SLOVENSKI KEMIJSKI DNEVI 2024
30th Annual Meeting of the Slovenian Chemical Society
18.-20. september 2024 • Portorož-Portorose, Slovenija

Considering the concepts of synergism in (corrosion) chemistry

Slovenski kemijski dnevi 2024

Anton Kokalj
Dept. of Physical and Organic Chemistry, Jožef Stefan Institute, Ljubljana, Slovenia

Bernardin, 20 September 2024

Synergism

…one plus one is greater than two …

…the combined is greater than the sum of its parts …

Synergism

Example of synergism in chemistry:
a mixture exhibiting properties superior to pure compounds.

In this presentation:
synergism in corrosion inhibition
(with a blend of corrosion inhibitors, one aims to boost corrosion protection).

Corrosion inhibitors: substances, used in relatively low concentration, that effectively reduce the corrosion rate of metals and alloys.

(used in cooling systems, storage tanks, boilers, oil pipelines, oil well drilling technology, architecture. . .)

How to quantify synergism?

performance of a mixture, P_{mixture} $\Leftrightarrow$ threshold performance, $P_{\mathrm{threshold}}$

How to quantify synergism?

performance of a mixture, P_{mixture} $\Leftrightarrow$ threshold performance, $P_{\text{threshold}}$

$$P_{\text{mixture}} > P_{\text{threshold}} \Rightarrow \text{synergism}$$

How to quantify synergism?

performance of a mixture, P_{mixture} $\Leftrightarrow$ threshold performance, $P_{\mathrm{threshold}}$

$P_{\mathrm{mixture}} > P_{\mathrm{threshold}} \Rightarrow$ synergism

$P_{\mathrm{mixture}} < P_{\mathrm{threshold}} \Rightarrow$ antagonism

Motivation

The concepts of **synergism** is often utilized in corrosion inhibition studies.

However, the foundations underlying this concept appear not to be always understood.

Corrosion inhibition efficiency

The performance of corrosion inhibitors is usually quantified with corrosion inhibition efficiency, η (to be defined later).

- perfect inhibitor, $\eta = 1$
- null inhibitor, $\eta = 0$
- corrosion activator, $\eta < 0$

Quantifying synergism

Synergistic parameter in corrosion inhibition

A typical equation for the synergistic parameter (S) one finds in the literature:

$$S = \frac{1 - \eta_{1+2}}{1 - \eta_{12}}$$

$\eta \equiv$ inhibition efficiency

Quantifying synergism
Synergistic parameter in corrosion inhibition

A typical equation for the synergistic parameter (S) one finds in the literature:

$$S = \frac{1 - \overset{?}{\boxed{\eta_{1+2}}}}{1 - \underset{?}{\boxed{\eta_{12}}}}$$

$\eta \equiv$ inhibition efficiency

Quantifying synergism

Synergistic parameter in corrosion inhibition

A typical equation for the synergistic parameter (S) one finds in the literature:

? threshold inhibition efficiency for a binary mixture

$$S = \frac{1 - \boxed{\eta_{1+2}}}{1 - \boxed{\eta_{12}}} = \frac{1 - \boxed{\eta_{12}^{\text{threshold}}}}{1 - \boxed{\eta_{12}^{\text{measured}}}}$$

? measured inhibition efficiency of a binary mixture

Quantifying synergism

Synergistic parameter in corrosion inhibition

A typical equation for the synergistic parameter (S) one finds in the literature:

?

threshold inhibition efficiency for a binary mixture

$$S = \frac{1 - \eta_{1+2}}{1 - \eta_{12}} = \frac{1 - \eta_{12}^{\text{threshold}}}{1 - \eta_{12}^{\text{measured}}}$$

?

measured inhibition efficiency of a binary mixture

where usually:

$$\eta_{12}^{\text{threshold}} = \eta_1 + \eta_2 - \eta_1 \eta_2$$

(K. Aramaki, N. Hackerman, J. Electochem. Soc. 116 (1969) 568)

Quantifying synergism

Synergistic parameter in corrosion inhibition

A typical equation for the synergistic parameter (S) one finds in the literature:

threshold inhibition efficiency for a binary mixture

?

$$S = \frac{1 - \eta_{1+2}}{1 - \eta_{12}} = \frac{1 - \eta_{12}^{\text{threshold}}}{1 - \eta_{12}^{\text{measured}}}$$

?

measured inhibition efficiency of a binary mixture

where usually:

$$\eta_{12}^{\text{threshold}} = \eta_1 + \eta_2 - \eta_1 \eta_2$$

(K. Aramaki, N. Hackerman, J. Electochem. Soc. 116 (1969) 568)

how this equation emerges is not explained in the paper

Quantifying synergism

Synergistic parameter in corrosion inhibition

A typical equation for the synergistic parameter (S) one finds in the literature:

threshold inhibition efficiency for a binary mixture

?

$$S = \frac{1 - \eta_{1+2}}{1 - \eta_{12}} = \frac{1 - \eta_{12}^{\text{threshold}}}{1 - \eta_{12}^{\text{measured}}}$$

?

measured inhibition efficiency of a binary mixture

where usually:

$$\eta_{12}^{\text{threshold}} = \eta_1 + \eta_2 - \eta_1\eta_2 \qquad \eta_{123}^{\text{threshold}} = \eta_1 + \eta_2 + \eta_3 - \eta_1\eta_2 - \eta_1\eta_3 - \eta_2\eta_3 + \eta_1\eta_2\eta_3$$

how this equation emerges is not explained in the paper [redacted], [redacted], [redacted], Mor. J. Chem. 14 (2023) 689–698.

Aramaki and Hackerman (Aramaki et al. (1987)), calculated the synergism parameter S_θ using the following equation:

$$S_\theta = \frac{1-\theta_{1+2}}{1-\theta'_{1+2}} = \frac{1-(\theta_1 + \theta_2) \overset{+}{\cancel{-}} (\theta_1\,\theta_2)}{1-\theta'_{1+2}}$$

where: $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\,\theta_2)$; θ_1 = surface coverage by anion; θ_2 = surface coverage by organic compound; θ'1+2 = measured surface coverage by both the anion and organic inhibitor. $S_\theta > 1$ means that the compound system has an obvious synergistic effect. $S_\theta \leq 1$ means that the synergy is not significant or there is an antagonistic effect. The larger the S_θ value, the stronger the synergy between the inhibitors. So, S_θ is defined only for two components acting on the metal surface; then, at our knowledge, there is no relationship to estimate the synergism parameter of more than two inhibitors (Bouklah et al (2006); Kokaji et al. (2023); Mobin et al. (2013)). By the way, the inhibition process is [redacted], Mor. J. Chem. 14 (2023) 689–698.

Aramaki and Hackerman (Aramaki et al. (1987)), calculated the synergism parameter S_θ using the following equation:

$$S_\theta = \frac{1-\theta_{1+2}}{1-\theta'_{1+2}} = \frac{1-(\theta_1 + \theta_2) \overset{+}{\cancel{-}} (\theta_1\,\theta_2)}{1-\theta'_{1+2}}$$

where: $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\,\theta_2)$; θ_1 = surface coverage by anion; θ_2 = surface coverage by organic compound; θ'1+2 = measured surface coverage by both the anion and organic inhibitor. $S_\theta > 1$ means that the compound system has an obvious synergistic effect. $S_\theta \leq 1$ means that the synergy is not significant or there is an antagonistic effect. The larger the S_θ value, the stronger the synergy between the inhibitors. So, S_θ is defined only for two components acting on the metal surface; then, at our knowledge, there is no relationship to estimate the synergism parameter of more than two inhibitors (Bouklah et al (2006); Kokaji et al. (2023); Mobin et al. (2013)). By the way, the inhibition process is

2

irect

ocate/corsci

Check for updates

Considering the concept of synergism in corrosion inhibition

Anton Kokalj

Department of Physical and Organic Chemistry, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

A R T I C L E I N F O

Keywords:
Corrosion inhibition
Synergism
Langmuir adsorption model

A B S T R A C T

Synergism in corrosion inhibition and how to best quantify it is explored conceptually. In the equation for the synergistic parameter, the mixture's inhibition efficiency is evaluated against a threshold inhibition efficiency based on the performance of pure compounds. However, the choice for the threshold value is not unique. In the literature, the threshold of Aramaki–Hackerman is usually used. Herein, several other reasonable choices are developed, which are based on (i) the Langmuir adsorption model, (ii) the requirement that a mixture's inhibition efficiency is higher than the highest inhibition efficiency of pure compounds, or (iii) that corrosion resistance in a mixture is higher than the sum of resistances in pure compounds. The presented synergistic models are also extended to multi-component mixtures.

Corros. Sci. 212 (2023) 110922

[redacted], [redacted], [redacted], Mor. J. Chem. 14 (2023) 689–698.

Aramaki and Hackerman (Aramaki et al. (1987)), calculated the synergism parameter S_θ using the following equation:

$$S_\theta = \frac{1-\theta_{1+2}}{1-\theta'_{1+2}} = \frac{1-(\theta_1 + \theta_2) \overset{+}{\cancel{-}} (\theta_1\, \theta_2)}{1-\theta'_{1+2}}$$

where: $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\, \theta_2)$; θ_1 = surface coverage by anion; θ_2 = surface coverage by organic compound; θ'1+2 = measured surface coverage by both the anion and organic inhibitor. $S_\theta > 1$ means that the compound system has an obvious synergistic effect. $S_\theta \leq 1$ means that the synergy is not significant or there is an antagonistic effect. The larger the S_θ value, the stronger the synergy between the inhibitors. So, S_θ is defined only for two components acting on the metal surface; then, at our knowledge, there is no relationship to estimate the synergism parameter of more than two inhibitors (Bouklah et al (2006); Kokaji et al. (2023); Mobin et al. (2013)). By the way, the inhibition process is

irect

ocate/corsci

CORROSION SCIENCE

Considering the concept of synergism in corrosion inhibition

Anton Kokalj

Department of Physical and Organic Chemistry, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

ARTICLE INFO

Keywords:
Corrosion inhibition
Synergism
Langmuir adsorption model

Corros. Sci. 212 (2023) 110922

ABSTRACT

Synergism in corrosion inhibition and how to best quantify it is explored conceptually. In the equation for the synergistic parameter, the mixture's inhibition efficiency is evaluated against a threshold inhibition efficiency based on the performance of pure compounds. However, the choice for the threshold value is not unique. In the literature, the threshold of Aramaki–Hackerman is usually used. Herein, several other reasonable choices are developed, which are based on (i) the Langmuir adsorption model, (ii) the requirement that a mixture's inhibition efficiency is higher than the highest inhibition efficiency of pure compounds, or (iii) that corrosion resistance in a mixture is higher than the sum of resistances in pure compounds. The presented synergistic models are also extended to multi-component mixtures.

resistance in a mixture is higher than the sum of resistances in pure compounds. The presented synergistic models are also extended to multi-component mixtures.

Preliminary definitions

- $r \equiv$ corrosion rate, $R \equiv$ corrosion resistance

$$R \propto r^{-1} \qquad r_0, R_0 \;\ldots\; \text{blank sample}$$
$$r, R,\ r_i, R_i,\ r_{ij}, R_{ij} \;\ldots\; \text{inhibited samples}$$

- Inhibition efficiency:

$$\eta = \frac{r_0 - r}{r_0} = \frac{R - R_0}{R}, \qquad \eta \in [0,1] \text{ (for inhibitors)}$$

- **Corrosion activity (α):**

$$\alpha = 1 - \eta = \frac{r}{r_0} = \frac{R_0}{R}, \qquad \alpha \in [0,1] \text{ (for inhibitors)}$$

equations are simpler with α than η

Preliminary definitions

- $r \equiv$ corrosion rate, $R \equiv$ corrosion resistance

$$R \propto r^{-1} \qquad r_0, R_0 \; \ldots \; \text{blank sample}$$

$$r, R,\; r_i, R_i,\; r_{ij}, R_{ij} \; \ldots \; \text{inhibited samples}$$

- Inhibition efficiency:

$$\eta = \frac{r_0 - r}{r_0} = \frac{R - R_0}{R}, \qquad \eta \in [0, 1] \;\; \text{(for inhibitors)}$$

- **Corrosion activity (α):**

$$\alpha = 1 - \eta = \frac{r}{r_0} = \frac{R_0}{R}, \qquad \alpha \in [0, 1] \;\; \text{(for inhibitors)}$$

equations are simpler with α than η

Preliminary definitions

- $r \equiv$ corrosion rate, $R \equiv$ corrosion resistance

$$R \propto r^{-1} \qquad r_0, R_0 \;\ldots\; \text{blank sample}$$
$$r, R,\; r_i, R_i,\; r_{ij}, R_{ij} \;\ldots\; \text{inhibited samples}$$

- Inhibition efficiency:

$$\eta = \frac{r_0 - r}{r_0} = \frac{R - R_0}{R}, \qquad \eta \in [0, 1] \;\; \text{(for inhibitors)}$$

- **Corrosion activity (α):**

$$\alpha = 1 - \eta = \frac{r}{r_0} = \frac{R_0}{R}, \qquad \alpha \in [0, 1] \;\; \text{(for inhibitors)}$$

equations are simpler with α than η

Preliminary definitions

- $r \equiv$ corrosion rate, $R \equiv$ corrosion resistance

$$R \propto r^{-1} \qquad r_0, R_0 \ \ldots \text{ blank sample}$$
$$r, R,\ r_i, R_i,\ r_{ij}, R_{ij} \ \ldots \text{ inhibited samples}$$

- Inhibition efficiency:

$$\eta = \frac{r_0 - r}{r_0} = \frac{R - R_0}{R}, \qquad \eta \in [0, 1] \ \text{(for inhibitors)}$$

- **Corrosion activity (α):**

$$\alpha = 1 - \eta = \frac{r}{r_0} = \frac{R_0}{R}, \qquad \alpha \in [0, 1] \ \text{(for inhibitors)}$$

equations are simpler with α than η

Derivation of the Aramaki–Hackerman threshold

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

$$S = \frac{1 - \eta_{12}^{\text{threshold}}}{1 - \eta_{12}^{\text{measured}}} = \frac{\alpha_{12}^{\text{threshold}}}{\alpha_{12}^{\text{measured}}}$$ (synergistic parameter)

$$\eta_{12}^{\text{threshold}} = \eta_1 + \eta_2 - \eta_1\eta_2 \quad \Rightarrow$$ confined within [0,1] (for inhibitors)

Derivation of the Aramaki–Hackerman threshold

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

$$S = \frac{1-\eta_{12}^{\text{threshold}}}{1-\eta_{12}^{\text{measured}}} = \frac{\alpha_{12}^{\text{threshold}}}{\alpha_{12}^{\text{measured}}}$$ (synergistic parameter)

$$\eta_{12}^{\text{threshold}} = \eta_1 + \eta_2 - \eta_1\eta_2 \quad \Rightarrow$$ confined within [0,1] (for inhibitors)

Proof.

- pure inhibitor-1: $\alpha_1 \in [0, 1]$
- pure inhibitor-2: $\alpha_2 \in [0, 1]$

Derivation of the Aramaki–Hackerman threshold

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

$$S = \frac{1-\eta_{12}^{\text{threshold}}}{1-\eta_{12}^{\text{measured}}} = \frac{\alpha_{12}^{\text{threshold}}}{\alpha_{12}^{\text{measured}}}$$ (synergistic parameter)

$$\eta_{12}^{\text{threshold}} = \eta_1 + \eta_2 - \eta_1\eta_2 \quad \Rightarrow$$ confined within [0,1] (for inhibitors)

Proof.

- pure inhibitor-1: $\alpha_1 \in [0, 1]$
- pure inhibitor-2: $\alpha_2 \in [0, 1]$
- threshold for a binary mixture: $\alpha_{12}^{\text{threshold}} = \alpha_1\alpha_2 \in [0, 1]$

Derivation of the Aramaki–Hackerman threshold

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

$$S = \frac{1-\eta_{12}^{\text{threshold}}}{1-\eta_{12}^{\text{measured}}} = \frac{\alpha_{12}^{\text{threshold}}}{\alpha_{12}^{\text{measured}}}$$ (synergistic parameter)

$\eta_{12}^{\text{threshold}} = \eta_1 + \eta_2 - \eta_1\eta_2 \quad \Rightarrow$ confined within [0,1] (for inhibitors)

Proof.

- pure inhibitor-1: $\alpha_1 \in [0, 1]$
- pure inhibitor-2: $\alpha_2 \in [0, 1]$
- threshold for a binary mixture: $\alpha_{12}^{\text{threshold}} = \alpha_1\alpha_2 \in [0, 1]$

$$\alpha_1\alpha_2 = (1-\eta_1)(1-\eta_2) = 1 - \eta_1 - \eta_2 + \eta_1\eta_2$$

Derivation of the Aramaki–Hackerman threshold

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

$$S = \frac{1-\eta_{12}^{\text{threshold}}}{1-\eta_{12}^{\text{measured}}} = \frac{\alpha_{12}^{\text{threshold}}}{\alpha_{12}^{\text{measured}}}$$ (synergistic parameter)

$$\eta_{12}^{\text{threshold}} = \eta_1 + \eta_2 - \eta_1\eta_2 \quad \Rightarrow$$ confined within [0,1] (for inhibitors)

Proof.

- pure inhibitor-1: $\alpha_1 \in [0,1]$
- pure inhibitor-2: $\alpha_2 \in [0,1]$
- threshold for a binary mixture: $\alpha_{12}^{\text{threshold}} = \alpha_1\alpha_2 \in [0,1]$

$$\alpha_1\alpha_2 = (1-\eta_1)(1-\eta_2) = 1 - \eta_1 - \eta_2 + \eta_1\eta_2$$

- But: $\alpha_{12}^{\text{threshold}} = 1 - \eta_{12}^{\text{threshold}} \quad \Rightarrow \quad \eta_{12}^{\text{threshold}} = \eta_1 + \eta_2 - \eta_1\eta_2$

$\square$

The Aramaki–Hackerman multi-component model

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

- n-component mixture:

$$\alpha^{\text{threshold}} = \prod_{i=1}^{n} \alpha_i$$

$$\eta^{\text{threshold}} = 1 - \prod_{i=1}^{n} \alpha_i = 1 - \prod_{i=1}^{n} (1 - \eta_i)$$

The Aramaki–Hackerman multi-component model

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

- n-component mixture:

$$\alpha^{\text{threshold}} = \prod_{i=1}^{n} \alpha_i$$

$$\eta^{\text{threshold}} = 1 - \prod_{i=1}^{n} \alpha_i = 1 - \prod_{i=1}^{n} (1 - \eta_i)$$

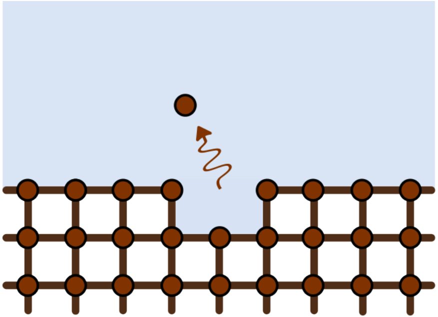
- 3-component mixture:

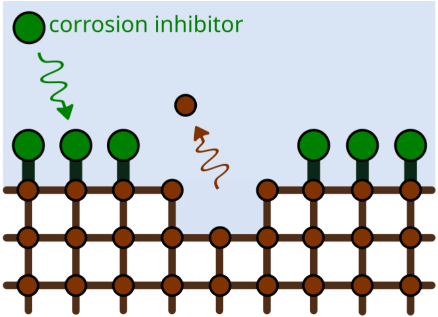
$$\alpha_{123}^{\text{threshold}} = \alpha_1 \alpha_2 \alpha_3$$
$$\eta_{123}^{\text{threshold}} = \eta_1 + \eta_2 + \eta_3 - \eta_1\eta_2 - \eta_1\eta_3 - \eta_2\eta_3 + \eta_1\eta_2\eta_3$$

How inhibitors impede corrosion?

Adsorption hypothesis: adsorbed inhibitor molecule protects the surface site at which it is adsorbed from corrosion.

Corrosion of metals: $M \rightarrow M^{z+} + ze^{-}$

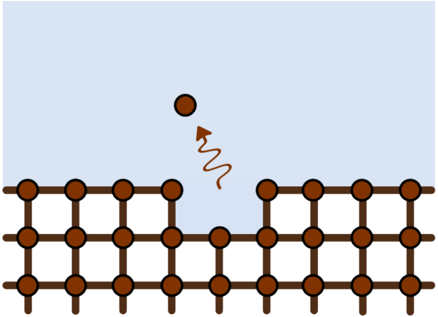


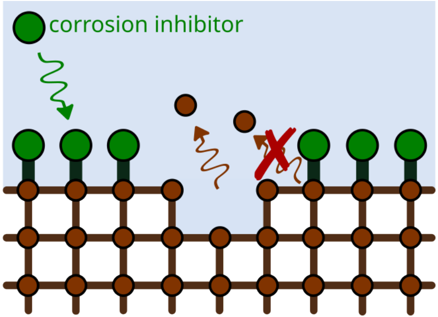


How inhibitors impede corrosion?

Adsorption hypothesis: adsorbed inhibitor molecule protects the surface site at which it is adsorbed from corrosion.

Corrosion of metals: $\mathrm{M} \rightarrow \mathrm{M}^{z+} + ze^{-}$





Inhibition efficiency vs. surface coverage

Perfect adsorption hypothesis: An adsorbed inhibitor molecule **perfectly** protects the site at which it is adsorbed from corrosion.

This hypothesis implies that $\eta = \underbrace{\theta}_{\text{fractional surface coverage}}$.

blank sample: $r_0 \propto \overbrace{A}^{\text{surface area of a sample}}$

inhibited sample: $r \propto A(1-\theta)$

$$\Downarrow$$

$$\eta = \frac{r_0 - r}{r_0} = \frac{A - A(1-\theta)}{A} = \theta$$

If $\eta = \theta \Rightarrow$ utilize the Langmuir adsorption model

Basic assumption of the **Langmuir model**:[1] **no interactions** between adsorbates

- if interactions between inhibitors 1 and 2 are **attractive**:

  $\theta_{12} > \theta_{\text{Langmuir}} \Rightarrow$ **synergism**

- if interactions between inhibitors 1 and 2 are **repulsive**:

  $\theta_{12} < \theta_{\text{Langmuir}} \Rightarrow$ **antagonism**

[1] Other assumptions are:

- all adsorption sites are equivalent
- 0 or 1 molecule is adsorbed at an adsorption site
- maximum coverage is a single monolayer

If $\eta = \theta \Rightarrow$ utilize the Langmuir adsorption model

Basic assumption of the **Langmuir model**:[1] $\boxed{\textbf{no interactions} \text{ between adsorbates}}$

- if interactions between inhibitors 1 and 2 are **attractive**:

  $\theta_{12} > \theta_{\text{Langmuir}} \Rightarrow$ **synergism**

- if interactions between inhibitors 1 and 2 are **repulsive**:

  $\theta_{12} < \theta_{\text{Langmuir}} \Rightarrow$ **antagonism**

[1] Other assumptions are:

- all adsorption sites are equivalent
- 0 or 1 molecule is adsorbed at an adsorption site
- maximum coverage is a single monolayer

If $\eta = \theta \Rightarrow$ utilize the Langmuir adsorption model

Basic assumption of the **Langmuir model**:[1] $\boxed{\textbf{no interactions} \text{ between adsorbates}}$

- if interactions between inhibitors 1 and 2 are **attractive**:

  $\theta_{12} > \theta_{\text{Langmuir}} \Rightarrow$ **synergism**

- if interactions between inhibitors 1 and 2 are **repulsive**:

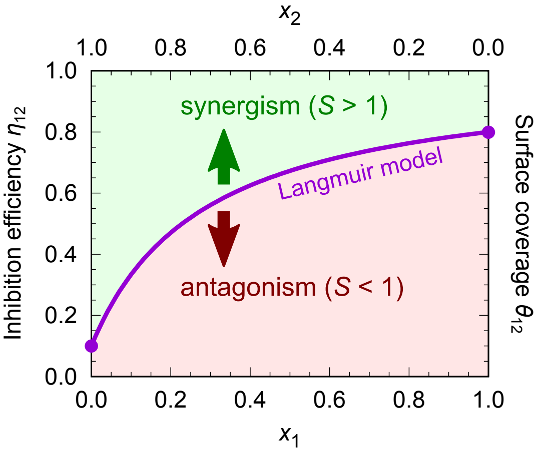
  $\theta_{12} < \theta_{\text{Langmuir}} \Rightarrow$ **antagonism**

[1] Other assumptions are:

- all adsorption sites are equivalent
- 0 or 1 molecule is adsorbed at an adsorption site
- maximum coverage is a single monolayer

The Langmuir synergistic model

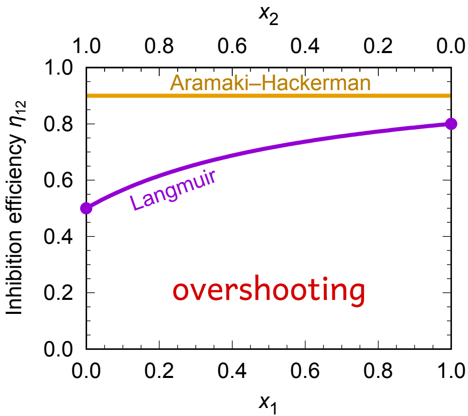
(A. Kokalj, Corros. Sci. 212 (2023) 110922)

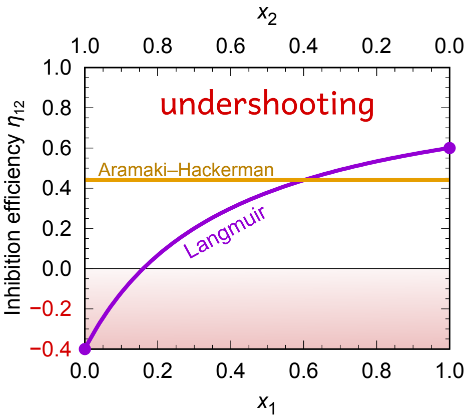


$$S = \frac{1-\eta^{\text{threshold}}}{1-\eta^{\text{measured}}} = \frac{1-\theta_{\text{Langmuir}}}{1-\theta_{\text{measured}}}$$

Drawbacks of the Aramaki–Hackerman model

$\eta_{12}^{\text{threshold}} = \eta_1 + \eta_2 - \eta_1\eta_2$ (A. Kokalj, Corros. Sci. 212 (2023) 110922)





$\eta_1^{\max} = 0.8$, $\eta_2^{\max} = 0.5$

$\eta_{12}^{\text{threshold}} = 0.9$

$\eta_1^{\max} = 0.6$, $\eta_2^{(x_2=1)} = -0.4$

$\eta_{12}^{\text{threshold}} = 0.44$

Absolute synergistic model

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

Practical consideration

For synergism, **the mixture should perform better than any pure inhibitor compound in the blend**, irrespective of the concentration.

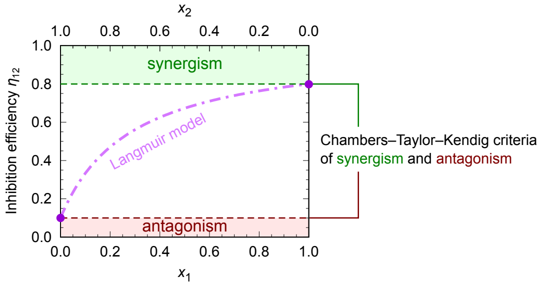
Absolute synergistic model

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

Practical consideration

For synergism, **the mixture should perform better than any pure inhibitor compound in the blend**, irrespective of the concentration.

Such a criterion was used by Chambers–Taylor–Kendig (Corrosion 61 (2005) 480), but they used it qualitatively.



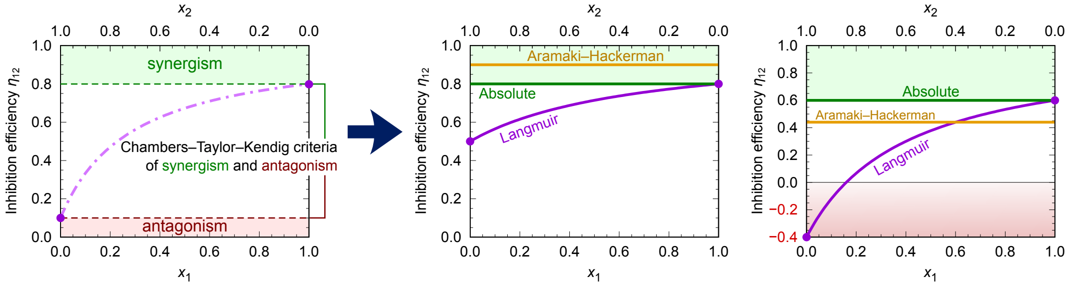
Absolute synergistic model

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

Practical consideration

For synergism, **the mixture should perform better than any pure inhibitor compound in the blend**, irrespective of the concentration.

Such a criterion was used by Chambers–Taylor–Kendig (Corrosion 61 (2005) 480), but they used it qualitatively.



Absolute synergistic model

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

Practical consideration

For synergism, **the mixture should perform better than any pure inhibitor compound in the blend**, irrespective of the concentration.

$$\eta_{\mathrm{abs}}^{\mathrm{threshold}} = \max(\eta_1^{\mathrm{opt}}, \eta_2^{\mathrm{opt}} \ldots\ \eta_n^{\mathrm{opt}})$$

$$\alpha_{\mathrm{abs}}^{\mathrm{threshold}} = \min(\alpha_1^{\mathrm{opt}}, \alpha_2^{\mathrm{opt}} \ldots\ \alpha_n^{\mathrm{opt}})$$

$$\boxed{S_{\mathrm{abs}} = \frac{1 - \eta_{\mathrm{abs}}^{\mathrm{threshold}}}{1 - \eta_{12\cdots n}^{\mathrm{measured}}} = \frac{\alpha_{\mathrm{abs}}^{\mathrm{threshold}}}{\alpha_{12\cdots n}^{\mathrm{measured}}}}$$

$\eta_i^{\mathrm{opt}} \equiv$ maximum inhibition efficiency of inhibitor i

$\alpha_i^{\mathrm{opt}} \equiv$ minimum inhibition activity of inhibitor i

Synergistic parameter — generalization

CASE–1: activity is bad
(goal = minimize activity)

$$S = \frac{\alpha^{\text{threshold}}}{\alpha^{\text{measured}}}$$

for synergism ($S > 1$):

$$\alpha^{\text{measured}} < \alpha^{\text{threshold}}$$

where for absolute model:

$$\alpha^{\text{threshold}} = \min(\alpha_1^{\text{opt}}, \alpha_2^{\text{opt}} \ldots \alpha_n^{\text{opt}})$$

CASE–2: activity is good
(goal = maximize activity)

$$S = \frac{\alpha^{\text{measured}}}{\alpha^{\text{threshold}}}$$

for synergism:

$$\alpha^{\text{measured}} > \alpha^{\text{threshold}}$$

where for absolute model:

$$\alpha^{\text{threshold}} = \max(\alpha_1^{\text{opt}}, \alpha_2^{\text{opt}} \ldots \alpha_n^{\text{opt}})$$

Synergistic parameter — generalization

CASE–1: activity is bad
(goal = minimize activity)

$$S = \frac{\alpha^{\text{threshold}}}{\alpha^{\text{measured}}}$$

for synergism ($S > 1$):

$$\alpha^{\text{measured}} < \alpha^{\text{threshold}}$$

where for absolute model:

$$\alpha^{\text{threshold}} = \min(\alpha_1^{\text{opt}}, \alpha_2^{\text{opt}} \ldots \alpha_n^{\text{opt}})$$

CASE–2: activity is good
(goal = maximize activity)

$$S = \frac{\alpha^{\text{measured}}}{\alpha^{\text{threshold}}}$$

for synergism:

$$\alpha^{\text{measured}} > \alpha^{\text{threshold}}$$

where for absolute model:

$$\alpha^{\text{threshold}} = \max(\alpha_1^{\text{opt}}, \alpha_2^{\text{opt}} \ldots \alpha_n^{\text{opt}})$$

Synergistic parameter — generalization

CASE–1: activity is bad
(goal = minimize activity)

$$S = \frac{\alpha^{\text{threshold}}}{\alpha^{\text{measured}}}$$

for synergism ($S > 1$):

$$\alpha^{\text{measured}} < \alpha^{\text{threshold}}$$

where for absolute model:

$$\alpha^{\text{threshold}} = \min(\alpha_1^{\text{opt}}, \alpha_2^{\text{opt}} \ldots\ \alpha_n^{\text{opt}})$$

CASE–2: activity is good
(goal = maximize activity)

$$S = \frac{\alpha^{\text{measured}}}{\alpha^{\text{threshold}}}$$

for synergism:

$$\alpha^{\text{measured}} > \alpha^{\text{threshold}}$$

where for absolute model:

$$\alpha^{\text{threshold}} = \max(\alpha_1^{\text{opt}}, \alpha_2^{\text{opt}} \ldots\ \alpha_n^{\text{opt}})$$

If some other measure (m) is used, express $\alpha = \mathrm{f}(m)$ and plug it into the S equation.

Synergistic parameter — generalization

CASE–1: activity is bad
(goal = minimize activity)

$$S = \frac{\alpha^{\text{threshold}}}{\alpha^{\text{measured}}}$$

for synergism ($S > 1$):

$$\alpha^{\text{measured}} < \alpha^{\text{threshold}}$$

where for absolute model:

$$\alpha^{\text{threshold}} = \min(\alpha_1^{\text{opt}}, \alpha_2^{\text{opt}} \ldots \alpha_n^{\text{opt}})$$

CASE–2: activity is good
(goal = maximize activity)

$$S = \frac{\alpha^{\text{measured}}}{\alpha^{\text{threshold}}}$$

for synergism:

$$\alpha^{\text{measured}} > \alpha^{\text{threshold}}$$

where for absolute model:

$$\alpha^{\text{threshold}} = \max(\alpha_1^{\text{opt}}, \alpha_2^{\text{opt}} \ldots \alpha_n^{\text{opt}})$$

If some other measure (m) is used, express $\alpha = \mathrm{f}(m)$ and plug it into the S equation.

$\alpha = 1 - \eta$

Conclusions

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

1. In corrosion inhibition literature, the synergistic parameter was limited to two inhibitors because the origin of the Aramaki–Hackerman threshold was not understood.

2. Synergistic parameter can be straightforwardly defined for a multi-component mixture.

3. In the corresponding equation, the mixture's performance is evaluated against a threshold performance:
   - the choice for the threshold value is not unique,
   - several reasonable choices can be used.

Conclusions

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

1. In corrosion inhibition literature, the synergistic parameter was limited to two inhibitors because the origin of the Aramaki–Hackerman threshold was not understood.

2. Synergistic parameter can be straightforwardly defined for a multi-component mixture.

3. In the corresponding equation, the mixture's performance is evaluated against a threshold performance:

   — the choice for the threshold value is not unique,

   — several reasonable choices can be used.

Conclusions

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

1. In corrosion inhibition literature, the synergistic parameter was limited to two inhibitors because the origin of the Aramaki–Hackerman threshold was not understood.

2. Synergistic parameter can be straightforwardly defined for a multi-component mixture.

3. In the corresponding equation, the mixture's performance is evaluated against a threshold performance:
   - the choice for the threshold value is not unique,
   - several reasonable choices can be used.

Conclusions

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

1. In corrosion inhibition literature, the synergistic parameter was limited to two inhibitors because the origin of the Aramaki–Hackerman threshold was not understood.

2. Synergistic parameter can be straightforwardly defined for a multi-component mixture.

3. In the corresponding equation, the mixture's performance is evaluated against a threshold performance:
   - the choice for the threshold value is not unique,
   - several reasonable choices can be used.

Conclusions

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

1. In corrosion inhibition literature, the synergistic parameter was limited to two inhibitors because the origin of the Aramaki–Hackerman threshold was not understood.

2. Synergistic parameter can be straightforwardly defined for a multi-component mixture.

3. In the corresponding equation, the mixture's performance is evaluated against a threshold performance:

   - the choice for the threshold value is not unique,
   - several reasonable choices can be used.

Want to know more?

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

Corrosion Science 212 (2023) 110922

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

ELSEVIER

Check for updates

Considering the concept of synergism in corrosion inhibition

Anton Kokalj

Department of Physical and Organic Chemistry, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

ARTICLE INFO

Keywords:
Corrosion inhibition
Synergism
Langmuir adsorption model

ABSTRACT

Synergism in corrosion inhibition and how to best quantify it is explored conceptually. In the equation for the synergistic parameter, the mixture's inhibition efficiency is evaluated against a threshold inhibition efficiency based on the performance of pure compounds. However, the choice for the threshold value is not unique. In the literature, the threshold of Aramaki–Hackerman is usually used. Herein, several other reasonable choices are developed, which are based on (i) the Langmuir adsorption model, (ii) the requirement that a mixture's

Acknowledgments

(A. Kokalj, Corros. Sci. 212 (2023) 110922)

Grant No. P2-0393

Slovenian Research and Innovation Agency

Department of Physical and Organic Chemistry

Thank you for your attention

Drawbacks of the Aramaki–Hackerman model