10.2478/v10063-009-0001-7

ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN – POLONIA

VOL. LXIII, 8 SECTIO AA 2008

Atmospheric oxidation of ascorbic acid in nonionic surfactant systems♣

J. Narkiewicz-Michałek*, M. Szymula* and K. A. Wilk**
*Faculty of Chemistry, Maria Curie Skłodowska University,
M.C. Skłodowska Sq. 3, 20-031 Lublin, Poland
**Department of Chemistry, Wroclaw University of Technology,
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

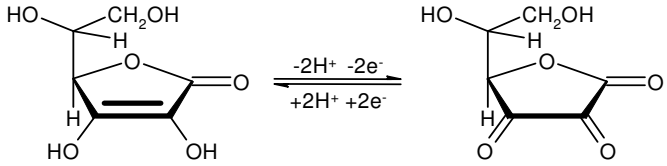
In our study we investigated the kinetics of atmospheric oxidation of ascorbic acid in the aqueous solutions of two non-ionic surfactants TRITON X-100 and commercial sugar ester C1616 (the most suitable emulsifier for food). For each surfactant the concentrations below and above the CMC were investigated. It was found that the micellar solutions of both surfactants showed faster oxidation rate than pure water. Less pronounced effects were observed with particular surfactant concentration change.

1. INTRODUCTION

Various natural and synthetic chemicals are incorporated into cosmetic, pharmaceutical and food emulsions to provide them with a long term stability and an appropriate consistency. The most important are surfactants and antioxidants. Surfactants are the system structure stabilizing agents whereas the ultimate mission of antioxidants is to slow down or inhibit the chemical oxidation reaction long enough for the product to be used by a consumer [1,2]. Antioxidants are usually classified into water soluble and oil soluble groups. The main representative of the hydrophilic antioxidants is naturally occurring vitamin C (ascorbic acid, AA). Vitamin C (L-ascorbic acid, AA, H_2A) is a water-soluble compound, which is characterized by a broad spectrum of antioxidant activities

♣ Dedicated to Professor Emil Chibowski on the occasion of his 65th birthday.

due to its capability of reacting with numerous aqueous free radicals and reactive oxygen species. Strong reducing power of AA is due to the two-step oxidation that results in hydrated dehydroascorbic acid (DHAA·H_2O) by the way of the intermediate ascorbate free-radical monodehydro ascorbic acid ($MDHA^-$). At neutral or alkaline pH, both rings of bicyclic structure of DHAA open to give 2,3-diketogulonic acid, which has a straight chain structure [3].



L-ascorbic acid L-dehydroascorbic acid

It is well known that AA activity in homogenous solutions is not the same as that in heterogeneous media. This environment dependence is the reason for investigating its activity in surfactant solutions [4-13]. In our earlier studies we investigated the kinetics of vitamin C atmospheric oxidation in the aqueous solutions of the four surfactants: SDS (anionic), AOT (anionic), TRITON X-100 (non-ionic) and CTAB (cationic). For each surfactant the concentrations below and above the CMC were investigated. We found that micellar environment influences significantly the vitamin C activity [3,4]. Its atmospheric oxidation rate changed in the following manner: it was the lowest in the AOT and SDS micellar solutions, somewhat higher in the TX-100 solution and the highest in the CTAB solution.

Nonionic surfactants differ from both cationic and anionic surfactants in that the molecules are actually uncharged. Traditionally, nonionic surfactants have used poly(ethylene oxide) chains as the hydrophilic group and can be classified into two groups: the alcohol ethoxylates and the alkylphenol ethoxylates. Triton X-100 belongs to the latter one. Another class of nonionic surfactants are the alkyl polyglycosides. For at least the last 20 years these have dubbed the "new generation nonionic surfactants". The predominant use of these surfacants is in foods and drinks, pharmaceuticals and skin-care products. It is thought that these surfactants are mild for the skin even at high loadings and long-term exposure (although they can lead to weakening of the skin barrier by promoting the transport of molecules).

The aim of this work was to compare the atmospheric oxidation of vitamin C in the solutions of two surfactants TX-100 and C1616 representing the above mentioned two classes of non-ionic surfactants. The knowledge how the type of

surfactant head group and surfactant concentration influence the kinetics of vitamin C oxidation may be useful for designing new products in food industry.

2. EXPERIMENTAL

The materials used were L-ascorbic acid and Triton X-100, produced by Fluka Chemie and RdH Labor Chemicalien, and sugar surfactant C1616 from Mitsubishi-Kagaku Foods Corporation. All surfactant solutions were prepared using doubly distilled water.

The kinetics of ascorbic acid decomposition was determined by ultraviolet spectroscopy using Specord M-42 Carl Zeiss Jena, a double-beam spectrophotometer. Stoppered quartz cells with an optical path length of 1.00 cm were used. In the experiment the initial AA concentration was 0.002% wt. The absorbance value of aqueous solution was around 1.2, i.e. it was in the region of linearity of concentration/absorbance relationship.

The surface tension of C1616 solutions was measured using a thermostated stalagmometer employing the "free drop" method of Lando et al. [14]. All measurements were taken at 22.5°C.

3. RESULTS AND DISCUSSION

Triton X-100 (octylphenol ethylene oxide containing on the average 9.5 oxyethylene units) is a comparatively mild, non-denaturing nonionic surfactant. It has no antimicrobial properties and is often used in biochemical applications to solubilize proteins. It is also known as an excellent detergent, dispersant and emulsifier for the oil-in-water systems (HLB=13.5). The CMC of TX-100 in the aqueous solution is about $0.22\text{-}0.24 \cdot 10^{-4}$ M and it forms globular aggregates with the mean aggregation number N_{agg}=140. Due to its good properties, it is often used as a model nonionic surfactant by many researchers.

The sugar surfactant C1616 is a representative of sucrose fatty acid esters which are nonionic surfactants consisting of sucrose as a hydrophilic group and fatty acid as a lipophilic group. As sucrose has the total of 8 hydroxyl groups, compounds ranging from sucrose mono- to octa- fatty acid esters can be produced. Being tasteless, odourless and nontoxic, they are the most suitable emulsifiers for foods. Being non-irritating for the eyes and skin, they are also suitable for pharmaceuticals and cosmetics. Because of their excellent biodegradability they do not cause environmental pollution. Sugar surfactants offer a full range of HLB values from 1 to 16, and in use all grades display exceptionally good surfactant functionality. The sugar surfactant C1616, used in our experiment, is a mixture of mono- and dipalmitate with a small amount of

monostearate. Its HLB is about 15 and the CMC, determined by us from the surface tension measurement, equals ≈ $1.0 \cdot 10^{-5}$ M (Figure 1).

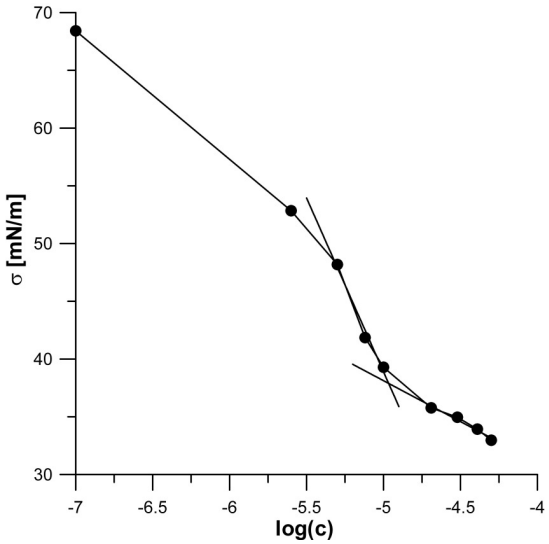


Fig. 1 The surface tension vs. C1616 concentration. CMC is determined by the extrapolation of the results at low and high concentrations to an intersection point.

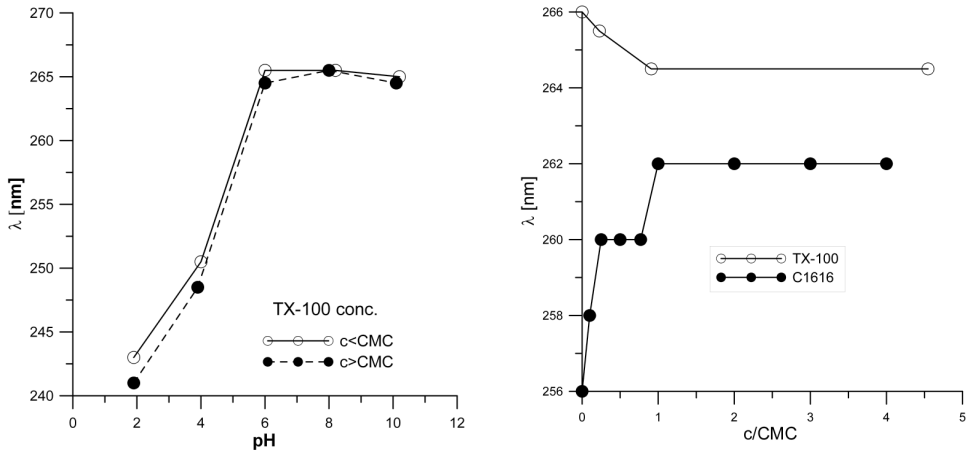


Fig. 2. (A) The wavelength corresponding to the maximum of AA absorbance in TX-100 as a function of the solution pH; (B) The wavelength corresponding to the maximum of AA absorbance in TX-100 (pH=6) and C1616 (free pH about 4-5) solutions as a function of the surfactant concentration. (AA concentration was 0.002% wt.).

The location of the absorption band of AA depends strongly on the solution pH. The UV spectrum of L-ascorbic acid at pH 2.0 reveals a λ_{max} of 243 nm (ε=10 000 mol^{-1} dcm^3 cm^{-1}) which undergoes a red shift to 265 nm (ε=16 500 mol^{-1} dcm^3 cm^{-1}) at pH 6.0. Below pH 4, ascorbic acid is present mainly in the undissociated form whereas at the neutral and alkaline pH the anionic form prevails as a result of ionization of the C-3-OH proton [3,15] (Figure 2A). At the same time the band location is almost independent of the TX-100 concentration at constant pH=6, indicating the weak interaction of AA molecules with the surfactant polar heads (Figure 2B). For the C1616 surfactant the band shifts to higher wavelength values with the increasing surfactant concentration. The main cause of this shift is the increasing ionisation of AA due to the increasing solution pH (from 4.7 for the aqueous AA solution to 6.4 for the system with the C1616 concentration above CMC).

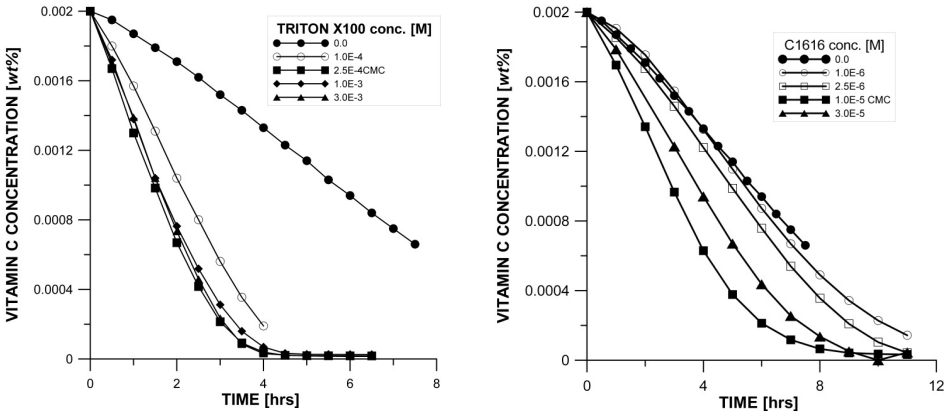


Fig. 3. Ascorbic acid concentration in the aqueous TX-100 solution (A) and the C1616 solution (B) as a function of atmospheric oxidation time.

In Figure 3 the results of ascorbic acid oxidative decomposition in the surfactant solutions are shown. It is clearly seen that the oxidation of ascorbic acid in both nonionic surfactant solutions proceeds more readily than in pure water. Depletion of AA becomes faster when the surfactant concentration increases. In the vicinity of CMC the rate of oxidation reaches the maximum value and then starts to decrease with the further increase of surfactant content. The initial rates of AA oxidation at different relative surfactant concentrations C/CMC are shown in Figure 4. The curve for TX-100 lies well above this for C1616. It means that the TX-100 micelles accelerate the oxidation of AA more than the C1616 micelles. If one assumes that the contact between AA and oxygen molecules is most effective at the surface of a micelle, the oxidation rate

will depend on the extent and properties of this surface. TX-100 forms large globular micelles with a slightly positively charged surface.

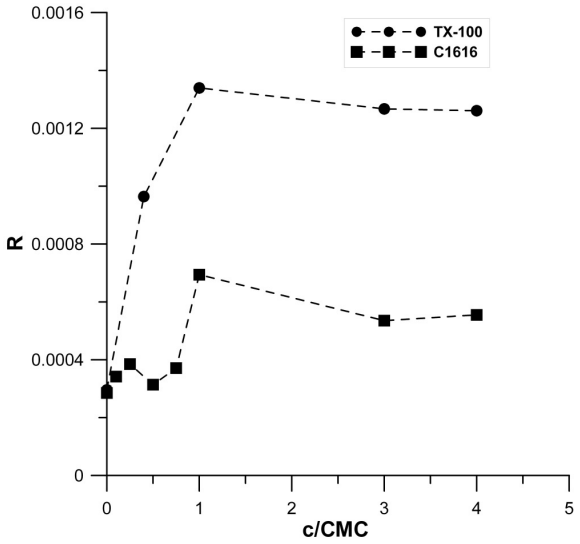


Fig. 4 The apparent initial oxidation rate R calculated from the linear regression of the experimental C(t) curves. n is a stoichiometric factor equal to 2 for AA.

The positive charge of the micelle surface attracts the ascorbic acid anions and causes the increase of their concentration in the interfacial region. It also stabilizes the anionic form of vitamin C. This stimulates the oxidation reaction.

The C1616 micelles are probably smaller and less compact than the TX-100 micelles because of their bulky and strongly hydrated polar heads. The compact hydration layer makes the contact of reagents located inside (oxygen) and outside the micelle (AA) more difficult [16,17].

For both surfactants the increasing number of micelles does not influence the oxidation rate of vitamin C substantially. It decreases slightly with the increasing number of micelles due to the decreasing surface concentration of vitamin C.

Another factor which may influence the oxidation of AA is the surface tension of solution which influences the oxygen transport from the air to the solution. At 22.5 ^{o}C the surface tension of TX-100 solution is about 29 mN/m at the CMC whereas for C1616 we found the value of about 40 mN/m at the CMC ($\approx 1 \cdot 10^{-5}$ M). As follows from paper [16] the lower the surface tension the faster is the oxygen transport through the solution/air interface. Thus we may expect higher oxygen concentration in the system containing TX-100 micelles and, consequently, the higher vitamin C oxidation rate.

4. REFERENCES

[1] Gallarate M., Carlotti M.E., Trota M., and Bravo S., *Int. J. Pharm.,* 188, 233 (1999).
[2] Zhang L., Lerner S., Rustrum W.V. and Hofmann G.A., *Bioelectrochem. Bioenerg.*, 48, 453 (1999).
[3] Davies M.B., Austin J. and Partridge D.A., Vitamin C: *Its Chemistry And Biochemistry,* The Royal Society of Chemistry Paperbacks*,* Thomas Graham House, 1991.
[4] Szymula M., Szczypa J. and Friberg S.E., *J. Dispersion Sci. Technol.,* **23,** 789 (2002).
[5] Szymula M. and Narkiewicz-Michałek J., *Colloid Polym. Sci.,* 281, 1142 (2003).
[6] Yu W., Zou A. and Guo R., *Colloids Surf., A,* 167, 293 (2000).
[7] Jaiswal P.V., Ijeri V.S. and Srivastava A.K., *Colloids Surf., B,* 46, 45 (2005).
[8] Suzuki M., Umetani S., Matsui M. and Kihara S., *J. Electroanal. Chem.,* 420, 119 (1997).
[9] Yoshimura Y., Honda K., Kondo T., Rao T.N., Tryk D.A. and Fujishima A., *Electroanalysis Acta*, 47, 4387 (2002).
[10] Wen X.-L., Han Z.-X., Rieker A. and Liu Z.L., *J. Chem. Res. Synop.,* 3, 108 (1997).
[11] Wen X.L., Zhang J., Liu Z.L., Han Z.-X. and Rieker A., *J. Chem. Soc., Perkin Trans*. *2*, 4, 905 (1998).
[12] Han Y.K., Oh S.G., Shin S.L., Joung W.D., Yi S.C. and Cho C.G., *Colloids Surf., B*, 24, 33 (2002).
[13] Issopoulos P.B. and Salta S.E., *Fresenius J. Anal. Chem.,* 357, 317 (1997).
[14] Lando J.L. and Oakley H.T., *J. Colloid Interface Sci.,* 25, 526 (1967).
[15] Fernandes J.C.B., de Oliveira Neto G. and Kubota L.T., *Analytica Chimica Acta,* 366, 11 (1998).
[16] Mathenson I.B.C. and King Jr. A.D., *J. Colloid Interface Sci.*, 66, 464 (1978).
[17] Subczyński W.K. and Wiśniewski A., *Acta Biochim. Pol.,* 47, 613 (2000).