# Considering the concept of synergism in corrosion inhibition

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## ARTICLE INFO

## 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.

## 1. Introduction

Synergism is of considerable interest in corrosion protection [1] because the phenomenon boosts corrosion inhibition when a proper combination of inhibitors is used, i.e., the resulting mixture displays superior corrosion inhibition performance compared to individual compounds in the mix. Many examples of synergistic blends are known, ranging from organic [2–11] to inorganic compounds [8,12–16] as well as combinations of organic compounds with halides [17–20], other anions [14,21,22], rare earth salts [12,23,24], and metal cations [8].

The purpose of this publication is neither to discuss which chemicals provide synergistic inhibition nor to consider inhibition mechanisms but to explore synergism conceptually and how to best quantify it with a synergistic parameter. In the corrosion inhibition literature, synergism is usually quantified with the synergistic parameter ($S$) derived by Aramaki and Hackerman [17]. In the corresponding equation, the mixture's inhibition efficiency ($\eta^{\text{measured}}$) is evaluated against a threshold inhibition efficiency ($\eta^{\text{threshold}}$) based on the performance of pure compounds, i.e., $S = (1 - \eta^{\text{threshold}})/(1 - \eta^{\text{measured}})$. If the mixture's inhibition efficiency is higher than the threshold value, the synergistic parameter is greater than one. So defined synergistic parameter is quite reasonable and well-founded. In contrast, the choice for the threshold value is not unique, and we will show that under some circumstances, the choice of Aramaki–Hackerman has some problems. In particular, it may predict a synergistic parameter greater than one for a mixture displaying inhibition efficiency inferior to a pure compound.

A different approach to qualifying synergism was pursued by Chambers et al. [12,13], who defined synergism as occurring when a mixture performs better than the best inhibitor (present in the mix) alone, and

antagonism as occurring when a mixture performs worse than the worst inhibitor alone.

Because the choice for the threshold inhibition efficiency is not unique, we will develop several other reasonable thresholds and argue that some are superior to that of Aramaki–Hackerman. The equations for presented synergistic parameters are also extended to multi-component mixtures. Furthermore, some pitfalls made occasionally in the literature when calculating the synergistic parameter will also be underlined, one of them being that percentage inhibition efficiencies are plugged into the equation suitable for inhibition efficiencies normalized to unity.

This paper is structured as follows: the next section details different choices of concentrations for mixtures and pure inhibitors when evaluating synergism. In Section 3 various synergistic models are developed and Section 4 discusses the performance and implications of these models. Finally, Section 5 contains the conclusions.

## 2. Choice of inhibitor concentrations

When considering mixtures of inhibitor compounds, a choice of inhibitor concentrations should deserve some attention. Herein, we will consider the following choices of inhibitor concentrations (binary mixtures are considered for simplicity), which are also used in the literature:

1. *Fixed total concentration:* Experiments are performed at a fixed total concentration ($c_0$) of inhibitors. In this case, the sum of concentrations of inhibitors 1 and 2 is constant for mixtures

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and pure compounds, $c_1 + c_2 = c_0$. Hence, for the pure compounds one concentration is set to $c_0$ and the other to zero. This concentration choice was used in, e.g., Refs. [5,7,12,13].

2. *Partial concentrations:* The concentrations of inhibitors 1 and 2 in a mixture are $c_1$ and $c_2$, and the pure compounds are analyzed at the partial concentration of $c_1$ for the inhibitor-1 and $c_2$ for the inhibitor-2. With this choice, the total concentration of inhibitors, $c_1 + c_2$, is usually not held constant but changes from mixture to mixture. Typically one chooses two discrete sets of concentrations, $c_1 \in \{c_1^{(1)}, c_1^{(2)} \dots c_1^{(n)}\}$ and $c_2 \in \{c_2^{(1)}, c_2^{(2)} \dots c_2^{(m)}\}$, and forms mixtures as their combinations, i.e., $\{c_1^{(i)}, c_2^{(j)}\}_{i,j=1}^{n,m}$. Partial concentrations are used quite often, e.g., see Refs. [9,10, 17,21,25,26].

3. *Optimum concentrations:* For each pure inhibitor compound, a concentration at which it displays the highest measured inhibition efficiency is used when evaluation the synergism of considered mixtures. Optimum concentrations were used in, e.g., Refs. [11,22].

## 3. Derivation of synergistic models

In this section, various synergistic models are presented. It contains about 50 equations that some readers may find inconvenient. For those readers who are not comfortable with equations, the summary of synergistic models is provided in Listing 1, and the quantities that appear therein are defined in Sections 3.1 and 3.2.

### 3.1. Preliminary definitions

In terms of corrosion rates ($r$) and corrosion resistances ($R$), the corrosion inhibition efficiency is defined as:

$$\eta = \frac{r_0 - r}{r_0} = \frac{R - R_0}{R} \quad \text{and} \quad R \propto \frac{1}{r}, \tag{1}$$

where $r_0$ and $r$ are the corrosion rates of a blank and inhibited sample, respectively, and likewise for $R_0$ and $R$. The so defined inhibition efficiency is unitless ($\eta \in [0, 1]$ for corrosion inhibitors, whereas for corrosion activators $\eta < 0$). The unitless $\eta$ is used explicitly herein, although inhibition efficiency is often expressed in percentages in the literature (the relation between the two is $\eta_\% = 100\eta$).

It turns out very convenient to define *corrosion activity* ($\alpha$) as a complement to inhibition efficiency:

$$\alpha = 1 - \eta. \tag{2}$$

Corrosion activity is normalized to a blank sample ($\eta = 0$), for which $\alpha = 1$. Furthermore, a perfect inhibitor ($\eta = 1$) should display a null corrosion activity, which is the value of $\alpha$ for $\eta = 1$, whereas corrosion activators ($\eta < 0$) display $\alpha > 1$. These arguments reveal that $\alpha$ is indeed a reasonable measure of corrosion activity. Hence, the name *corrosion activity* is appropriate.

By combining Eqs. (1) and (2), it is straightforward to show that:

$$\frac{r}{r_0} = \frac{R_0}{R} = 1 - \eta = \alpha. \tag{3}$$

### 3.2. Definition of synergistic parameter

A *synergistic parameter* ($S$) can be generally defined in terms of corrosion activities as:

$$S = \frac{\alpha^{\text{threshold}}}{\alpha^{\text{measured}}}, \tag{4}$$

where $\alpha^{\text{measured}}$ is the measured corrosion activity of the inhibitor mixture and $\alpha^{\text{threshold}}$ is the threshold corrosion activity. By this definition, $S > 1$ implies synergism, and $S < 1$ corresponds to antagonism. If the measured mixture's corrosion activity is smaller than the threshold

value, then the synergistic parameter $S > 1$. In terms of inhibition efficiencies, Eq. (4) reads:

$$S = \frac{1 - \eta^{\text{threshold}}}{1 - \eta^{\text{measured}}}, \tag{5}$$

where $\eta^{\text{threshold}}$ is the threshold inhibition efficiency and $\eta^{\text{measured}}$ is the measured mixture's inhibition efficiency.

A different approach was used by Wieczorek and Szklarska-Smialowska [2], who defined the *synergistic effect* ($s$) as a difference between the measured and threshold inhibition efficiencies:

$$s = \eta^{\text{measured}} - \eta^{\text{threshold}}. \tag{6}$$

By this definition, $s > 0$ corresponds to synergism, and $s < 0$ to antagonism. However, herein, we will only consider the synergistic parameter $S$.

Beware that unitless inhibition efficiencies normalized to unity ($\eta \in [0, 1]$ for inhibitors) must be plugged into Eq. (5). However, in some studies (e.g., Refs. [10,26]), the values in percentages were used instead, as found by recalculating the tabulated data. Also Ref. [20] wrongly suggested that percentage inhibition efficiencies should be used in Eq (5).[1] Instead, if inhibition efficiencies are expressed with percentages ($\eta_\%$), the corresponding equations is:

$$S = \frac{100 - \eta_\%^{\text{threshold}}}{100 - \eta_\%^{\text{measured}}}. \tag{7}$$

For a binary inhibitor mixture, Eqs. (4) and (5) can be written as:

$$S = \frac{\alpha^{\text{threshold}}}{\alpha_{12}} = \frac{1 - \eta^{\text{threshold}}}{1 - \eta_{12}}, \tag{8}$$

where $\alpha_{12}$ is the measured corrosion activity of the binary mixture and $\eta_{12}$ is the corresponding inhibition efficiency.

The reason that the synergistic parameter is defined as $(1 - \eta^{\text{threshold}})/(1 - \eta_{12})$ and not as $\eta_{12}/\eta^{\text{threshold}}$ can easily be understood by a simple example. Let us take that $\eta_1 = \eta_2 = 0.9$ and $\eta_{12} = 0.99$, where $\eta_1$ and $\eta_2$ are the inhibition efficiencies of the pure inhibitors 1 and 2, respectively. This is a clear case of synergism because the binary mixture displays a 10-fold reduction of corrosion rate with respect to either of the pure inhibitors. Hence, in this case, one would expect a high value for the synergistic parameter. If we assume that the value of $\eta^{\text{threshold}}$ is 0.9, then Eq. (8) gives the value of 10, whereas $\eta_{12}/\eta^{\text{threshold}}$ is only 1.1.

For the threshold value, the choice of Aramaki and Hackerman [17] is usually used in the literature. However, we will show that several other reasonable thresholds can be chosen. These synergistic models are presented below. For simplicity, they are first derived for a binary mixture and then extended to a multi-component combination of $n$ inhibitors, $n \geq 2$.

### 3.3. The Aramaki–Hackerman model

Aramaki and Hackerman [17] defined the threshold value of $\eta^{\text{threshold}}$ as[2]:

$$\eta_{\text{Aramaki}}^{\text{threshold}} = \eta_1 + \eta_2 - \eta_1\eta_2. \tag{9}$$

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[1] Ref. [20] states that Eq. (5) is *"generally appropriate for relative numbers such as percentage inhibition efficiency"*. In contrast, inhibition efficiencies normalized to unity should be used in Eq. (5).

[2] As stressed above, inhibition efficiencies normalized to unity must be used. If instead inhibition efficiencies in percentages are used, the threshold $\eta_\%$ is:

$$\eta_{\text{Aramaki}}^{\text{threshold}}\% = \eta_{1\%} + \eta_{2\%} - \frac{\eta_{1\%}\eta_{2\%}}{100},$$

and, furthermore, Eq. (7) should be used instead of Eq. (5).

Let us explain how this definition emerges. For the threshold value of $\alpha$, Aramaki and Hackerman used:

$$\alpha_{\text{Aramaki}}^{\text{threshold}} = \alpha_1 \alpha_2. \tag{10}$$

It should be noted that Aramaki and Hackerman did not use the term corrosion activity but utilized the $r/r_0$ ratio, which is equivalent to the currently defined corrosion activity, Eq. (3).

A probable reason why Aramaki and Hackerman used such a definition is that for inhibitors $\alpha \in [0, 1]$. Hence, also the $\alpha_1 \alpha_2$ product is confined to the $[0, 1]$ range and this is a neat property.[3] They explicitly stated that $\eta_{\text{Aramaki}}^{\text{threshold}}$ of Eq. (9) is limited to less than 1. In contrast, the $\eta_1 + \eta_2$ sum, used in an older study of Hackerman [27], can be greater than 1, as explicitly stated in the Aramaki–Hackerman publication [17]. Still, some publications (e.g., Refs. [10,19,25,26,28–30]) used the $\eta_1 + \eta_2$ sum for the threshold value of $\eta^{\text{threshold}}$ despite citing the Aramaki–Hackerman's paper [17].

It may not be immediately evident that $\eta_{\text{Aramaki}}^{\text{threshold}}$ cannot exceed 1. Hence, let us show that this is so. By using the Aramaki–Hackerman's threshold value of $\alpha$, Eq. (10), together with Eqs. (2) and (8), we get:

$$\begin{aligned} S^{\text{Aramaki}} &= \frac{\alpha_1 \alpha_2}{\alpha_{12}} \\ &= \frac{(1 - \eta_1)(1 - \eta_2)}{1 - \eta_{12}} \\ &= \frac{1 - \eta_1 - \eta_2 + \eta_1 \eta_2}{1 - \eta_{12}} = \frac{1 - \eta_{\text{Aramaki}}^{\text{threshold}}}{1 - \eta_{12}}. \end{aligned} \tag{11}$$

The last line of this equation explains why $\eta_{\text{Aramaki}}^{\text{threshold}}$ is defined by Eq. (9) as $\eta_{\text{Aramaki}}^{\text{threshold}} = \eta_1 + \eta_2 - \eta_1 \eta_2$. It follows from the first and the last line of the above Eq. (11) that:

$$\eta_{\text{Aramaki}}^{\text{threshold}} = 1 - \alpha_1 \alpha_2. \tag{12}$$

However, for inhibitors:

$$\alpha_1 \alpha_2 \in [0, 1], \qquad \text{hence} \quad \eta_{\text{Aramaki}}^{\text{threshold}} \in [0, 1], \tag{13}$$

which proves the assertion of Aramaki and Hackerman that $\eta_{\text{Aramaki}}^{\text{threshold}}$ is confined to less than one; note that in Eq. (13) we allow for the value of 1 of the perfect inhibitor, although in practice it is not achievable.

Another instructive explanation of the Aramaki–Hackerman threshold was given by Wieczorek and Szklarska-Smialowska [2]. Their reasoning goes as follows: inhibitor-1 covers a $\Theta_1$ fraction of the surface, whereas inhibitor-2 covers the remaining $(1 - \Theta_1)$ fraction of the surface with the efficiency of $\Theta_2$. Therefore, the resulting total coverage ($\Theta$) is:

$$\Theta = \Theta_1 + (1 - \Theta_1)\Theta_2 = \Theta_1 + \Theta_2 - \Theta_1 \Theta_2. \tag{14}$$

By virtue of the *perfect adsorption hypothesis*, (cf. Section 3.4), the fractional surface coverage and inhibition efficiency are synonymous. Hence, by replacing $\Theta_i$ with $\eta_i$ and $\Theta$ with the Aramaki–Hackerman threshold value of $\eta$, one obtains Eq. (9).

It is also worth expressing the Aramaki–Hackerman synergistic parameter with corrosion rates and corrosion resistances because the resulting expressions are quite simple, i.e.:

$$S^{\text{Aramaki}} = \frac{\alpha_1 \alpha_2}{\alpha_{12}} = \frac{r_1 r_2}{r_{12} r_0} = \frac{R_{12} R_0}{R_1 R_2}. \tag{15}$$

The Aramaki–Hackerman model can easily be extended to mixtures of $n$ inhibitors. In this case, the threshold value of $\alpha$ is a product of inhibition activities of pure compounds:

$$\alpha_{\text{Aramaki}}^{\text{threshold}} = \prod_{i=1}^{n} \alpha_i \qquad \text{and} \qquad S^{\text{Aramaki}} = \frac{\alpha_{\text{Aramaki}}^{\text{threshold}}}{\alpha_{12 \cdots n}}, \tag{16}$$

where $\alpha_{12 \cdots n}$ is the measured corrosion activity of a mixture of $n$ inhibitor compounds. The expression for the threshold value of $\eta$ is more cumbersome:

$$\eta_{\text{Aramaki}}^{\text{threshold}} = 1 - \prod_{i=1}^{n} (1 - \eta_i), \tag{17}$$

which for three inhibitors reads:

$$\eta_{\text{Aramaki}}^{\text{threshold}} = \eta_1 + \eta_2 + \eta_3 - \eta_1 \eta_2 - \eta_1 \eta_3 - \eta_2 \eta_3 + \eta_1 \eta_2 \eta_3. \tag{18}$$

### 3.4. Perfect adsorption hypothesis

Under the assumption that corrosion inhibition is due to adsorbed inhibitor molecules, such that corrosion ceases at sites where inhibitor molecules are adsorbed, the corrosion rate is proportional to the "unprotected" surface area, where by "unprotected" we mean surface sites where inhibitor molecules are not adsorbed. In this case, the inhibition efficiency is equivalent to a fractional surface coverage ($\Theta$). For uninhibited sample, the corrosion rate is proportional to the surface area ($A$), $r_0 \propto A$, and for inhibited sample to the unprotected surface area, $r \propto A(1 - \Theta)$. Hence:

$$\eta = \frac{r_0 - r}{r_0} \approx \frac{A - A(1 - \Theta)}{A} = \Theta. \tag{19}$$

Let us call the $\eta = \Theta$ assumption the *perfect adsorption hypothesis* ("perfect" because it presupposes that adsorption perfectly blocks the corrosion at occupied sites). Although this hypothesis has recently been criticized by Lindsay et al. [31], we will utilize it to define the Langmuir threshold value in the synergistic parameter equation.

### 3.5. Synergistic parameters based on the Langmuir model

One of the basic assumptions of the Langmuir model [32] is the absence of lateral interactions between adsorbed molecules, and this criterion can be used to define the threshold value for inhibition efficiency. Let us assume that inhibitors 1 and 2 follow the Langmuir adsorption model when used alone. The surface coverage for the binary inhibitor mixture should be higher (lower) than the Langmuir surface coverage if the lateral interactions between inhibitors 1 and 2 are attractive (repulsive). In this context, attractive lateral interactions imply synergism and repulsive lateral interactions antagonism.

For a single compound, the Langmuir adsorption isotherm is given by:

$$\Theta_i = \frac{k_i c_i}{1 + k_i c_i} \tag{20}$$

or equivalently:

$$k_i c_i = \frac{\Theta_i}{1 - \Theta_i}, \tag{21}$$

whereas for a binary mixture, the total surface coverage given by the Langmuir model is:

$$\Theta_{\text{Langmuir}} = \frac{k_1 c_1 + k_2 c_2}{1 + k_1 c_1 + k_2 c_2}, \tag{22}$$

where $k_i$ and $c_i$ stand for the adsorption equilibrium constant and the concentration of the inhibitor $i$, respectively. By virtue of the perfect adsorption hypothesis ($\eta = \Theta$), Eq. (22) can be used to define the Langmuir threshold value of the inhibition efficiency, i.e., $\eta_{\text{Langmuir}}^{\text{threshold}} = \Theta_{\text{Langmuir}}$.

### 3.5.1. Langmuir model at a fixed total concentration of inhibitors

In the case of a fixed total concentration of inhibitors, it is convenient to use fractional concentrations:

$$x_1 = c_1 / c_0 \qquad \text{and} \qquad x_2 = c_2 / c_0. \tag{23}$$

Because $c_1 + c_2 = c_0$, it follows that:

$$x_1 + x_2 = 1. \tag{24}$$

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[3] It should be noted that for corrosion activators, $\alpha > 1$. Hence, $\alpha_1 \alpha_2$ can become larger than 1.

It is also convenient to define:

$$k'_i = k_i c_0, \qquad \text{hence} \quad k'_i x_i = k_i c_i. \tag{25}$$

For a pure compound $i$ at the $c_0$ concentration, $x_i = 1$, and correspondingly:

$$k'_i x_i = k'_i \qquad \text{for } x_i = 1. \tag{26}$$

By using the $\Theta = \eta$ assumption together with Eqs. (21) and (26), $k'_i$ can be expressed as:

$$k'_i = \frac{\Theta^0_i}{1 - \Theta^0_i} = \frac{\eta^0_i}{1 - \eta^0_i}, \tag{27}$$

where $\Theta_i$ and $\eta_i$ are annotated by superscript 0 to indicate that they correspond to the $c_i = c_0$ concentration. Plugging this relation into the expression for the Langmuir total surface coverage, Eq. (22), we get:

$$
\begin{aligned}
\Theta_{\text{Langmuir}}(x_1) &= \frac{k'_1 x_1 + k'_2 x_2}{1 + k'_1 x_1 + k'_2 x_2} \\
&= \frac{\dfrac{\eta^0_1}{1 - \eta^0_1} x_1 + \dfrac{\eta^0_2}{1 - \eta^0_2} x_2}{1 + \dfrac{\eta^0_1}{1 - \eta^0_1} x_1 + \dfrac{\eta^0_2}{1 - \eta^0_2} x_2}.
\end{aligned}
\tag{28}
$$

After some algebraic manipulation and using the $\eta^{\text{threshold}}_{\text{Langmuir}} = \Theta_{\text{Langmuir}}$ equality, we obtain the following equation for the Langmuir threshold inhibition efficiency[4]:

$$\eta^{\text{threshold}}_{\text{f-Lang}}(x_1) = \frac{\eta^0_1 x_1 + \eta^0_2 x_2 - \eta^0_1 \eta^0_2}{1 - \eta^0_1 x_2 - \eta^0_2 x_1}, \qquad \text{where } x_2 = 1 - x_1. \tag{29}$$

The subscript "f-Lang" stands for "fixed Langmuir" and indicates that $\eta^{\text{threshold}}_{\text{f-Lang}}$ was derived at a fixed total concentration. This equation corresponds to the following threshold corrosion activity:

$$\alpha^{\text{threshold}}_{\text{f-Lang}}(x_1) = \frac{\alpha^0_1 \alpha^0_2}{\alpha^0_1 x_2 + \alpha^0_2 x_1}. \tag{30}$$

Note that $\eta^{\text{threshold}}_{\text{f-Lang}}$ and $\alpha^{\text{threshold}}_{\text{f-Lang}}$ are functions of partial inhibitor concentrations, implying that each considered mixture has its own threshold value. The corresponding Langmuir synergistic parameter ($S^{\text{Langmuir}}_{\text{fix}}$) can thus be written as:

$$S^{\text{Langmuir}}_{\text{fix}}(x_1) = \frac{\alpha^{\text{threshold}}_{\text{f-Lang}}(x_1)}{\alpha_{12}(x_1)} = \frac{1 - \eta^{\text{threshold}}_{\text{f-Lang}}(x_1)}{1 - \eta_{12}(x_1)}, \tag{31}$$

where the subscript "fix" indicates that the parameter is applicable to the case of a fixed total concentration. Note that the measured inhibition efficiency $\eta_{12}$ of a mixture is also a function of $x_1$ because each mixture displays its own value of inhibition efficiency.

For a mixture of $n$-inhibitors, the threshold value of $\alpha^{\text{threshold}}$ is:

$$\alpha^{\text{threshold}}_{\text{f-Lang}} = \frac{\displaystyle\prod_{i=1}^{n} \alpha^0_i}{\displaystyle\sum_{i=1}^{n} \left( x_i \prod_{j \neq i}^{n} \alpha^0_j \right)}, \tag{32}$$

where $j \neq i$ indicates that the $\alpha^0_i$ term is excluded from the product. For a mixture of three inhibitors, this equation reads:

$$\alpha^{\text{threshold}}_{\text{f-Lang}} = \frac{\alpha^0_1 \alpha^0_2 \alpha^0_3}{x_1 \alpha^0_2 \alpha^0_3 + x_2 \alpha^0_1 \alpha^0_3 + x_3 \alpha^0_1 \alpha^0_2}. \tag{33}$$

### 3.5.2. Langmuir model at partial concentrations of inhibitors

Langmuir model is also applicable to analyze the synergism of a binary mixture when pure inhibitor compounds are measured at partial concentrations of $c_1$ and $c_2$ used in the mixture. Aramaki et al. [21] used such a model but did not wholly derive the corresponding equations. To do so, it is more convenient to use corrosion activities. Furthermore, we will use the following two relations based on Eqs. (21) and (22):

$$\alpha^{\text{threshold}}_{\text{p-Lang}} = 1 - \Theta_{\text{Langmuir}} = \frac{1}{1 + k_1 c_1 + k_2 c_2} \tag{34}$$

and

$$k_i c_i = \frac{1 - \alpha_i}{\alpha_i}. \tag{35}$$

Here, the subscript "p-Lang" stands for "partial Langmuir" and indicates that we are considering partial concentrations of inhibitors. By plugging Eq. (35) into Eq. (34), we obtain:

$$\alpha^{\text{threshold}}_{\text{p-Lang}} = \frac{1}{1 + \dfrac{1 - \alpha_1}{\alpha_1} + \dfrac{1 - \alpha_2}{\alpha_2}} = \frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2 - \alpha_1 \alpha_2}. \tag{36}$$

From this equation, we can also derive the corresponding equation for $\eta^{\text{threshold}}$, which is:

$$\eta^{\text{threshold}}_{\text{p-Lang}} = \frac{\eta_1 + \eta_2 - 2\eta_1 \eta_2}{1 - \eta_1 \eta_2}. \tag{37}$$

By comparing Eq. (36) with Eq. (10), we see that:

$$\alpha^{\text{threshold}}_{\text{p-Lang}} = \frac{1}{\alpha_1 + \alpha_2 - \alpha_1 \alpha_2} \, \alpha^{\text{threshold}}_{\text{Aramaki}} \tag{38}$$

and correspondingly (cf. Eq. (8)):

$$S^{\text{Langmuir}}_{\text{partial}} = \frac{1}{\alpha_1 + \alpha_2 - \alpha_1 \alpha_2} S^{\text{Aramaki}} \tag{39}$$

or equivalently:

$$S^{\text{Langmuir}}_{\text{partial}} = \frac{1}{1 - \eta_1 \eta_2} S^{\text{Aramaki}}, \tag{40}$$

where the subscript "partial" indicates that the Langmuir synergistic parameter corresponds to the case of partial concentrations.

The partial Langmuir model can be extended to mixtures of $n$ inhibitors, but the corresponding equation for the threshold value of $\alpha$ is cumbersome:

$$\alpha^{\text{threshold}}_{\text{p-Lang}} = \frac{\displaystyle\prod_{i=1}^{n} \alpha_i}{\displaystyle\sum_{i=1}^{n} \left( \prod_{j \neq i}^{n} \alpha_j \right) - (n-1) \prod_{i=1}^{n} \alpha_i}. \tag{41}$$

For three inhibitors, this equation reads:

$$\alpha^{\text{threshold}}_{\text{p-Lang}} = \frac{\alpha_1 \alpha_2 \alpha_3}{\alpha_2 \alpha_3 + \alpha_1 \alpha_3 + \alpha_1 \alpha_2 - 2\alpha_1 \alpha_2 \alpha_3}. \tag{42}$$

### 3.6. Absolute synergistic parameter

Another reasonable choice—actually, the most reasonable one according to the author's opinion—for the threshold value of $\eta$ is to require for synergism that the inhibition efficiency of a mixture must be higher than the maximum measured inhibition efficiency of any pure inhibitor compound (present in the blend). Such a definition for synergism has been used by Chambers, Taylor, and Kendig (CTK) [12], but they used it qualitatively and did not formalize it with a synergistic parameter (a formalization of the CTK conditions with synergistic and

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[4] It is easy to see that Eq. (29) gives correct values at the two endpoints, $x_1 = 0$ and $x_1 = 1$, i.e.:

for $x_1 = 0$ : $\quad \eta^{\text{threshold}}_{\text{f-Lang}} = \dfrac{\eta^0_2 - \eta^0_1 \eta^0_2}{1 - \eta^0_1} = \dfrac{\eta^0_2(1 - \eta^0_1)}{1 - \eta^0_1} = \eta^0_2,$

for $x_1 = 1$ : $\quad \eta^{\text{threshold}}_{\text{f-Lang}} = \dfrac{\eta^0_1 - \eta^0_1 \eta^0_2}{1 - \eta^0_2} = \eta^0_1.$

Namely, for a pure compound, the threshold value should equal the value of the pure compound so that $S = 1$.

antagonistic parameters is presented in Appendix). For this condition the threshold inhibition efficiency can be defined as:

$$\eta_{abs}^{threshold} = \max(\eta_1^{opt}, \eta_2^{opt}), \tag{43}$$

where $\eta_1^{opt}$ and $\eta_2^{opt}$ are the optimum inhibition efficiencies of the pure inhibitor compounds 1 and 2, respectively. The corresponding synergistic parameter is thus:

$$S^{abs} = \frac{1 - \eta_{abs}^{threshold}}{1 - \eta_{12}} = \frac{1 - \max(\eta_1^{opt}, \eta_2^{opt})}{1 - \eta_{12}}. \tag{44}$$

Let us name $S^{abs}$ as the *absolute synergistic parameter* because, by its definition, a mixture displays synergism only if it has a higher inhibition efficiency than any of the pure constituent compounds alone at optimum concentration.

This definition is the most suitable for the so-called optimum concentrations, where one searches for optimum concentrations of pure compounds and uses the corresponding inhibition efficiency values when quantifying the synergism (this is why $\eta_1$ and $\eta_2$ are annotated with the "opt" superscripts in the above equations). $S^{abs}$ is also applicable for fixed total concentrations but less so for partial concentrations because, at partial concentrations, pure compounds may not perform well enough, implying too weak a condition for the synergism (see the Results and discussion section).

With corrosion activities, the absolute synergistic parameter is defined as:

$$S^{abs} = \frac{\min(\alpha_1^{opt}, \alpha_2^{opt})}{\alpha_{12}}, \qquad \text{where } \alpha_i^{opt} = 1 - \eta_i^{opt}. \tag{45}$$

It is straightforward to generalize the absolute synergistic parameter to a mixture of $n$ inhibitor compounds. In this case, the threshold values of $\eta$ and $\alpha$ are:

$$\eta_{abs}^{threshold} = \max(\eta_1^{opt}, \eta_2^{opt} \dots \eta_n^{opt}) \tag{46}$$

and

$$\alpha_{abs}^{threshold} = \min(\alpha_1^{opt}, \alpha_2^{opt} \dots \alpha_n^{opt}). \tag{47}$$

### 3.7. The "1+1>2" synergistic parameter

The synergism is often expressed with the phrase "*one plus one is greater than two*", meaning that the combined is greater than the sum of its parts. This phrase seems particularly applicable for situation, where measurements of pure compounds 1 and 2 are performed at partial concentrations of $c_1$ and $c_2$, respectively. However, with respect to corrosion inhibition the phrase cannot be expressed as $\eta_{12} > \eta_1 + \eta_2$ because $\eta_1 + \eta_2$ can be greater than one, which is physically meaningless. Hence, we need to find a suitable physical property that can be added without creating a physical nonsense. A corrosion resistance ($R$) is such a property. Hence, for synergism, we can require the following:

$$R_{12} > R_1 + R_2, \qquad \text{hence } R^{threshold} = R_1 + R_2, \tag{48}$$

where $R_{12}$ is the measured corrosion resistance in a binary inhibitor mixture. Although this relation is appealing, it has a problem because it fails to converge to the two endpoints, $x_1 \to 0$ and $x_1 \to 1$ (i.e., it fails to converge to a pure compound when the concentration of the other compound in the mixture approaches zero; see the next subsection).

By using the $R \propto r^{-1}$ relation, the synergistic parameter can be expressed with corrosion resistances as:

$$S = \frac{\alpha^{threshold}}{\alpha_{12}} = \frac{r^{threshold}/r_0}{r_{12}/r_0} = \frac{R_{12}}{R^{threshold}}. \tag{49}$$

By using the condition (48), the synergistic parameter becomes:

$$S^{1+1>2} = \frac{R_{12}}{R_1 + R_2}. \tag{50}$$

Let us nickname this synergistic parameter as "*one plus one is greater than two*", which is why it is designated by the "1+1>2" superscript. As

its threshold is defined by the $R$ sum of the pure constituents, it seems the most suited to the partial concentrations; it may also be applied to fixed and optimum concentrations, though in these cases, it may give too strong a condition.

The $S^{1+1>2}$ parameter expressed with corrosion rates, corrosion activities, and corrosion efficiencies is:

$$S^{1+1>2} = \frac{r_1 r_2}{(r_1 + r_2) r_{12}} = \frac{\alpha_1 \alpha_2}{(\alpha_1 + \alpha_2) \alpha_{12}}$$
$$= \frac{1}{\alpha_1 + \alpha_2} S^{Aramaki} = \frac{1}{2 - \eta_1 - \eta_2} S^{Aramaki}. \tag{51}$$

It is straightforward to extend the "1+1>2" model to mixtures of $n$ inhibitors by requiring:

$$R_{12 \cdots n} > \sum_{i=1}^n R_i, \qquad \text{hence} \quad S^{1+1>2} = \frac{R_{12 \cdots n}}{\sum_i R_i}, \tag{52}$$

where $R_{12 \cdots n}$ is the measured corrosion resistance in a mixture of $n$ inhibitors. While the expression for the threshold value of $R$ is very simple, $R^{threshold} = \sum_i R_i$, the expressions for $\eta^{threshold}$ and $\alpha^{threshold}$ are quite cumbersome. For a mixture of three inhibitors, the corresponding $\alpha^{threshold}$ reads:

$$\alpha_{1+1>2}^{threshold} = \frac{\alpha_1 \alpha_2 \alpha_3}{\alpha_1 \alpha_2 + \alpha_1 \alpha_3 + \alpha_2 \alpha_3}. \tag{53}$$

### 3.8. The "adjusted 1+1>2" model and its equivalence to the partial Langmuir model

As mentioned above, the "1+1>2" model has a problem because it fails to converge to the two endpoints, $x_1 \to 0$ and $x_1 \to 1$. To foresee the problem, let us consider the $x_1 \to 1$ endpoint, implying that the mixture approaches the pure compound-1 and the corresponding corrosion resistance approaches the value of $R_1$. In contrast, the sum of corrosion resistances of the samples immersed into solutions of the two corresponding pure compounds is $R_1 + R_0$ because the sample immersed into a solution of compound-2 (with $x_2 \to 0$) approaches the corrosion resistance of the blank sample ($R_0$). Hence, in this case we have:

$R_1 =$ corrosion resistance in a mixture,

$R_1 + R_0 =$ sum of resistances in pure compounds,

and correspondingly:

$$S = \frac{R_1}{R_1 + R_0} < 1, \tag{54}$$

which is incorrect because for a pure compound, the synergistic parameter must be $S = 1$.

This drawback can be corrected by replacing the gross corrosion resistance with the inhibitor's effect on the corrosion resistance, i.e., $R_i - R_0$. Hence, for synergism, we require:

$$R_{12} - R_0 > (R_1 - R_0) + (R_2 - R_0), \tag{55}$$

which leads to:

$$R^{threshold} = R_1 + R_2 - R_0. \tag{56}$$

This is a weaker requirement compared to Eq. (48) of the "1+1>2" model, hence the "1+1>2" model can be considered as a majorant (this is why the "1+1>2" model is useful despite its problem of failing to converge to the endpoints). Let us call the model of Eq. (56) the "*adjusted 1+1>2*" model. The corresponding synergistic parameter is:

$$S^{adj.1+1>2} = \frac{R_{12}}{R_1 + R_2 - R_0}. \tag{57}$$

**Listing 1:** Summary of various synergistic models, along with the equations for their threshold values for binary mixtures. Synergistic parameters are reported for multi-compound mixtures, defined with either $\alpha$, $\eta$, or $R$, depending on which equation is the simplest. For each model, the best-suited choice of concentration and its applicability to other concentration choices are also stated.

| Synergistic model | $\eta^{\text{threshold}}$ equation (for binary mixture) | $\alpha^{\text{threshold}}$ equation (for binary mixture) | $S$ equation (for $n$ inhibitors) | best suited for concentration | applicable to other concentrations |
|---|---|---|---|---|---|
| Aramaki–Hackerman | $\eta^{\text{threshold}} = \eta_1 + \eta_2 - \eta_1\eta_2$ | $\alpha^{\text{threshold}} = \alpha_1\alpha_2$ | $S = \dfrac{\alpha_1\alpha_2\cdots\alpha_n}{\alpha_{12\cdots n}}$ | n/a$^\dagger$ | yes (to all) |
| Langmuir (fixed) | $\eta^{\text{threshold}} = \dfrac{\eta_1^0 x_1 + \eta_2^0 x_2 - \eta_1^0\eta_2^0}{1 - \eta_1^0 x_2 - \eta_2^0 x_1}$ | $\alpha^{\text{threshold}} = \dfrac{\alpha_1^0\alpha_2^0}{\alpha_1^0 x_2 + \alpha_2^0 x_1}$ | $S = \dfrac{\alpha_1^0\alpha_2^0\cdots\alpha_n^0}{\alpha_{12\cdots n}\sum\limits_{i=1}^{n}\left(x_i\prod\limits_{j\neq i}\alpha_j^0\right)}$ | fixed | no |
| Langmuir (partial) & "adjusted 1+1>2" | $\eta^{\text{threshold}} = \dfrac{\eta_1 + \eta_2 - 2\eta_1\eta_2}{1 - \eta_1\eta_2}$ | $\alpha^{\text{threshold}} = \dfrac{\alpha_1\alpha_2}{\alpha_1 + \alpha_2 - \alpha_1\alpha_2}$ | $S = \dfrac{R_{12\cdots n}}{\sum\limits_{i=1}^{n} R_i - (n-1)R_0}$ | partial | yes (to all) |
| Absolute | $\eta^{\text{threshold}} = \max(\eta_1^{\text{opt}}, \eta_2^{\text{opt}})$ | $\alpha^{\text{threshold}} = \min(\alpha_1^{\text{opt}}, \alpha_2^{\text{opt}})$ | $S = \dfrac{\min(\alpha_1^{\text{opt}}, \alpha_2^{\text{opt}}\cdots\alpha_n^{\text{opt}})}{\alpha_{12\cdots n}}$ | optimum | yes (to fixed) |
| "1+1>2" | $\eta^{\text{threshold}} = \dfrac{1 - \eta_1\eta_2}{2 - \eta_1 - \eta_2}$ | $\alpha^{\text{threshold}} = \dfrac{\alpha_1\alpha_2}{\alpha_1 + \alpha_2}$ | $S = \dfrac{R_{12\cdots n}}{R_1 + R_2 + \cdots + R_n}$ | partial | yes (to all) |

$\dagger$ Not assigned (partial concentrations were used in the Aramaki–Hackernam original work [17]).

Surprisingly, the *"adjusted 1+1>2"* model is equivalent to the partial Langmuir model,[5] which is quite interesting because the underlying assumptions of the two models appear different (but apparently, they are equivalent, although this is not obvious). This model can be straightforwardly extended to a mixture of $n$ compounds. The corresponding expression is:

$$S^{\text{adj.1+1>2}} = \frac{R_{12\cdots n}}{\sum\limits_{i=1}^{n} R_i - (n-1)R_0}. \tag{58}$$

Note that this equation is much simpler that the equivalent Eq. (41), derived above for the partial Langmuir model.

## 4. Results and discussion

To facilitate comprehension of the various synergistic models defined and discussed above, Listing 1 summarizes them along with the equations for their threshold values and lists which choice of concentration is the most suitable for a given model and whether the model is applicable also for other concentration choices.

For the sake of simplicity, the results presented below focus only on binary mixtures.

### 4.1. A fixed total concentration, $c_0 = c_1 + c_2$

We will first analyze how the synergistic models behave in the case of a *fixed total concentration* of inhibitor compounds (i.e., $c_i = c_0$ for pure compounds and $\sum_i c_i = c_0$ for mixtures). This choice of

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[5] By using the $\alpha_i = R_0/R_i$ relation and dividing the numerator and denominator of Eq. (57) by $R_0$, we obtain:

$$S^{\text{adj.1+1>2}} = \frac{\dfrac{R_{12}}{R_0}}{\dfrac{R_1}{R_0} + \dfrac{R_2}{R_0} - \dfrac{R_0}{R_0}} = \frac{\alpha_{12}^{-1}}{\alpha_1^{-1} + \alpha_2^{-1} - 1} = \frac{\alpha_1\alpha_2}{\alpha_{12}(\alpha_1 + \alpha_2 - \alpha_1\alpha_2)}.$$

The equivalence becomes evident by plugging the expression for $\alpha_{\text{p–Lang}}^{\text{threshold}}$ of Eq. (36) into the above equation, i.e.:

$$S^{\text{adj.1+1>2}} = \frac{\alpha_1\alpha_2}{\alpha_{12}(\alpha_1 + \alpha_2 - \alpha_1\alpha_2)} = \frac{\alpha_{\text{p–Lang}}^{\text{threshold}}}{\alpha_{12}} = S_{\text{partial}}^{\text{Langmuir}}.$$

concentrations can be considered as a fair play because in all cases the total concentration of inhibitors is the same.

Let us consider a continuous transition from a pure inhibitor compound-1 to binary mixtures by decreasing (increasing) fractional concentration $x_1$ ($x_2$) until we arrive at a pure inhibitor compound-2. It seems reasonable to expect that inhibition efficiency will change smoothly from $\eta_1^0$ to $\eta_2^0$.[6] The Langmuir model is a simple physical model that predicts such smooth variation of inhibition efficiency from $x_1 = 1$ to $x_1 = 0$ under the assumption that inhibitor surface coverage is synonymous with inhibition efficiency, Eq. (19). It is a particularly relevant model for synergism because its basic premise is that there are no lateral interactions between adsorbates. Consequently, this premise implies synergism (antagonism) for attractive (repulsive) interactions between different inhibitors. Hence, the synergistic (antagonistic) mixture should display the inhibition efficiency above (below) that predicted by the Langmuir model, as shown schematically by Fig. 1a for an example with $\eta^0 = 0.8$ and $\eta_2^0 = 0.1$.

Fig. 1a reveals that according to the Langmuir model at a fixed total concentration (also called the "fixed" Langmuir model), Eq. (29), two compounds can act synergistically even if a mixture's measured $\eta_{12}$ is lower than the highest inhibition efficiency of the two pure compounds. In this respect, the fixed Langmuir model gives a relatively weak synergistic condition, which is not very useful in practice, despite being physically sound. Namely, in practice, one aims to increase the inhibition efficiency by mixing inhibitor compounds. A practically useful criterion for inhibition synergism, particularly for experiments performed at a fixed total concentration, is to require that a mixture is superior to all pure inhibitor compounds. This requirement formally reads (for simplicity, we focus on binary mixtures): $\eta_{12} > \max(\eta_1^0, \eta_2^0)$, which is compatible with the definition of the absolute synergistic parameter, Eqs. (43) and (44). In contrast to the fixed Langmuir model of Fig. 1a, where a curve divides synergistic and antagonistic regions (i.e., the threshold value depends on $x_1$), the threshold for the absolute synergistic parameter at a fixed total concentration is a single value (i.e., a horizontal line divides the synergistic and antagonistic regions).

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[6] Any discontinuity in inhibition efficiency occurring from $x_1 = 1$ to $x_1 = 0$ would indicate a phase transition. A possible such phase transition would be that at a critical concentration of the second compound, the corrosion inhibition mechanism of the first compound abruptly changes (for example, by a phase transition in the adsorption structure).
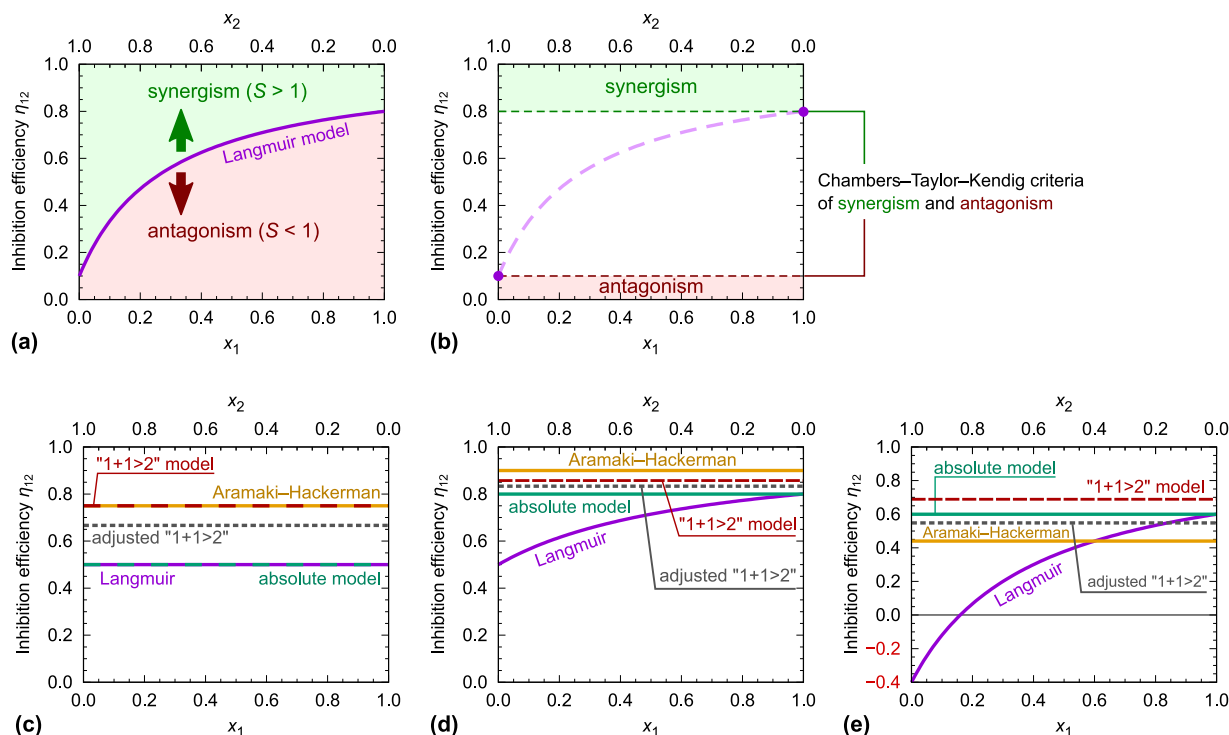
**Fig. 1.** Performance of various synergistic models at a fixed total concentration ($c_1 = c_2 = c_0$ for pure compounds and $c_1 + c_2 = c_0$ for binary mixtures). (a) Schematic explanation of how to read the plots: the curve represents the model's $\eta^{\text{threshold}}$ as a function of $x_1$ (lower $x$-axis) or $x_2$ (upper $x$-axis), implying that the model predicts a synergism at specific $x_1$ if the measured inhibition efficiency of the corresponding mixture ($\eta_{12}$) is above the curve's value at $x_1$, and antagonism if $\eta_{12}$ is below the curve. (b) Schematic illustration of the Chambers–Taylor–Kendig (CTK) synergistic and antagonistic criteria [12], according to which synergism occurs when a mixture performs better than the best inhibitor (present in the mix) alone, and antagonism occurs when a mixture performs worse than the worst inhibitor alone; the two points at $x_1 = 0$ and $x_1 = 1$ indicate the performance of the two inhibitors alone. Various cases with different $\eta_1^0$ and $\eta_2^0$ values are shown in (c–e). (c) $\eta_1^0 = \eta_2^0 = 0.5$; (d) $\eta_1^0 = 0.8$ and $\eta_2^0 = 0.5$; and (e) $\eta_1^0 = 0.6$ and $\eta_2^0 = -0.4$.
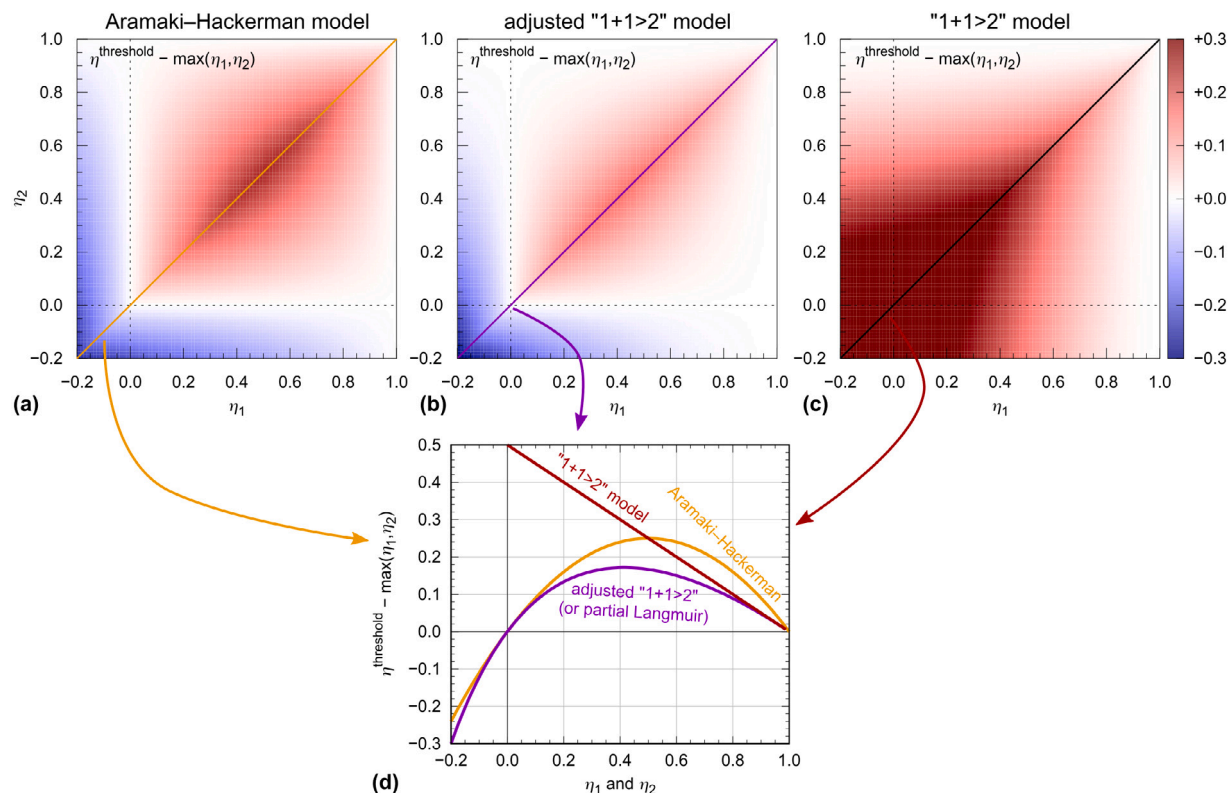


**Fig. 2.** Comparison of various synergistic models in terms of the $\eta^{\text{threshold}} - \max(\eta_1, \eta_2)$ difference, i.e., the absolute model is taken as a reference. (a–c) 2D plots of the $\eta^{\text{threshold}} - \max(\eta_1, \eta_2)$ difference as a function of $\eta_1$ and $\eta_2$ of pure compounds. Red (blue) regions represent positive (negative) differences, implying a stronger (weaker) synergistic condition than given by the absolute model. (d) The $\eta^{\text{threshold}} - \max(\eta_1, \eta_2)$ differences along the $\eta_1 = \eta_2$ diagonal.

The absolute synergistic parameter is compatible with the Chambers–Taylor–Kendig (CTK) criterion for synergism [12], according to which synergism occurs when a mixture performs better than the best inhibitor (present in the blend) alone, whereas the CTK criterion for antagonism requires that a mixture performs worse than the worst inhibitor alone (Fig. 1b); because Chambers–Taylor–Kendig did not transform their conditions into equations, a formalization of their requirements is presented in Appendix. Figs. 1a and 1b illustrate the conceptual difference between a criterion based on the synergistic parameter and the CTK synergism/antagonism criteria. For a criterion based on the synergistic parameter, there is a sharp transition at $S = 1$ between synergism ($S > 1$) and antagonism ($S < 1$). In contrast, for the CTK criteria, there are two boundary lines, a line for synergism and a line for antagonism. Hence, the transition between the two is not sharp. Such a gradual transition between synergism and antagonism may seem more reasonable than the sharp transition based on the synergistic parameter. However, the $S = 1$ limiting line is the most suitable for the latter, whereas other choices of $S$ for synergism and antagonism would be arbitrary.

Going back to criteria based on the synergistic parameter, Figs. 1c–e present different models for a fixed total concentration. In addition to the absolute model, the Aramaki–Hackerman, "1+1>2", and "adjusted 1+1>2" models also give a single value for the synergistic threshold. Figs. 1c and 1d reveal that for corrosion inhibitors ($\eta_1^0 > 0$ and $\eta_2^0 > 0$), the Aramaki–Hackerman, "1+1>2", and "adjusted 1+1>2" models give too strong requirements for synergistic inhibition because the threshold inhibition efficiency for synergism is above the $\max(\eta_1^0, \eta_2^0)$ value. To illustrate the point, let us consider a simple example with $\eta_1^0 = 0.5$ and $\eta_2^0 = 0.6$. It seems practical to consider any mixture that displays $\eta_{12} > 0.6$ as synergistic, yet the Aramaki–Hackerman threshold value for synergistic inhibition efficiency is $\eta_1^0 + \eta_2^0 - \eta_1^0 \eta_2^0 = 0.8$. Hence, only mixtures with $\eta_{12} > 0.8$ will exhibit $S^{\text{Aramaki}} > 1$. It will be shown below that for the Aramaki–Hackerman model, the overshooting is the highest for $\eta_1^0 = \eta_2^0 = 0.5$, where it gives the threshold value of $\eta^{\text{threshold}} = 0.75$, corresponding to an excess of 25 percentage points (Fig. 1c); Fig. 1c also shows that for $\eta_1^0 = \eta_2^0$ cases, the fixed Langmuir model gives the same result as the absolute model.

In addition to giving too strong synergistic requirements for inhibitors, the Aramaki–Hackerman and "adjusted 1+1>2" models also give too weak conditions when one of the pure compounds activate corrosion as shown by Fig. 1e for $\eta_1^0 = 0.6$ and $\eta_2^0 = -0.4$. In contrast, the absolute and "1+1>2" models are not susceptible to this shortcoming because even for activators their thresholds are always greater or equal to $\max(\eta_1^0, \eta_2^0)$.

In Fig. 1e, the pure compound-2 is a corrosion activator ($\eta_2^0 = -0.4$), which, strictly speaking, is out of the scope of the Langmuir model that is based on the perfect adsorption hypothesis ($\eta = \Theta$) for which $\eta = 0$ is the lowest possible value. Nevertheless, the Langmuir model gives well-defined answers even in such cases as shown in Fig. 1e.

## 4.2. A direct comparison of synergistic models

The above brief analysis reveals that in the case of a fixed total concentration, the Aramaki–Hackerman and "adjusted 1+1>2" models have some problems because they give too weak requirements for synergism when one of the pure compounds accelerates corrosion ($\eta_i < 0$). This issue, therefore, deserves more detailed scrutiny.

Here, we extend the analysis and alleviate the constraint of a fixed total concentration. Hence, we compare the models without any assumption on concentrations. Let $\eta_1$ and $\eta_2$ be the inhibition efficiencies of pure compounds measured at concentrations of experimenter choice, and $\eta_{12}$ the inhibition efficiency of a mixture also at a concentration of experimenter choice. In the comparison, we will also include the partial Langmuir model—i.e., a Langmuir model derived for partial concentrations—which is equivalent to the "adjusted 1+1>2" model,

as demonstrated in Section 3.8 (hence, partial Langmuir model $\equiv$ "adjusted 1+1>2" model).

In Fig. 2, the Aramaki–Hackerman, "adjusted 1+1>2" (or partial Langmuir), and "1+1>2" models are evaluated with respect to the absolute model, serving as a reference, although the last model is justified only for fixed and optimum concentrations. In particular, the comparison is performed in terms of the difference between $\eta^{\text{threshold}}$ and $\max(\eta_1, \eta_2)$:

$$\Delta\eta^{\text{threshold}} = \eta^{\text{threshold}} - \max(\eta_1, \eta_2). \tag{59}$$

Negative values of $\Delta\eta^{\text{threshold}}$ indicate too weak a synergistic requirement. In contrast, positive values imply too strong a synergistic condition only for fixed and optimum concentrations but not necessarily for partial and arbitrary concentrations. Positive and negative $\Delta\eta^{\text{threshold}}$ values are represented in Figs. 2a–c by red and blue colors, respectively.

For the Aramaki–Hackerman and "adjusted 1+1>2" (or partial Langmuir) models, Fig. 2 reveals blue colored region when at least one of the compounds has $\eta_i < 0$. Hence, in this case, these two models give too weak conditions for synergism because they can predict $S > 1$ even if $\eta_{12} < \max(\eta_1, \eta_2)$. In contrast, the "1+1>2" model does not have this drawback (note that it lacks the blue region). Therefore, its requirement for synergism is stronger than for the other two models (Fig. 2).

The $\Delta\eta^{\text{threshold}}$ difference is particularly large when $\eta_1$ and $\eta_2$ have similar values, and Fig. 2d specifically plots the $\eta_1 = \eta_2$ case. For the "1+1>2" model, $\Delta\eta^{\text{threshold}}$ linearly increases with decreasing inhibition efficiencies. In contrast, for the Aramaki–Hackerman model the difference displays the maximum at $\eta_1 = \eta_2 = 0.5$ with $\Delta\eta^{\text{threshold}} = 0.25$, and for the "adjusted 1+1>2" (or partial Langmuir) model the maximum appears at $\eta_1 = \eta_2 = \sqrt{2} - 1$ with $\Delta\eta^{\text{threshold}} = 0.174$.[7]

Two further remarks can be made from Fig. 2d. (i) The "adjusted 1+1>2" (or partial Langmuir) model asymptotically approaches the Aramaki–Hackerman model at $\eta_1, \eta_2 \rightarrow 0$, whereas at $\eta_1, \eta_2 \rightarrow 1$, it asymptotically approaches the "1+1>2" model. (ii) The Aramaki–Hackerman and partial Langmuir models are not too different in the shown range: the former gives a somewhat stronger condition for synergism than the latter. This observation, to some extent, justifies inferences in the literature [30,33], which, based on the Aramaki–Hackerman synergistic parameter, evaluate interactions between inhibitors 1 and 2. Instead, it is the Langmuir model that has this capacity.

## 4.3. Partial inhibitor concentrations

For *partial concentrations*, the concentrations of inhibitors 1 and 2 in a mixture are $c_1$ and $c_2$, and the pure compounds are measured at the partial concentration of $c_1$ for the inhibitor-1 and $c_2$ for the inhibitor-2. In this case, the synergistic parameter depends on two variables, $c_1$ and $c_2$, and the corresponding analysis implies complicated 3D plots. To simplify the analysis, let us use fractional concentrations $x_1$ and $x_2$—i.e., $x_i = c_i/(c_i + c_j)$—which reduce two variables ($c_1$ and $c_2$) to a single variable $x_1$ because $x_2 = 1 - x_1$. However, fractional concentrations mandate that $c_1 + c_2 = \text{constant}$, which is otherwise not required for partial concentrations. Due to this constraint, such concentrations can be named *constrained partial concentrations*. Fig. 3 presents the analysis of various synergistic models for *constrained partial concentrations*. The figure utilizes the perfect adsorption hypothesis ($\eta = \Theta$) and the Langmuir adsorption model for pure compounds 1 and 2 to provide a simple relation between inhibition efficiency and concentration of pure compounds (inhibition efficiencies of pure compounds are plotted by thin dashed lines).

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[7] It should be further noted that for $\eta_i < 0$, the $\Delta\eta^{\text{threshold}}$ difference of the Aramaki–Hackerman model smoothly decreases with decreasing $\eta_i$, whereas the partial Langmuir model has a pole at $\eta_1 \eta_2 = 1$ due to the $(1 - \eta_1 \eta_2)$ denominator in Eq. (37).
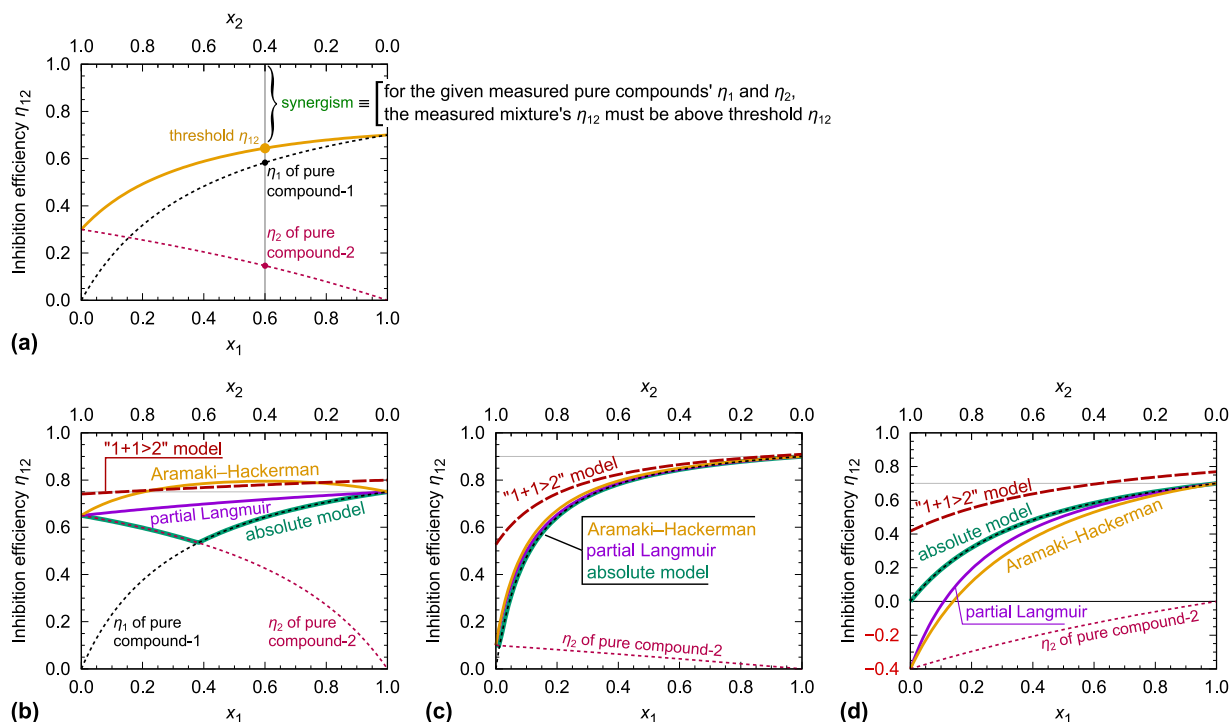
**Fig. 3.** Performance of various synergistic models at constrained partial concentrations ($x_1$ and $x_2$ for pure compounds and $x_1 + x_2$ for binary mixtures). (a) Schematic explanation of how to read the plots: the thick solid curve represents a model's predicted $\eta^{\text{threshold}}$ as a function of $x_1$ (lower $x$-axis) or $x_2$ (upper $x$-axis), and the thin dashed curves represent $\eta_1(x_1)$ and $\eta_2(x_2)$ of pure compounds. At a given $x_1$ (indicated by the thin vertical line), the inhibition efficiencies of pure compounds are $\eta_1$ and $\eta_2$, and a synergistic model predicts synergism if the measured inhibition efficiency of the $x_1 + x_2$ mixture is higher than the model's threshold value. Various cases with different $\eta_1$ and $\eta_2$ values of pure compounds are shown in (b–d). In (c) and (d), the $\eta_1$ black dashed curve of the pure compound-1 is difficult to spot because it coincides with the absolute model green curve.

Fig. 3a schematically explains how to read the plots: a specific concentration $x_1$ (note that $x_2 = 1 - x_1$) corresponds to a thin vertical line at which the inhibition efficiencies of pure compounds are $\eta_1$ and $\eta_2$ (points at the intersections of the vertical line and dashed curves). For these $\eta_1$ and $\eta_2$ values, a given model predicts a specific threshold value of $\eta^{\text{threshold}}$ (point at the intersection of the vertical line and the model's curve). If the measured mixture's $\eta_{12}$ value is above $\eta^{\text{threshold}}$, the model predicts synergism. Note that different synergistic models predict different threshold values of $\eta^{\text{threshold}}$ (Figs. 3b–d).

Three specific cases are considered in Figs. 3b–d. Fig. 3b presents the case where the performances of pure compounds 1 and 2 are similar, with $\eta_1 = 0.75$ and $\eta_2 = 0.65$ at $x_1 = 1$ and $x_2 = 1$, respectively. The Aramaki–Hackerman and "1+1>2" models give stronger synergistic conditions than the partial Langmuir (or "adjusted 1+1>2") and absolute models; here, the $\eta_1$ and $\eta_2$ values, measured at partial $x_1$ and $x_2$ concentrations of pure compounds, are used for the absolute model. If the highest inhibition efficiency of the pure compounds is taken as the reference, then the Aramaki–Hackerman and "1+1>2" models give too strong requirements, unless $x_1$ becomes too low. In contrast, the partial Langmuir and absolute models give too week conditions. Note also that, as pointed out in the theory section, the "1+1>2" model does not converge toward a pure compound when the concentration of the other compound goes to zero.

Fig. 3c presents the case of a good inhibitor-1 ($\eta_1 = 0.9$ at $x_1 = 1$) and a lousy inhibitor-2 ($\eta_2 = 0.1$ at $x_2 = 1$). Here, the Aramaki–Hackerman, partial Langmuir (or "adjusted 1+1>2"), and absolute models give very similar threshold values, whereas threshold values of the "1+1>2" model are higher, particularly at low $x_1$. Note that in this case all the models appear to give too weak conditions for synergism, with the exception of the "1+1>2" model at very high $x_1$, because they may predict synergism even if the mixture's $\eta_{12}$ is below the highest inhibition efficiency of the pure compound-1. Therefore, partial concentrations are the least appropriate among the three considered

concentration choices because they may result in falsely predicted synergism.

Fig. 3d presents the case of a modest inhibitor-1 ($\eta_1 = 0.7$ at $x_1 = 1$) and a corrosion activator-2 ($\eta_2 = -0.4$ at $x_2 = 1$). Also in this case, the Aramaki–Hackerman, partial Langmuir (or "adjusted 1+1>2"), and absolute models (also the "1+1>2" model at low $x_1$) predict too weak conditions for synergism. Furthermore, at low $x_1$ values, the Aramaki–Hackerman and partial Langmuir (or "adjusted 1+1>2") models may predict synergism even if a mixture activates corrosion, $\eta_{12} < 0$. In contrast, the "1+1>2" and absolute models do not have this drawback.

As already discussed in Section 4.1, due to the use of the perfect adsorption hypothesis, the Langmuir synergistic model should not be applicable when corrosion activators are present in the blend (Fig. 3d). However, it was shown in the theory section that the "partial" Langmuir model is equivalent to the "adjusted 1+1>2" model for which the perfect adsorption hypothesis is not used. This observation justifies the use of the Langmuir model even when some compounds in the mixture are corrosion activators.

Regarding the problem of the "1+1>2" model not converging toward a pure compound when the concentration of the other compound goes to zero, Fig. 3 reveals that this discrepancy is significant for lousy inhibitors, whereas, for efficient inhibitors, the discrepancy becomes insignificant, which is easy to understand because for efficient inhibitors corrosion resistances are high and, in a relative sense, $R_1 + R_2 - R_0 \approx R_1 + R_2$.

Let us also analyze synergistic models for the unconstrained partial concentrations using the "actual" $c_1$ and $c_2$ concentrations. Because 3D plots would be unreadable, 2D contour plots will be used instead. Such a contour plot can analyze one model at a time, so a proper reference to compare with is required. A good choice for such a reference is the absolute model at optimum concentrations, $\max(\eta_1^{\text{opt}}, \eta_2^{\text{opt}})$, where $\eta_i^{\text{opt}}$ is the highest inhibition efficiency of the pure compound $i$ for $c_i \in [0, c_i^{\text{max}}]$. This way, the following differences are plotted in contour
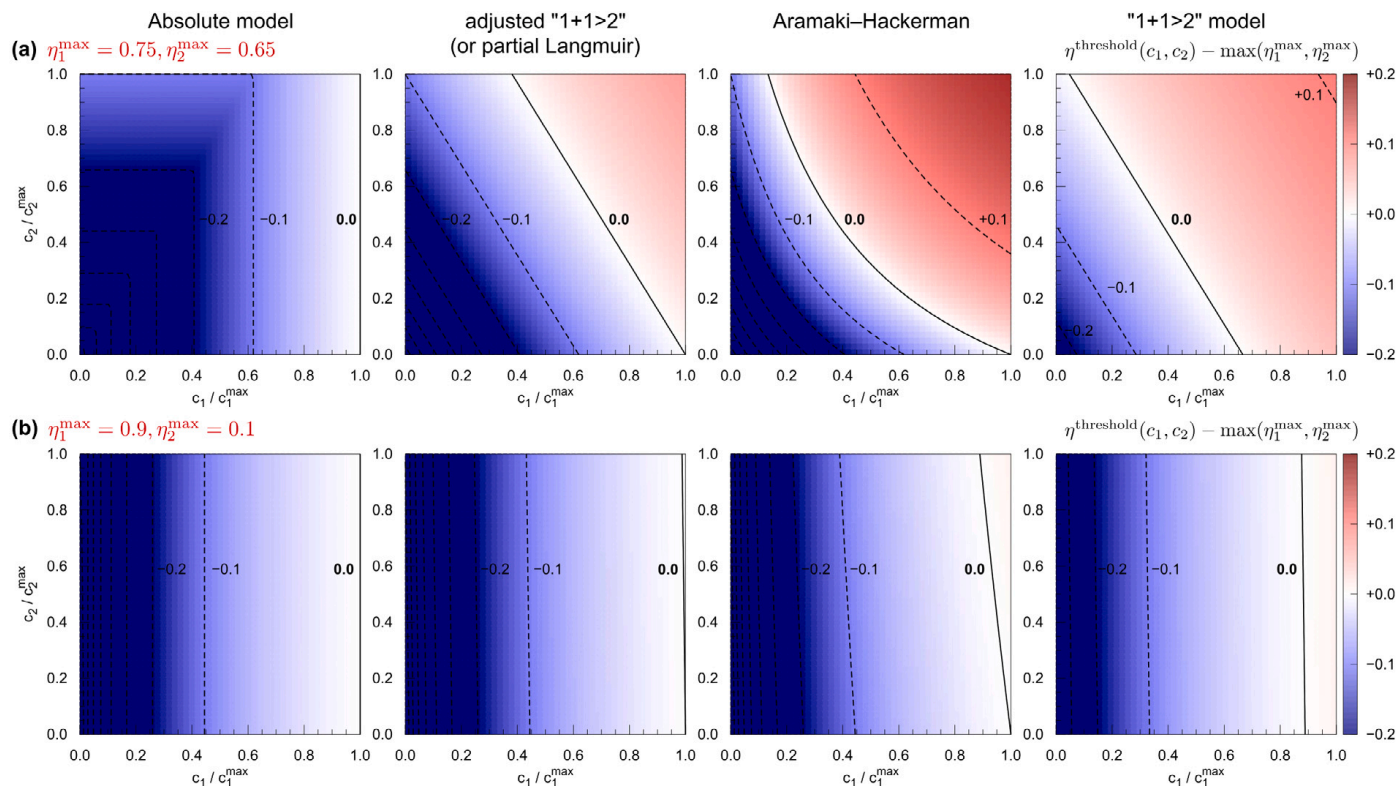
**Fig. 4.** Comparison of synergistic models at partial concentrations in terms of the $\eta^{\mathrm{threshold}}(c_1, c_2) - \max(\eta_1^{\max}, \eta_2^{\max})$ difference (for the absolute model, $\eta_1$ and $\eta_2$ measured at partial $c_1$ and $c_2$ concentrations of pure compounds are used). Red (blue) regions represent positive (negative) differences. Two cases—compatible with Figs. 3b,c—are shown, corresponding to (a) moderate+moderate and (b) efficient+lousy inhibitors. In particular, the inhibition efficiencies at the highest $c_1^{\max}$ and $c_2^{\max}$ concentrations are (a) $\eta_1^{\max} = 0.75, \eta_2^{\max} = 0.65$ and (b) $\eta_1^{\max} = 0.9, \eta_2^{\max} = 0.1$.

plots of Fig. 4:

$$\Delta\eta^{\mathrm{threshold}}(c_1, c_2) = \eta^{\mathrm{threshold}}(c_1, c_2) - \max(\eta_1^{\mathrm{opt}}, \eta_2^{\mathrm{opt}}). \quad (60)$$

Among the models presented in Fig. 4 is also the absolute model, corresponding to partial concentrations with $\eta^{\mathrm{threshold}} = \max(\eta_1, \eta_2)$, where $\eta_1$ and $\eta_2$ are inhibition efficiencies of pure compounds at $c_1$ and $c_2$. Do not confuse this with the $\max(\eta_1^{\mathrm{opt}}, \eta_2^{\mathrm{opt}})$ reference in Eq. (60), which uses pure compounds' inhibition efficiencies at optimum concentrations.

Fig. 4 shows two cases that are compatible with Figs. 3b,c and correspond to (a) moderate+moderate and (b) efficient+lousy inhibitors. In Fig. 4, red (blue) regions represent positive (negative) $\Delta\eta^{\mathrm{threshold}}(c_1, c_2)$ differences. The dominant impression from the figure is the prevalence of blue regions, indicating that, for partial concentrations, models can predict synergism even if the measured inhibition efficiency of a mixture is lower than the highest inhibition efficiency among pure standalone compounds at the optimum concentration. In this respect, the Aramaki–Hackerman and "1+1>2" models fare better than others, as indicated by their higher incidence of red regions. Fig. 4 further reveals that the absolute model is not applicable for partial concentrations, as the corresponding contour plots are completely blue-colored.

The important message from Figs. 3 and 4 is that when synergism is analyzed at partial concentrations, models can predict synergism even if the mixture's $\eta_{12}$ is below the highest inhibition efficiency of pure compounds. In this sense, the fixed and optimum concentrations are more reliable for determining if a given mixture is superior to pure compounds.

## 5. Conclusions

In this paper, synergism in corrosion inhibition and how to adequately quantify it was scrutinized conceptually. To this end, corrosion

activity was introduced as a complement to corrosion efficiency. The majority of equations, including the equation for the synergistic parameter, are simpler if expressed with corrosion activities instead of corrosion inhibition efficiencies.

While the definition of the synergistic parameter as the ratio between the threshold and measured mixture's corrosion activities is well-founded, the choice for the threshold value is not unique, and several reasonable thresholds can be chosen. In the literature, the threshold of Aramaki and Hackerman is usually used. Nevertheless, several other rational choices and the corresponding models have been developed herein. The Aramaki–Hackerman and the newly developed models were also extended to multi-component inhibitor mixtures.

In addition to the choice of the threshold, the selection of concentrations of pure compounds is also important when quantifying the synergism. The three commonly used options are (i) fixed total concentration, where pure compounds are analyzed at the total inhibitors' concentration used in the mixture; (ii) partial concentrations, where each pure compound is analyzed at the corresponding partial concentration used in the mixture; and (iii) optimum concentrations of pure compounds. Among these concentration types, the partial concentrations are the least appropriate for scrutinizing synergism because all the models considered herein may give a synergistic parameter greater than one for a mixture displaying inhibition efficiency inferior to a pure compound. In contrast, the fixed and optimum concentrations are more robust and reliable for quantifying synergism. However, even for these concentrations, the Aramaki–Hackerman and Langmuir models may wrongly predict synergism if a compound in the mixture accelerates corrosion when used alone.

Among the newly developed synergistic models, two are based on the Langmuir adsorption model. They are named *fixed* and *partial Langmuir models* to indicate that they were derived for the fixed and partial concentrations, respectively.

The third developed model is the *absolute synergistic model*, which is based on the requirement that for synergism, the mixture's inhibition efficiency must be higher than the highest optimum inhibition efficiency of pure compounds. From a practical point of view, this is the essential condition because by mixing compounds, one aims to surpass the best inhibition efficiency of pure compounds. This model is applicable for the fixed and optimum concentrations but may fail if corrosion inhibition efficiencies of pure compounds are evaluated at partial concentrations.

The fourth developed model is the *"1+1>2" model*. It is based on the premise that, for synergism, the *combined is greater than the sum of its parts* and requires that the corrosion resistance in a mixture is higher than the sum of corrosion resistances in pure compounds. This model is robust, reliable, and applicable to any concentration choice. However, it does not converge to a pure compound when the concentration of the other compound in the mixture approaches zero. The fifth developed model (named the *"adjusted 1+1>2" model*) is the "1+1>2" model corrected for the convergence problem. Surprisingly, so corrected model is equivalent to the partial Langmuir model, which is quite interesting because the underlying assumptions of the two models appear quite different.

Current analyses suggest using optimum or at least fixed concentrations of pure compounds and the absolute synergistic model to determine if a given mixture is synergistic. If the partial concentrations are used instead, the "1+1>2" model is recommended. The Aramaki–Hackerman model also performs well for partial concentrations but only if none of the compounds used in the mixture accelerate corrosion when used as a standalone.

## CRediT authorship contribution statement

**Anton Kokalj:** Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft, Writing – review & editing, Visualization.

## Declaration of competing interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

The manuscript does not use any raw data. Graphs were generated with the Gnuplot software [34], and the corresponding scripts will be made available on request.

## Acknowledgments

## Appendix. Formalization of the Chambers–Taylor–Kendig synergistic and antagonistic criteria

Chambers–Taylor–Kendig (CTK) [12] did not formalize their conditions for synergism and antagonism with synergistic and antagonistic parameters. Hence, a plausible formalization is presented below. Let us first recall that the absolute model's requirement for synergism (Section 3.6) is synonymous with the CTK criterion for synergism. Both require that for synergism, a mixture must perform better than the best inhibitor (present in the mix) alone. The corresponding threshold value for $\eta$ is:

$$\eta_{\text{abs}}^{\text{threshold}} = \eta_{\text{CTK}}^{\text{synergism}} = \max(\eta_1^{\text{opt}}, \eta_2^{\text{opt}} \dots \eta_n^{\text{opt}}), \tag{A.1}$$

where $\eta_{\text{CTK}}^{\text{synergism}}$ is the CTK threshold value for synergism. Analogously, the CTK criterion for antagonism, which requires that a mixture performs worse than the worst inhibitor (present in the blend) alone, can be defined with the threshold value for antagonism:

$$\eta_{\text{CTK}}^{\text{antagonism}} = \min(\eta_1^{\text{opt}}, \eta_2^{\text{opt}} \dots \eta_n^{\text{opt}}). \tag{A.2}$$

To complete the formalization, we need the antagonistic parameter ($A$), which can be reasonably defined as the inverse of synergistic parameter (cf. Eq. (5)):

$$A = S^{-1} = \frac{1 - \eta^{\text{measured}}}{1 - \eta^{\text{threshold}}}. \tag{A.3}$$

This way, $A > 1$ when antagonism occurs. However, for the CTK model, the threshold values for synergism and antagonism are not the same ($\eta_{\text{CTK}}^{\text{synergism}} \neq \eta_{\text{CTK}}^{\text{antagonism}}$). Hence, also:

$$A_{\text{CTK}} \neq S_{\text{CTK}}^{-1}, \tag{A.4}$$

where $A_{\text{CTK}}$ and $S_{\text{CTK}}$ are the CTK antagonistic and synergistic parameters, respectively. Based on the above, the $S_{\text{CTK}}$ and $A_{\text{CTK}}$ parameters can be defined as:

$$\text{if } \eta^{\text{measured}} > \eta_{\text{CTK}}^{\text{synergism}} \Rightarrow S_{\text{CTK}} = \frac{1 - \eta_{\text{CTK}}^{\text{synergism}}}{1 - \eta^{\text{measured}}}, \tag{A.5}$$

$$\text{if } \eta^{\text{measured}} < \eta_{\text{CTK}}^{\text{antagonism}} \Rightarrow A_{\text{CTK}} = \frac{1 - \eta^{\text{measured}}}{1 - \eta_{\text{CTK}}^{\text{antagonism}}}. \tag{A.6}$$

Note that for the so-formalized CTK conditions, the synergistic parameter is defined only for cases where synergism occurs. Likewise, the antagonistic parameter is defined only for instances where antagonism occurs.

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