{d+e+n}} = \frac{\alpha_1}{\text{CMC}_1} + \frac{\alpha_2}{\text{CMC}_2} + \frac{\alpha_3}{\text{CMC}_3}
\]

where CMC\(_1\), CMC\(_2\), CMC\(_3\) represent CMC for single surfactants and \(\alpha_1\), \(\alpha_2\), \(\alpha_3\) the mass fractions of individual surfactants.

The ideal CMC value obtained with the above formula for mixture NaLSar+L7+AO, 4.4x10\(^{-3}\) %, is lower than the experimental CMC value, resulting in a negative deviation of the ideal behavior. The synergism of mixtures of ionic and nonionic surfactants is given by the higher entropy of the double layer of counterions far from the micelle interface and lower chemical potential of aggregated surfactant [12].
3.2. Evaluation of surfactant stability in hydrogen peroxide

Hydrogen peroxide is an oxidizing agent widely used due to the low price, easy handling and its decomposition products consisting in water and oxygen [13]. A destabilizing effect on the hydrogen peroxide may occur by adding organic components such as surfactants [14]. The need to use stable surfactants in hydrogen severely limits choices. The most common choice is amine oxide type surfactants [15]. In order to diversify surfactant classes used in decontamination we propose a mixed surfactant system containing an amino acid based surfactant (NaLSar), used in combination with AO and L7. Evaluation of active oxygen content in function of time for H$_2$O$_2$ – surfactant combinations are presented in Figure 2.

![Figure 2. Active oxygen content variation in function of time for hydrogen peroxide-based formulations.](image)

The slow decrease of active oxygen content for all the formulations during the 60 days of observation shows a good stability, so that the surfactant system can be used in formulating decontamination agents. The tests performed with GC-MS technique on the NaLSar + L7 + AO surfactant system in 4% hydrogen peroxide to neutralize the dimethyl methylphosphonate (DMMP) used as a neurotoxic warfare chemical simulant resulted in the total neutralization of the simulant used.

3.3. Corrosion testing and evaluation

Surfactant-based decontamination systems must take into account corrosive effects on the metal surfaces of the oxidizing component, hydrogen peroxide, which ensures the decontamination effect of some chemical contaminants. Hydrogen peroxide is an oxidizing agent with no negative effects on the environment used in industrial applications and as antimicrobial agent for medical applications. The oxidizing character of hydrogen peroxide causes an inherent potential for metal corrosion. Therefore, in the corrosion tests several corrosion inhibitors were used. Triethanolamine (TEA) helps prevent corrosion of zinc and steel, is an organic amine corrosion inhibitor widely used for corrosion protection of metals in metal working fluids or water systems. Organic amines inhibit corrosion on metals by a mechanism of adsorption on metal surface and the subsequent formation of a passivated protective film [16-18]. Sodium silicate is inhibitor for iron and steel in cooling water systems. Soluble sodium silicate is an industrial chemical compound used extensively in corrosion inhibition. Silicates form protective films of silica and iron oxides [19, 20]. The deposition of thin silicate coatings on aluminum and its alloys have been investigated [21]. Benzotriazole (BTA) and its derivatives are organic corrosion inhibitors for copper alloys used in aqueous environment. BTA is also used to protect against corrosion the steel and aluminum alloys [22].
The use of the above corrosion inhibitors (triethanolamine, sodium silicate and benzotriazole) on corrosion protection on metal surfaces was evaluated in this study. Mixtures of NaLSar+L7+AO with mass ratio 1:2:3, 4% hydrogen peroxide and 12% mixture of propylene glycol and polyethylene glycol were prepared, and different corrosion inhibitors were added. Sample D3 contains 5% triethanolamine, sample D4 contains 1.5% sodium silicate and sample D5 contains 0.2% benzotriazole.

The results obtained by applying the test method presented above on the gray cast iron plate and aluminum is presented in Figures 3 and 4.

![Figure 3](image1.png)

**Figure 3.** Initial appearance (a) of the surface of cast iron plate and after 24 hours (b) for samples SD3, SD4 and SD5.

![Figure 4](image2.png)

**Figure 4.** Initial appearance (a) of the surface of aluminum plate and after 24 hours (b) for sample SD3.

The examination of the cast iron plate takes into account the proportion of stained surface and the colour intensity of the stains as well as the number of pinches. Corrosion tests performed on grey cast iron plate with formulations containing different corrosion inhibitors led to the conclusion that the most efficient corrosion inhibitor is triethanolamine (sample SD3), the metallic surface is free of stains or pinches. Sodium silicate is not as effective as triethanolamine on preventing corrosion of cast iron, it can be observed a stained surface hardly noticeable on an area of less than 10% of the test surface (sample SD4), while in the case of benzotriazole used as corrosion inhibitor pinches can be observed, as well as a stained surface on an area of less than 10% of the test surface (sample SD4). For sample SD3, the aluminum plate showed no signs of corrosion.

4. Conclusions

The use of an amino acid-based surfactant, namely sodium lauroyl sarcosinate, in a ternary surfactant system intended to be used in formulations with oxidizing agents for the neutralization of hazardous materials proved to be efficient in terms of surface properties and also in terms of stability in hydrogen peroxide solutions. The experimental critical micelle concentration value for the mixture of sodium lauroyl sarcosinate with lauryl dimethyl amine oxide and C12-C14 alcohol ethoxylated 7EO are lower than the ideal critical micelle concentration, demonstrating the synergistic action of the mixture, due to the greater interaction between the chemical species involved than the individual surfactants. Stability
in hydrogen peroxide solutions are high for all the surfactants included in the study. In the presence of an appropriate corrosion inhibitor, the formulations containing surfactants and hydrogen peroxide present no signs of corrosion on grey cast iron or aluminum surfaces. The results obtained lead us to the conclusion that it can be used in such formulations amino-acid-based surfactants, due to their stability in hydrogen peroxide and the compatibility and synergism with nonionic surfactants, but also due to their low toxicity and high biodegradability.

Acknowledgments
This work was financially supported by the Romanian National Authority for Scientific Research and Innovation – UEFISCDI, Contract No. 70PCCDI/2018.

5. References
[1] Kumar V, Goel R, Chawla R, Silambarasan M and Sharma R K 2010 Journal of Pharmacy And Bioallied Sciences 2(3) 220-238
[2] Fitzgerald G J 2008 American journal of public health 98(4) 611-625
[3] Purdon J G, Claude L C and Burczyk A F H 1999 Broad spectrum decontamination formulation and method of use WO2000048684A1
[4] Cronce D T 1998 Chemical warfare agent decontaminant solution using quaternary ammonium complexes US Patent No. 5760089
[5] Maciejewski P, Zielonka Z and Wrzesiński J 2011 Bezpieczeństwo i Technika Pożarnicza 51-58
[6] Khan A W, Kotta S, Ansari S H, Ali J and Sharma R K 2013 Defence Science Journal 63(5) 487-496
[7] Brown J S, Hodge R C and Schilling A S 2003 NAVAL SURFACE WARFARE CENTER DAHLGREN DIV VA
[8] Brame J A, Medina V F, Smith I and Procell L 2016 (No. ERDC/EL-SR-16-2) Army Engineer Research and Development Center Vicksburg, United States
[9] Singh B, Prasad G K, Pandey K S, Danikhel R K and Vijayaraghavan R 2010 Defence science journal 60(4) 428-441
[10] Chican I E, Vărășteanu D, Fierăscu I, Fierăscu R C and Deaconu M 2019 In IOP Conference Series: Materials Science and Engineering 572(1) 012009
[11] Akisada H, Kuwahara J, Noyori K, Kuba R, Shimooka T and Yamada A 2005 Journal of colloid and interface science 288(1) 238-246
[12] Bergström M and Eriksson J C 2004 Trends in Colloid and Interface Science XVI (pp. 16-22). Springer, Berlin, Heidelberg
[13] Lesage G, Penate I Q, Cognet P and Poux M 2012 International Journal of Chemical Reactor Engineering 10(1) 1-18
[14] Bonislawski D J, Lovetro D C and Schneidewind L 2014 U.S. Patent Application No. 20140005090
[15] Johansson I and Somasundaran P (Eds.). 2007 Handbook for Cleaning/decontamination of Surfaces. Elsevier
[16] Choi H, Song Y K, Kim K Y and Park J M 2012 Surface and Coatings Technology 206(8-9) 2354-2362
[17] Tang Z. 2019 Current Opinion in Solid State and Materials Science 23 100759
[18] Shang W, He C, Wen Y, Wang Y and Zhang Z 2016 RSC advances, 6(115) 113967-113980
[19] Rushing J C, McNeill L S and Edwards M 2003 Water Research 37(5) 1080-1090
[20] Gao H, Li Q, Chen F N, Dai Y, Luo F and Li L Q 2011 Corrosion Science 53(4) 1401-1407
[21] Hamdy A S 2006 Surface and Coatings Technology 200(12-13) 3786-3792
[22] Bokati K S and Delghanian C 2018 Journal of Environmental Chemical Engineering 6(2) 1613-1624