

HALAMID® BIOCIDAL MODE OF ACTION

Historical view on the biocidal mode of action

Since the first publication by Chattaway(1) in 1905 on Chloramine T and the first introduction as a disinfectant by Dakin(2) in 1916, this product has been seen as slow hypochlorite (HOCI and/or OCI⁻) releasing agent. This despite some authors reported about properties conflicting with this theory(3,4).

Product properties conflicting with the theory of slow hypochlorite release in comparison to hypochlorite and chloro-isocyanurates are:

- excellent stability of the aqueous solution
- moderate pH dependence of the biocidal efficacy
- moderate influence of organic matter on the biocidal
 efficacy
- hardly any skin irritation
- hardly any chlorination ability

New Studies I

Recently some studies have been published that prove that the biocidal mode of action of Halamid[®] is not based on the release of hypochlorite but must be explained by a different chemical mechanism.

Gottardi(5) calculated the theoretical composition of an aqueous Chloramine-T solution at various pH values. In an aqueous solution of Chloramine-T the following equilibriums exist: $(R = CH_3 - C_6H_4 - SO_2)$

R-NCINa	\longleftrightarrow	R-NCI [−] + Na+
R-NCI [−] + H+	\longleftrightarrow	R-NHCI
2 R-NHCI	\longleftrightarrow	R-NH ₂ + R-NCl ₂
R-NCI, + H20	\longleftrightarrow	R-NHCI + HOCI
HOCI	\longleftrightarrow	OCI [–] + H+
R-NH,	\longleftrightarrow	R-NH [−] + H+

According to these equilibriums, seven different compounds can be present in a Chloramine-T solution.

Based on the known equilibrium constants, Gottardi calculated for various pH values the concentrations of the individual compounds. If Chloramine-T would be a slow hypochlorite-releasing agent, then the compounds HOCI and/or OCF should be present at a significant level. However Gottardi showed that for a 0.1 % Chloramine-T solution the hypochlorite concentrations [OCF] and [HOCI] are:

at pH 3 :	$[\text{ OCI}^-] = < 0.01 \ \mu\text{g/l},$	[HOCI] = 14 µg/I
at pH 7 :	[OCI⁻] = 4 µg/l,	[HOCI] = 14 µg/I
at pH 10 :	[OCI⁻] = 35 µg/l,	[HOCI] = 0.5 µg/l
at pH 12 :	[OCI⁻] = 200 µg/l,	$[$ HOCI $] = < 0.01 \ \mu\text{g/I}$

The biocidal effects of Chloramine-T can never be explained by these minimal quantities of hypochlorite.

New Studies II

Hahn et al(6) proved the theory of Gottardi by analysis. They developed an electrochemical analytical method by which they could detect very low concentrations of hypochlorite in a Chloramine-T solution. They found that in an aqueous solution containing 2.5 g Chloramine-T per liter, the hypochlorite concentration is lower than $100 \mu g/L$ (this is the detection limit of the analytical method). Even if they deliberately add hypochlorite to the solution, it reacts quickly with solution components. At neutral and alkaline pH values, it reacts with R-NH₂ (para-toluenesulfonamide), which -as Gottardi showsis present at minor concentrations in a Chloramine-T solution, to form Chloramine-T. At acidic pH values it is reported to react with R-NHCl to form RNCl₂ (dichloramine-T).

So based on theoretical as well as analytical proven facts one has to conclude that Halamid[®] is not a slow hypochlorite releasing agent.

Present view on the biocidal mode of action of Halamid®

Gottardi calculated that the compounds responsible for the biocidal properties of a Chloramine-T solution are:

R-NHCI and R-NCI ₂ (Chloramine-T acid	
and Dichloramine-T)	
R-NHCI, R-NCI ⁻ and	
R-NCl ₂ (Chloramine-T acid;	
Chloramine-T ion and Dichloramine-T)	
R-NCI ⁻ (Chloramine-T ion)	

At all pH values, these molecules represent more than 99.99 % of the total amount of Chloramine-T present in the solution.

Biocidal mode of action of Halamid®

Halamid[®], dissolved in water, ionizes and forms the Chloramine-T ion. This ion reacts directly with microorganisms such as bacteria, fungi, viruses, with which it comes into contact. Its action is based on an irreversible destruction of the envelope and cell material of microorganisms. This oxidizing action ensures that microorganisms are effectively killed and do not have a chance to develop resistance to Halamid[®].

References:

- 1 F.D. Chattaway, J. Chem. Soc. 87, 151 (1905)
- 2 H.D Dakin, J.B. Cohen, M. Daufresne, J. Kenyon, Proc. Royal Soc. London Ser. B. 232-251, 1916
- 3 Kirk-Othmer, Encyclopedia of Chemical Technology,5th edition, Volume 5, page 921
- 4 Ullmann's Encyclopedia of Industrial Chemistry, 4th edition, Band 9, page 389
- 5 W. Gottardi, Arch. Pharm., 325, 377-384, (1992)
- 6 M. Hahn, A. Liebau, H.H. Rüttinger, R. Thamm, Anal. Chim. Acta, 289, 35-42, (1994)

Use biocides safely. Always read the label and product information before use.

Halamid[®] is an Axcentive product available in various packages, from 2 kg buckets to 1000 kg big bags.

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