



# On the use of the Langmuir and other adsorption isotherms in corrosion inhibition

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## ABSTRACT

In corrosion inhibition studies, the standard adsorption Gibbs energy is often estimated via the linear regression of the Langmuir isotherm in the  $c/\theta = 1/K + c$  form, where both the intercept and the slope are estimated, although the Langmuir isotherm requires the slope of 1. Hence,  $c/\theta = 1/K + mc$  is actually used, where  $m$  is the slope. Herein, a theoretical basis for this equation is established. It is demonstrated to be an effective equation that can decently describe various adsorption models and provide relatively accurate estimates of the standard adsorption Gibbs energy, provided surface coverages are reliably determined experimentally. However, any significant deviation from the slope of 1 signals non-Langmuir adsorption due to inter-adsorbate interactions, multi-site adsorption, or surface heterogeneity. Among these three causes, only attractive inter-adsorbate interactions lead to a slope of less than 1.

## 1. Introduction

The Langmuir adsorption isotherm [2] is often used in corrosion inhibition studies when estimating the standard adsorption Gibbs energy ( $\Delta G_{\text{ads}}^{\circ}$ ) based on measured inhibition efficiencies at several different inhibitor concentrations. The estimation basically consists of three steps. (i) The inhibitor fractional surface coverage ( $\theta$ ) is considered to be synonymous with its corrosion inhibition efficiency ( $\eta$ ), i.e.,  $\theta = \eta$ . (ii) An adsorption isotherm is assumed to link the fractional surface coverage with the equilibrium adsorption constant, and here the Langmuir adsorption isotherm is most often used. (iii) The chosen adsorption isotherm is used to fit the relation between inhibitor surface coverage and inhibitor concentration in the bulk solution. As a result of this fit, one obtains the adsorption equilibrium constant from which the standard adsorption Gibbs energy is calculated. The so-estimated  $\Delta G_{\text{ads}}^{\circ}$  is usually used to distinguish between physisorption and chemisorption based on the so-called 20/40 rule, which was recently criticized by arguing that it is not a reliable criterion to distinguish between the two adsorption modes [3].

In the case of the Langmuir adsorption isotherm (see Appendix A), the relation between fractional surface coverage and inhibitor concentration in the bulk solution ( $c$ ) is given by:

$$Kc = \frac{\theta}{1 - \theta}, \quad (1)$$

where  $K$  is the adsorption equilibrium constant. This equation is usually rearranged to the following form:

$$\frac{c}{\theta} = \frac{1}{K} + c, \quad (2)$$

so that  $K$  is calculated from the estimated intercept on the  $c/\theta$  vs.  $c$  plot, where the data are fitted with Eq. (2). The standard adsorption Gibbs energy is then often estimated via the following thermodynamic relation:

$$K = \frac{1}{c_{\text{H}_2\text{O}}} \exp\left(-\frac{\Delta G_{\text{ads}}^{\circ}}{RT}\right), \quad (3)$$

where  $c_{\text{H}_2\text{O}}$  is the molar concentration of liquid water (55.34 M at 25 °C).<sup>1</sup> The  $1/c_{\text{H}_2\text{O}}$  factor stems from considering the aqueous-phase adsorption as substitutional adsorption where an inhibitor molecule replaces a water molecule on the surface (for details, see Appendix A.2).

Note that Eq. (2) mandates the slope of the  $c/\theta$  vs.  $c$  line must be equal to 1. This implies that only the intercept  $1/K$  should be fitted. In contrast, a large majority of studies fit both the intercept and the slope. Effectively this means that the following equation is used instead:

$$\frac{c}{\theta} = \frac{1}{K} + mc, \quad (4)$$

where  $m$  is the slope of the  $c/\theta$  vs.  $c$  line. However, the so-estimated  $K$  differs from the one estimated by Eq. (2) that corresponds to the Langmuir isotherm. Fitting the slope can be used to query the deviation

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<sup>1</sup> Instead, a value of 55.5 M is often used, corresponding to a density of water of 1 kg/L. But the correct density at 25 °C is 0.997048 kg/L [1].

from the Langmuir adsorption model, i.e., if  $m$  appreciably differs from 1, the Langmuir model is not applicable. But does fitting the slope have any other utility? The primary purpose of this manuscript is, therefore, to analyze whether fitting the slope is physically acceptable and what  $m \neq 1$  means.

Two explanations are found in the literature of why the slope differs from 1. The first argues that the deviation is due to interactions between adsorbates [4–11], while the second interprets  $m$  in Eq. (4) as either the (average) number of sites that a single adsorbed inhibitor molecule occupies [12–15] or the (average) number of adsorbed water molecules displaced from the surface by one adsorbed inhibitor molecule [16,17]. However, to the author's knowledge, none of these explanations is based on adequate theoretical analysis. Such an analysis is therefore provided herein.

Some studies that interpret the slope  $m$  as the number of adsorption sites occupied by an inhibitor molecule refer to the modified Langmuir adsorption isotherm of Villamil et al. [12,13]:

$$\frac{c}{\theta} = \frac{m}{K} + mc. \quad (5)$$

However, Villamil et al. did not explain how this equation emerges. Because the adsorption equilibrium constants estimated from Eqs. (4) and (5) differ, it is worth scrutinizing which of the two gives a more accurate estimate of the standard adsorption Gibbs energy.

The analysis of the above-formulated issues is provided in two parts. In this publication, we assume that the inhibition efficiency corresponds to the inhibitor's fractional surface coverage,  $\theta \approx \eta$ . It is worth pointing out that this assumption, named as *perfect adsorption hypothesis* in Ref. [18] ("perfect" because it presupposes that adsorption perfectly blocks the corrosion at occupied sites), was recently criticized by Lindsay et al. [19]. For this reason, in the subsequent publication [20], we will consider the  $\theta \neq \eta$  case and develop a simple model where surface coverage depends on inhibition efficiency through a functional dependence.

In Section 2, we analyze the functional dependence of various isotherms on the  $c/\theta$  vs.  $c$  plot and then, in Section 3, perform further analysis by means of virtual experiments. To this end, several different adsorption models are considered with which the data are generated. The data are then fitted to Eq. (4), where both intercept and slope are estimated. The following adsorption models are considered: Frumkin [21] to account for intermolecular interactions, Flory–Huggings to account for molecular size [22], and Temkin [23] to account for surface heterogeneity. These models and the accompanying standard states are explained in the appendices.

It is demonstrated that Eq. (4), where both the slope and the intercept are fitted, is an effective equation that can decently describe various adsorption models. This finding explains why so many studies find that Eq. (4) is able to fit their experimental data. The analysis reveals that any significant deviation from the slope of 1 signals non-Langmuir adsorption. Intermolecular interactions, multi-site adsorption (i.e., a replacement of  $n$  adsorbed water molecules by a single inhibitor molecule), and surface heterogeneity result in slope deviating from 1. However, in the case of multi-site adsorption, the slope  $m$  does not correspond to the number of displaced water molecules  $n$  because it is shown that  $m < n$ .

Based on the insight from the analysis presented herein, a new general-purpose Type-I adsorption isotherm is derived in a parallel publication [24], which fits the experimental data better than Eq. (4).

## 2. Analysis

For simplicity, we consider only Type-I adsorption isotherms [25], where adsorbates form up to a full monolayer coverage. In general, adsorption isotherms can be written as:

$$Kc = f(\theta), \quad (6)$$

so that  $Kc$  is a function of the surface coverage. With the aid of an adsorption isotherm, the expression for the adsorption Gibbs energy can be written as (see Appendix B):

$$\Delta G_{\text{ads}} = \Delta G_{\text{ads}}^{\circ} + RT \ln f(\theta) - RT \ln \frac{c}{c^{\circ}}, \quad (7)$$

where  $\Delta G_{\text{ads}}^{\circ}$  is the standard adsorption Gibbs energy and  $c^{\circ}$  the standard state concentration. This equation implies that  $\Delta G_{\text{ads}}^{\circ}$  corresponds to the adsorbate standard state, where  $f(\theta) = 1$  so that the logarithmic term vanishes.

When Eq. (6) is transformed into the form compatible with Eq. (2) or Eq. (4) that is used for fitting, then it can be written as:

$$\frac{c}{\theta} = g(c), \quad (8)$$

so that  $c/\theta$  is a function of the inhibitor concentration  $c$ . For a particular isotherm, it may be too difficult to transform Eq. (6) into Eq. (8) such that  $g(c)$  is written in an explicit closed form. However, a closed form is not needed for the analysis because  $g(c)$  can be plotted parametrically, where the coverage  $\theta$  is used as a parameter. In particular,  $g(c)$  can be drawn by plotting the  $x \equiv c = f(\theta)/K$  and  $y \equiv (c/\theta) = f(\theta)/(\theta K)$  pairs for  $\theta$  ranging from 0 to almost 1.

For all Type-I isotherms for which the saturation coverage is normalized to 1, the  $c/\theta$  eventually becomes proportional to  $c$  with the slope of 1:

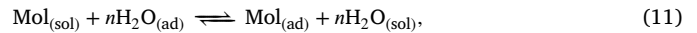
$$\frac{c}{\theta} = \text{intercept} + c \quad (\text{for Type-I isotherms at high } c). \quad (9)$$

The reason is that coverage increases with increasing concentration until eventually a full monolayer coverage is reached,  $\theta \approx 1$ . From this point on,  $c/\theta \approx c/1 = c$ . It may happen that, for a given solute, a saturation (monolayer) coverage requires concentration beyond the saturation concentration. In such a case, a hypothetical auxiliary solute can be envisaged that is equivalent to the real solute but displays an unlimited solubility.

The above Eqs. (6)–(9) correspond to plain adsorption:



where Mol stands for a molecule, and the (sol) and (ad) subscripts indicate a solvated molecule in the bulk solution and an adsorbed molecule, respectively. However, in the majority of corrosion inhibition studies, standard adsorption Gibbs energies are estimated with Eq. (3) that corresponds to substitutional adsorption:



where  $n = 1$  for the Langmuir, Frumkin, and Temkin adsorption models, whereas for the Flory–Huggings model,  $n \neq 1$ . The standard adsorption Gibbs energies of the substitutional and plain adsorptions are related by (see Eq. (A.14) in Appendix A.2):

$$\Delta G_{\text{ads}}^{\circ \text{ substitutional}} = \Delta G_{\text{ads}}^{\circ \text{ plain}} - 10 \text{ kJ/mol} \quad \text{at } T = 298.15 \text{ K}. \quad (12)$$

There is also a difference with respect to adsorbate standard states. Let us illustrate this for the Langmuir adsorption model. For plain adsorption, the explicit form of Eq. (7) for the Langmuir adsorption model is (see Appendix A):

$$\Delta G_{\text{ads}} = \Delta G_{\text{ads}}^{\circ} + RT \ln \frac{\theta}{1 - \theta} - RT \ln \frac{c}{c^{\circ}}, \quad (13)$$

which implies that the adsorbate standard state is  $\theta = 0.5$ . In contrast, for substitutional adsorption, the corresponding equation is (see Appendix A):

$$\Delta G_{\text{ads}} = \Delta G_{\text{ads}}^{\circ} + RT \ln \frac{\theta_{\text{Mol}}}{\theta_{\text{H}_2\text{O}}} - RT \ln \frac{c}{c_{\text{H}_2\text{O}}}, \quad (14)$$

where  $\theta_{\text{Mol}}$  and  $\theta_{\text{H}_2\text{O}}$  correspond to surface coverages of Mol and  $\text{H}_2\text{O}$ , respectively. Hence,  $\Delta G_{\text{ads}}^{\circ}$  corresponds to  $\theta_{\text{Mol}} = \theta_{\text{H}_2\text{O}}$ , which requires

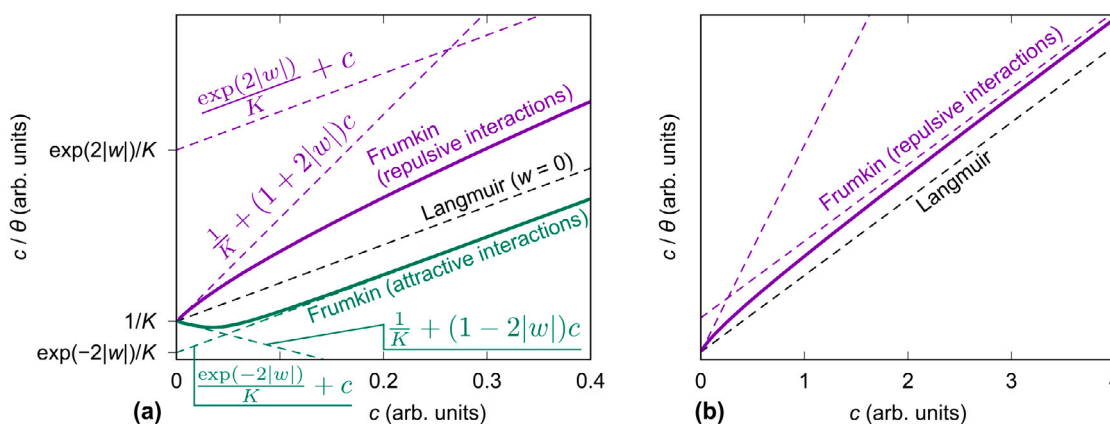


Fig. 1. The  $c/\theta$  vs.  $c$  plots of exemplar Frumkin isotherms for attractive (green) and repulsive (purple) lateral interactions. In (b), the concentration range is expanded to ten times higher concentration to illustrate that also for repulsive interactions, the slope of 1 is eventually reached. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

only that reactant  $\text{H}_2\text{O}_{(\text{ad})}$  and product  $\text{Mol}_{(\text{ad})}$  are considered at the same coverage.

For a more detailed discussion of the standard states, see Appendix B.

## 2.1. Frumkin adsorption model

The Frumkin adsorption isotherm [21] takes into account lateral interactions between adsorbed molecules and is given by (see Appendix C)<sup>2</sup>:

$$Kc = \frac{\theta}{1-\theta} \exp(2w\theta). \quad (15)$$

The corresponding equation rearranged to the  $c/\theta$  form is:

$$\frac{c}{\theta} = \frac{\exp(2w\theta)}{K} + c. \quad (16)$$

By analyzing this equation, it can be shown that at  $c = 0$ , the isotherm follows the line<sup>3</sup>:

$$\left(\frac{c}{\theta}\right)_{c \rightarrow 0} = \frac{1}{K} + (1 + 2w)c, \quad \text{hence} \quad (17)$$

at  $c = 0$ : intercept =  $\frac{1}{K}$ , slope =  $1 + 2w$ .

Therefore, for attractive interactions ( $w < 0$ ), the slope at  $c = 0$  is lower than 1, whereas for repulsive interactions ( $w > 0$ ), the slope is higher than 1.

In contrast, at very high concentrations, where saturation coverage is reached, the isotherm follows the line:

$$\left(\frac{c}{\theta}\right)_{\theta \rightarrow 1} = \frac{\exp(2w)}{K} + c, \quad (18)$$

implying that the slope is 1.

On the  $c/\theta$  vs.  $c$  plot, the Frumkin isotherm corresponds to a curve whose slope ranges from  $1 + 2w$  at a very small concentration to 1 at a very high concentration. This suggests that when the Frumkin isotherm is fitted with the Eq. (4), the slope will be different from 1 unless the fitting is performed only for relatively high concentrations. These

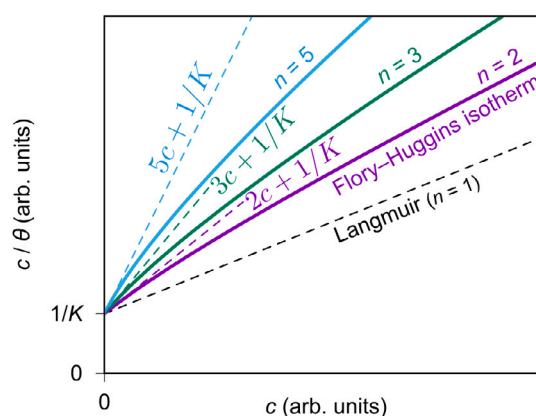


Fig. 2. The  $c/\theta$  vs.  $c$  plot of exemplar Flory-Huggins type isotherms (solid curves), Eq. (19), for  $n = 2, 3, 5$ . The Flory-Huggins slopes at  $c = 0$  are indicated by color-dashed lines, and the Langmuir isotherm is shown by the back-dashed line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

features are illustrated in Fig. 1, which shows two exemplar Frumkin adsorption isotherms, plotted in the  $c/\theta$  vs.  $c$  form, one for attractive and the other for repulsive lateral intermolecular interactions. The Langmuir adsorption isotherm corresponding to the same  $K$  value is also shown. For attractive interactions, the Frumkin isotherm is below the Langmuir isotherm and vice-versa for repulsive interactions. The reason is that due to attractive (repulsive) interactions, the coverage is higher (lower) than in the Langmuir case, resulting in smaller (higher)  $c/\theta$  values, and, consequently, the saturation coverage is reached at lower (higher) concentrations. Hence, the slope of 1 is reached much earlier for attractive than repulsive interactions. Fig. 1 reveals that Frumkin isotherms contact the Langmuir isotherm at the  $(c, c/\theta) = (0, 1/K)$  point. This observation suggests that for Frumkin isotherms,  $K$  and consequently  $\Delta G_{\text{ads}}^\circ$  correspond to adsorbate standard states, where lateral interactions vanish. Such standard states correspond to reactant  $\theta_{\text{H}_2\text{O}} \rightarrow 0$  and product  $\theta_{\text{Mol}} \rightarrow 0$ ; the other possibility is the so-called “ideal”  $\theta_{\text{Mol}} = 1$  and  $\theta_{\text{H}_2\text{O}} = 1$  (for more details, see Appendix C).

For cases that are well described by Frumkin isotherms, Fig. 1a suggests that the intercept obtained by the linear regression, Eq. (4), will be higher than  $1/K$  for repulsive interactions, whereas, for attractive interactions, it will be lower than  $1/K$ . This issue is considered in more detail in the results section.

<sup>2</sup> The exponential term is often written with the minus sign as  $\exp(-2w\theta)$  or even without the factor 2 as  $\exp(-w\theta)$ . Here, we use  $\exp(2w\theta)$  so that  $w$  follows the standard thermodynamic sign convention (i.e.,  $w < 0$  for attraction).

<sup>3</sup> In the limit of zero concentration, the coverage is zero (note from Eq. (15) that  $\theta = 0$  corresponds to  $Kc = 0$ ). Furthermore, it is evident from Eq. (16) that  $c/\theta = 1/K$  at  $c = 0$ , which implies  $\theta = Kc$ . At a very small coverage,  $\exp(2w\theta) \approx 1 + 2w\theta$ , and Eq. (16) can be written as:

$$\frac{c}{\theta} \approx \frac{1 + 2w\theta}{K} + c = \frac{1 + 2wKc}{K} + c = \frac{1}{K} + (2w + 1)c.$$

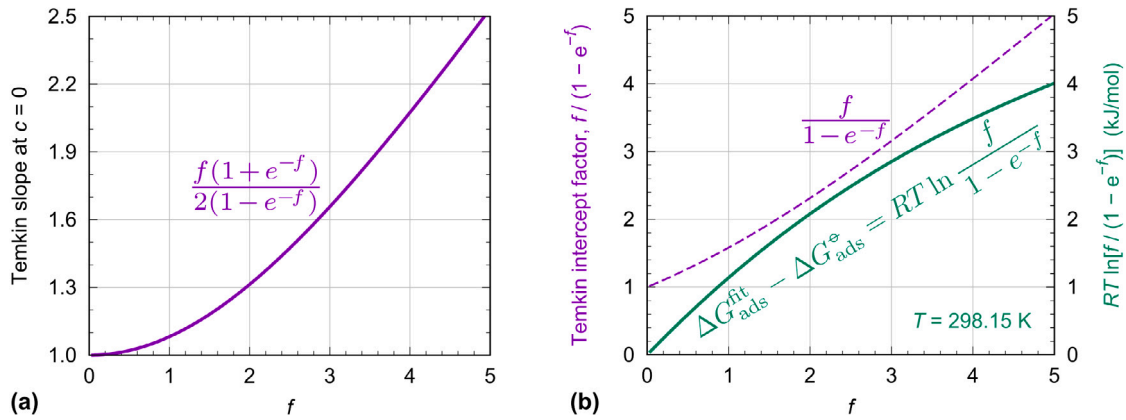


Fig. 3. (a) The  $c/\theta$  slope of the Temkin isotherm at  $c = 0$  depending on the parameter  $f$ , i.e.,  $\frac{f(1+e^{-f})}{2(1-e^{-f})}$  vs.  $f$ . (b) The Temkin intercept factor  $\frac{f}{1-e^{-f}}$  vs.  $f$  (purple dashed curve) and the dependence of the  $\Delta G_{\text{ads}}^{\text{fit}} - \Delta G_{\text{ads}}^{\circ}$  difference (at room temperature) on  $f$  (green), cf. Eq. (27). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

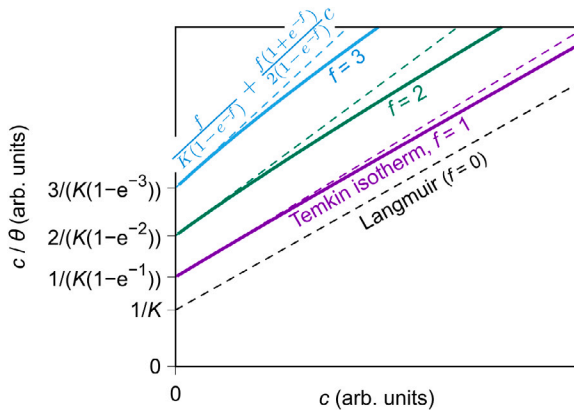


Fig. 4. The  $c/\theta$  vs.  $c$  plot of exemplar Temkin isotherms (solid curves) for  $f = 1, 2, 3$ . The Temkin slopes at  $c = 0$  are indicated by color-dashed lines, and the Langmuir isotherm is shown by the back-dashed line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

## 2.2. Flory–Huggins adsorption model

The Flory–Huggins adsorption model takes into account molecular size, i.e., it considers that a molecule replaces  $n$  adsorbed water molecules during adsorption. Let us consider the simplest form of the Flory–Huggins type adsorption isotherm (for other forms, see Appendix D):

$$Kc = \frac{\theta}{(1-\theta)^n}, \quad (19)$$

which is based on the thermodynamic consideration [26] of the substitutional adsorption reaction (11).

At a very small coverage,  $(1-\theta)^n \approx 1 - n\theta$ , and Eq. (19) can be rearranged to the following  $c/\theta$  form:

$$\left(\frac{c}{\theta}\right)_{\theta \rightarrow 0} = \frac{1}{K} + nc, \quad (20)$$

hence at  $c = 0$ : intercept =  $\frac{1}{K}$ , slope =  $n$ .

Note that this equation is equivalent to Eq. (4) that is used for fitting, which suggests that it is more appropriate than the “competing” Villamil Eq. (5). Eq. (20) indicates that the slope of Eq. (4) may indeed be related to the number of displaced water molecules or to the number of surface sites that a molecule adsorbs to; in the Flory–Huggins model the two are equivalent. However, beware that Eq. (20) holds only for  $\theta \ll 1$ .

In contrast, at very high concentrations, where saturation coverage is reached, the  $c/\theta$  slope is 1 (see Appendix F), although the approach to the slope of 1 is very slow. These observations suggest that when the Flory–Huggins type isotherm is fitted with the linear regression, Eq. (4), the slope of the regression line is less than  $n$  but greater than 1.

Multi-site adsorption thus results in a slope greater than 1. However, the slope is smaller than the number of displaced water molecules by an inhibitor molecule. This reasoning is supported by Fig. 2, which shows exemplar Flory–Huggins type adsorption isotherms for several values of  $n$ , plotted in the  $c/\theta$  vs.  $c$  form. It is evident that the slopes of the isotherms are within  $n$  and 1 and reduce as the concentration increases. This observation suggests that the intercepts obtained by the linear regression, Eq. (4), will be higher than  $1/K$ .

For the Flory–Huggins type isotherm of Eq. (19),  $K$  and  $\Delta G_{\text{ads}}^{\circ}$  correspond to adsorbate standard states of reactant  $\theta_{\text{H}_2\text{O}} = 1$  and product  $\theta_{\text{Mol}} = 1$  (see Appendix D).

## 2.3. Temkin adsorption model

The Temkin adsorption model accounts for surface heterogeneity. The exact form of the Temkin adsorption isotherm [22,23] is (see Appendix E):

$$Kc = \frac{e^{f\theta} - 1}{1 - e^{f(\theta-1)}}, \quad (21)$$

where  $f$  is a parameter describing surface heterogeneity and is taken to be positive; for  $f = 0$ , the Temkin isotherm reduces to the Langmuir isotherm, see Eq. (E.5).

For a small coverage,  $Kc$  can be approximated with the Taylor series, which up to the second order is:

$$Kc \approx \frac{f}{1-e^{-f}}\theta + \frac{f^2(1+e^{-f})}{2(1-e^{-f})^2}\theta^2. \quad (22)$$

This expression can be rearranged to:

$$\frac{c}{\theta} \approx \frac{1}{K} \left[ \frac{f}{1-e^{-f}} + \frac{f^2(1+e^{-f})}{2(1-e^{-f})^2}\theta \right]. \quad (23)$$

The first order term in the above expansion yields a useful relation for the coverage at  $c \rightarrow 0$ , i.e.:

$$\theta \approx Kc \frac{1-e^{-f}}{f}. \quad (24)$$

By plugging this expression into the right side of Eq. (23), we obtain:

$$\left(\frac{c}{\theta}\right)_{c \rightarrow 0} = \frac{f}{K(1-e^{-f})} + \frac{f(1+e^{-f})}{2(1-e^{-f})}c, \quad \text{hence at } c = 0 : \quad (25)$$

$$\text{intercept} = \frac{f}{K(1-e^{-f})}, \quad \text{slope} = \frac{f(1+e^{-f})}{2(1-e^{-f})}.$$



**Table 1**

The expressions for the Langmuir, Frumkin, Flory–Huggins, and Temkin adsorption isotherms, along with the corresponding  $c/\theta$  intercepts and slopes at  $c = 0$ , as well as the expressions for standard adsorption Gibbs energies corresponding to several choices of adsorbate standard states; these choices are summarized in Table 2.

Isotherm	Intercept	$c/\theta$ slope at $c = 0$	Standard adsorption Gibbs energy expressions
Langmuir	$Kc = \frac{\theta}{1 - \theta}$	$\frac{1}{K}$	$1$ $\Delta G_{\text{ads}}^{\text{fit}} = \Delta G_{\text{ads}}^{\circ} = \Delta G_{\text{ads}}^{(0)} = \Delta G_{\text{ads}}^{(1/2)} = \Delta G_{\text{ads}}^{(1)}$
Frumkin	$Kc = \frac{\theta}{1 - \theta} \exp(2w\theta)$	$\frac{1}{K}$	$1 + 2w$ $\Delta G_{\text{ads}}^{\text{fit}} = \Delta G_{\text{ads}}^{\circ} = \Delta G_{\text{ads}}^{(0)}$ $\Delta G_{\text{ads}}^{(1/2)} = \Delta G_{\text{ads}}^{\circ} + RTw$ $\Delta G_{\text{ads}}^{(1)} = \Delta G_{\text{ads}}^{\circ} + 2RTw$ $\Delta G_{\text{ads}}^{\circ}$ also corresponds to ideal $\theta_{\text{Mol}} = 1$ and $\theta_{\text{H}_2\text{O}} = 1$ ; “ideal” implies $w = 0$
Flory–Huggins type	$Kc = \frac{\theta}{(1 - \theta)^n}$	$\frac{1}{K}$	$n$ $\Delta G_{\text{ads}}^{\text{fit}} = \Delta G_{\text{ads}}^{\circ} = \Delta G_{\text{ads}}^{(1)}$ $\Delta G_{\text{ads}}^{(0)}$ is undefined for $n > 1$ $\Delta G_{\text{ads}}^{(1/2)} = \Delta G_{\text{ads}}^{\circ} + (n - 1)RT \ln 2$
Temkin	$Kc = \frac{e^{f\theta} - 1}{1 - e^{f(\theta - 1)}}$	$\frac{f}{K(1 - e^{-f})}$	$\frac{f(1 + e^{-f})}{2(1 - e^{-f})}$ $\Delta G_{\text{ads}}^{\text{fit}} = \Delta G_{\text{ads}}^{(0)} = \Delta G_{\text{ads}}^{\circ} + RT \ln \frac{f}{1 - e^{-f}}$ $\Delta G_{\text{ads}}^{(1/2)} = \Delta G_{\text{ads}}^{\circ} + RT \frac{f}{2}$ $\Delta G_{\text{ads}}^{(1)} = \Delta G_{\text{ads}}^{\circ} + RT \ln \frac{e^f - 1}{f}$ $\Delta G_{\text{ads}}^{\circ}$ corresponds to ideal $\theta_{\text{Mol}} = 1$ and $\theta_{\text{H}_2\text{O}} = 1$ ; “ideal” implies $f = 0$

**Table 2**

Summary of the adsorbate standard states for substitutional adsorption, defined in Appendix B. Each choice of the standard state is labeled by a specific superscript label.

Adsorbate standard state	Coverage	Relation between $\theta_{\text{Mol}}$ and $\theta_{\text{H}_2\text{O}}$
$\theta^{(0)}$	$\theta \rightarrow 0^a$	$\theta_{\text{Mol}}^{(0)} = \theta_{\text{H}_2\text{O}}^{(0)}$
$\theta^{(1/2)}$	$\theta = 0.5$	$\theta_{\text{Mol}}^{(1/2)} = \theta_{\text{H}_2\text{O}}^{(1/2)}$
$\theta^{(1)}$	$\theta = 1$	$\theta_{\text{Mol}}^{(1)} = \theta_{\text{H}_2\text{O}}^{(1)}$
Ideal $\theta = 1$	Corresponds to hypothetical ideal Langmuir case with $\theta = 1$	

<sup>a</sup>For practical purposes, very low coverage can be used.

The expression for the slope is sufficiently complicated that its value is not immediately obvious. At  $f = 0$ , the slope is 1 as it should be because the Temkin isotherm reduces to the Langmuir isotherm, whereas for  $f > 0$ , the slope  $> 1$  (Fig. 3a).

While other isotherms considered above yield  $1/K$  for the intercept, for the Temkin isotherm, the intercept is “ $1/K$  multiplied by the factor  $f/(1 - e^{-f})$ ”; the dependence of this factor on  $f$  is shown in Fig. 3b (purple dashed curve). However, when the Temkin isotherm is fitted with Eq. (4), which is of the  $c/\theta = 1/K_{\text{fit}} + mc$  form, the intercept is interpreted as the inverse of the equilibrium constant. The relation between  $K$  and fitted  $K_{\text{fit}}$  is therefore:

$$K_{\text{fit}} = K \frac{(1 - e^{-f})}{f}. \quad (26)$$

This  $K_{\text{fit}}$  is equivalent to the adsorption equilibrium constant corresponding to the mean surface reactivity, Eq. (E.19). In contrast,  $K$  corresponds to the reactivity of the most reactive surface patch, cf. Eq. (E.18).  $K_{\text{fit}}$  thus better represents heterogeneous surface than  $K$ . That this is so can also be realized by noting that, generally, for linear adsorption isotherms [27] at very low coverage, the  $\theta \approx Kc$  relation holds.<sup>4</sup> But for the Temkin model, this relation holds for  $K_{\text{fit}}$ , i.e., by combining Eqs. (24) and (26), we get  $\theta \approx K_{\text{fit}}c$ .

<sup>4</sup> An example of a non-linear adsorption isotherm at low coverage is the Langmuir–Freundlich (or Sips) isotherm [28,29] with  $n > 1$ ,  $Kc = \theta^n/(1 - \theta)^n$ , for which  $c/\theta = 0$  at  $c = 0$ .

The standard adsorption Gibbs energies corresponding to  $K_{\text{fit}}$  and  $K$  are related by:

$$\Delta G_{\text{ads}}^{\text{fit}} = \Delta G_{\text{ads}}^{\circ} + RT \ln \frac{f}{1 - e^{-f}}. \quad (27)$$

This equation reveals that  $\Delta G_{\text{ads}}^{\text{fit}}$  is equivalent to  $\Delta G_{\text{ads}}^{(0)}$  of Eq. (E.15), that is, to standard adsorption Gibbs energy corresponding to adsorbate standard states of reactant  $\theta_{\text{H}_2\text{O}} \rightarrow 0$  and product  $\theta_{\text{Mol}} \rightarrow 0$ . In contrast,  $\Delta G_{\text{ads}}^{\circ}$  corresponds to particular reactant  $\theta_{\text{H}_2\text{O}}$  and product  $\theta_{\text{Mol}}$  coverages, whose expressions are complicated and depend on the value of  $f$  (see Appendix E); the other possibility that corresponds to  $\Delta G_{\text{ads}}^{\circ}$  is the so-called “ideal”  $\theta_{\text{Mol}} = 1$  and  $\theta_{\text{H}_2\text{O}} = 1$  standard state (this “ideal” standard state corresponds to a hypothetical situation with  $f = 0$ ; for more details, see Appendix E).

The difference between  $\Delta G_{\text{ads}}^{\text{fit}}$  and  $\Delta G_{\text{ads}}^{\circ}$  at room temperature is shown in Fig. 3b (solid green curve). Note that for  $f > 0$ ,  $\Delta G_{\text{ads}}^{\text{fit}} > \Delta G_{\text{ads}}^{\circ}$  because even at small coverage, some molecules adsorb to less reactive surface patches due to entropic reasons. Hence, the average adsorption binding is weaker compared to that on the most reactive surface patch. In this sense,  $\Delta G_{\text{ads}}^{\text{fit}}$  is the representative standard adsorption Gibbs energy because it corresponds to the actual heterogeneous surface. In contrast,  $\Delta G_{\text{ads}}^{\circ}$  corresponds to a hypothetical “ideal” surface that displays the reactivity of the most reactive surface patch (i.e.,  $f = 0$ ).

Fig. 4 shows exemplar Temkin isotherms for several values of  $f$ , plotted in the  $c/\theta$  vs.  $c$  form. For  $f = 1$ , the isotherm appears similar to the Langmuir isotherm but is upshifted. In contrast, the deviation from the linearity is more apparent for higher values of  $f$ .

### 3. Results

In the preceding section, a dependence of  $c/\theta$  on the concentration  $c$  was analyzed for the Frumkin, Flory–Huggins, and Temkin adsorption isotherms as to account for intermolecular interactions, molecular size, and surface heterogeneity. To aid in the comprehension of the material related to these isotherms, Table 1 lists the intercepts, slopes, and relations between standard adsorption Gibbs energies corresponding to different choices of the adsorbate standard states, listed in Table 2. Note that among the three considered non-Langmuir isotherms, the  $c/\theta$  slope at  $c = 0$  is less than 1 only for the attractive Frumkin isotherm.

Below, we consider how the linear regression of Eq. (4) is able to fit these isotherms and what errors are introduced by doing so. For each isotherm, three “virtual” experiments are performed, where the

**Table 3**

Summary of the results of the three virtual experiments, presented in Figs. 5–7. In addition to the estimated slopes ( $\text{slope}_{\text{fit}}$ ), equilibrium constants ( $K_{\text{fit}}$ ), and standard adsorption Gibbs energies ( $\Delta G_{\text{ads}}^{\text{fit}}$ ), obtained by the linear regression based on Eq. (4), also the true intercepts and slopes (at  $c = 0$  and 1 M) are reported for each isotherm. The isotherms correspond to the true equilibrium constant of  $K = 3.24 \cdot 10^3 \text{ M}^{-1}$ , corresponding to  $\Delta G_{\text{ads}}^* = -30 \text{ kJ/mol}$  at  $T = 298.15 \text{ K}$ . For the Temkin isotherm, the  $\Delta G_{\text{ads}}^{\text{fit}}$  values need to be corrected by Eq. (27) to obtain the  $\Delta G_{\text{ads}}^*$  values (reported in parentheses).

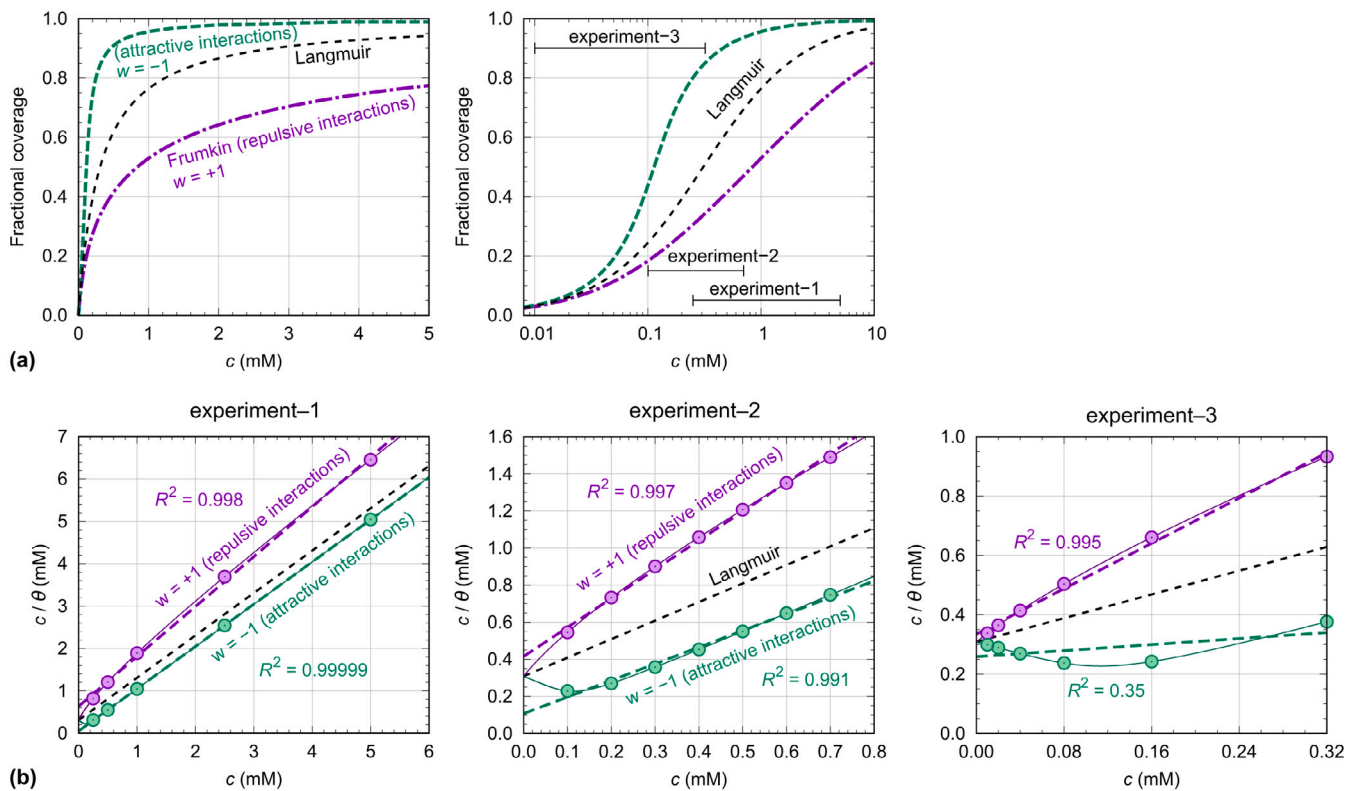
Isotherm	Intercept <sup>a</sup> (M)	Slope <sup>b</sup> at $c = 0$	Slope <sup>b</sup> at $c = 1 \text{ M}$	Experiment-1: $c \in [1, 6] \text{ mM}$			Experiment-2: $c \in [0.1, 0.7] \text{ mM}$			Experiment-3: $c \in [0.01, 0.32] \text{ mM}$		
				Slope <sub>fit</sub>	$K_{\text{fit}}$ ( $\text{M}^{-1}$ )	$\Delta G_{\text{ads}}^{\text{fit}}$ (kJ/mol)	Slope <sub>fit</sub>	$K_{\text{fit}}$ ( $\text{M}^{-1}$ )	$\Delta G_{\text{ads}}^{\text{fit}}$ (kJ/mol)	Slope <sub>fit</sub>	$K_{\text{fit}}$ ( $\text{M}^{-1}$ )	$\Delta G_{\text{ads}}^{\text{fit}}$ (kJ/mol)
Frumkin	$w = -1$	$3.09 \cdot 10^{-4}$	-1	1.00	$1.85 \cdot 10^4$	-34.3	0.89	$9.33 \cdot 10^3$	-32.6	0.25	$3.86 \cdot 10^3$	-30.4
	$w = +1$	$3.09 \cdot 10^{-4}$	+3	1.00	$1.58 \cdot 10^3$	-28.2	1.56	$2.41 \cdot 10^3$	-29.3	1.91	$2.98 \cdot 10^3$	-29.8
Flory–Huggins	$n = 2$	$3.09 \cdot 10^{-4}$	2	1.01	$2.03 \cdot 10^3$	-28.8	1.42	$2.77 \cdot 10^3$	-29.6	1.60	$3.13 \cdot 10^3$	-29.9
	$n = 3$	$3.09 \cdot 10^{-4}$	3	1.05	$1.61 \cdot 10^3$	-28.3	1.79	$2.48 \cdot 10^3$	-29.3	2.10	$3.02 \cdot 10^3$	-29.8
	$n = 5$	$3.09 \cdot 10^{-4}$	5	1.18	$1.21 \cdot 10^3$	-27.6	2.46	$2.11 \cdot 10^3$	-28.9	2.99	$2.83 \cdot 10^3$	-29.7
Temkin	$f = 1$	$4.88 \cdot 10^{-4}$	1.08	1.00	$1.97 \cdot 10^3$	-28.8 (-29.9) <sup>c</sup>	1.03	$2.02 \cdot 10^3$	-28.8 (-29.9) <sup>c</sup>	1.05	$2.04 \cdot 10^3$	-28.9 (-30.0) <sup>c</sup>
	$f = 2$	$7.14 \cdot 10^{-4}$	1.31	1.03	$1.26 \cdot 10^3$	-27.7 (-29.8) <sup>c</sup>	1.14	$1.36 \cdot 10^3$	-27.9 (-30.0) <sup>c</sup>	1.21	$1.39 \cdot 10^3$	-27.9 (-30.0) <sup>c</sup>
	$f = 3$	$9.74 \cdot 10^{-4}$	1.66	1.11	$8.67 \cdot 10^2$	-26.7 (-29.6) <sup>c</sup>	1.36	$9.90 \cdot 10^2$	-27.1 (-30.0) <sup>c</sup>	1.49	$1.02 \cdot 10^3$	-27.1 (-30.0) <sup>c</sup>
Langmuir	$3.09 \cdot 10^{-4}$	1	1	(Taken as the reference with $\Delta G_{\text{ads}}^* = -30 \text{ kJ/mol} \Rightarrow K = 3.24 \cdot 10^3 \text{ M}^{-1}$ )								

<sup>a</sup>The exact value of  $c/\theta$  at  $c = 0$  given by the isotherm.

<sup>b</sup>The exact slope,  $\partial(c/\theta)/\partial c$ , given by the isotherm.

<sup>c</sup>Value corrected to  $\Delta G_{\text{ads}}^*$  via Eq. (27); the corrections at  $T = 298.15 \text{ K}$  for  $f = 1, 2, 3$  are -1.1, -2.1, and -2.9 kJ/mol, respectively.

### Frumkin isotherms



**Fig. 5.** (a) Frumkin adsorption isotherms for attractive ( $w = -1$ ) and repulsive ( $w = +1$ ) lateral interactions for the equilibrium constant  $K$  corresponding to  $\Delta G_{\text{ads}}^* = -30 \text{ kJ/mol}$  at  $T = 298.15 \text{ K}$ . On the right plot, the concentration axis is logarithmic, and the concentration ranges used for the three virtual experiments in (b) are indicated. The Langmuir adsorption isotherm is shown for comparison (black dashed). (b) Data points, generated at selected concentrations with the Frumkin isotherms shown in (a), fitted with the linear  $c/\theta = 1/K + mc$  ansatz; concentrations are the highest for the virtual experiment-1 and the lowest for the virtual experiment-3. Thick dashed color lines are the fitted lines, and thin curves are the Frumkin isotherms. The coefficient of determination ( $R^2$ ) is also stated for each linear fit. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

## Flory–Huggins isotherms

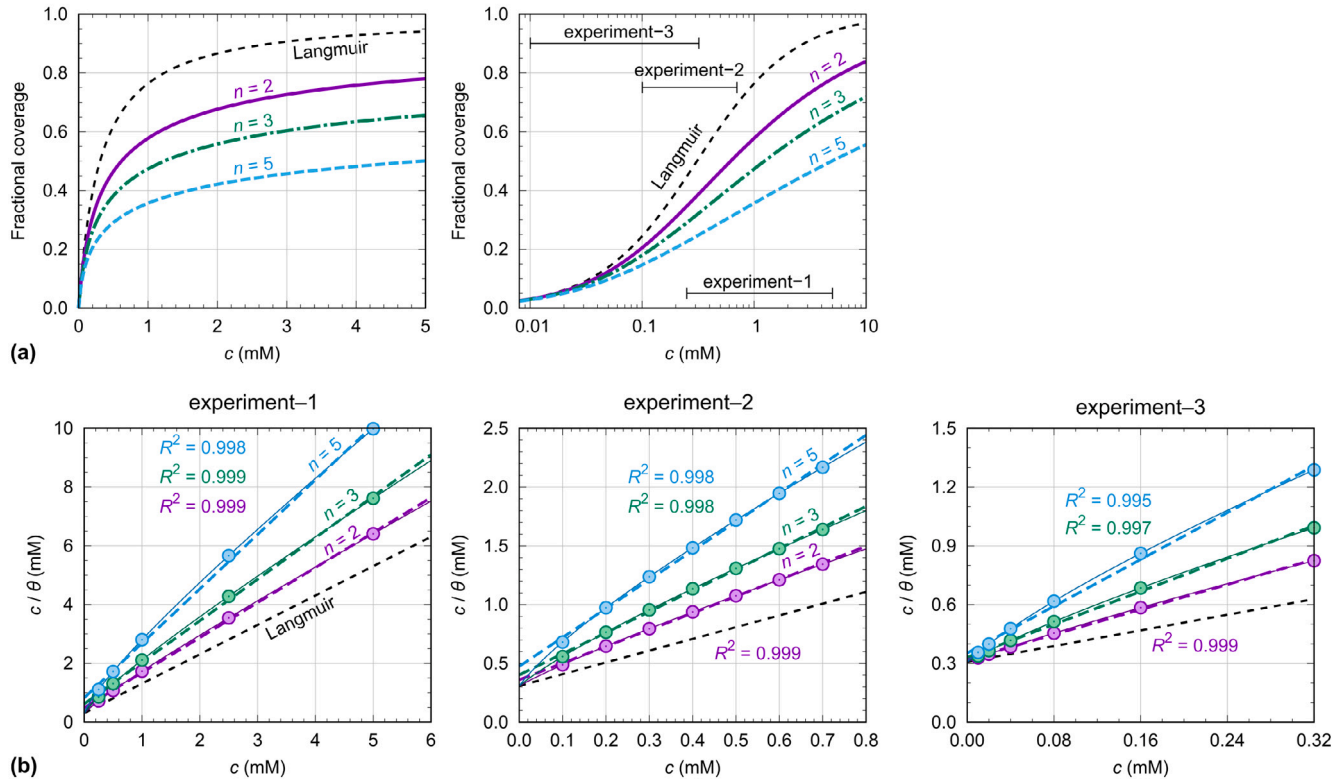


Fig. 6. Analogous to Fig. 5, but for the Flory–Huggins type adsorption isotherms. (a) Flory–Huggins type isotherms with  $n = 2, 3$ , and  $5$  for the equilibrium constant  $K$  corresponding to  $\Delta G_{\text{ads}}^{\circ} = -30$  kJ/mol at  $T = 298.15$  K. (b) Data points of the three virtual experiments fitted the linear  $c/\theta = 1/K + mc$  ansatz.

## Temkin isotherms

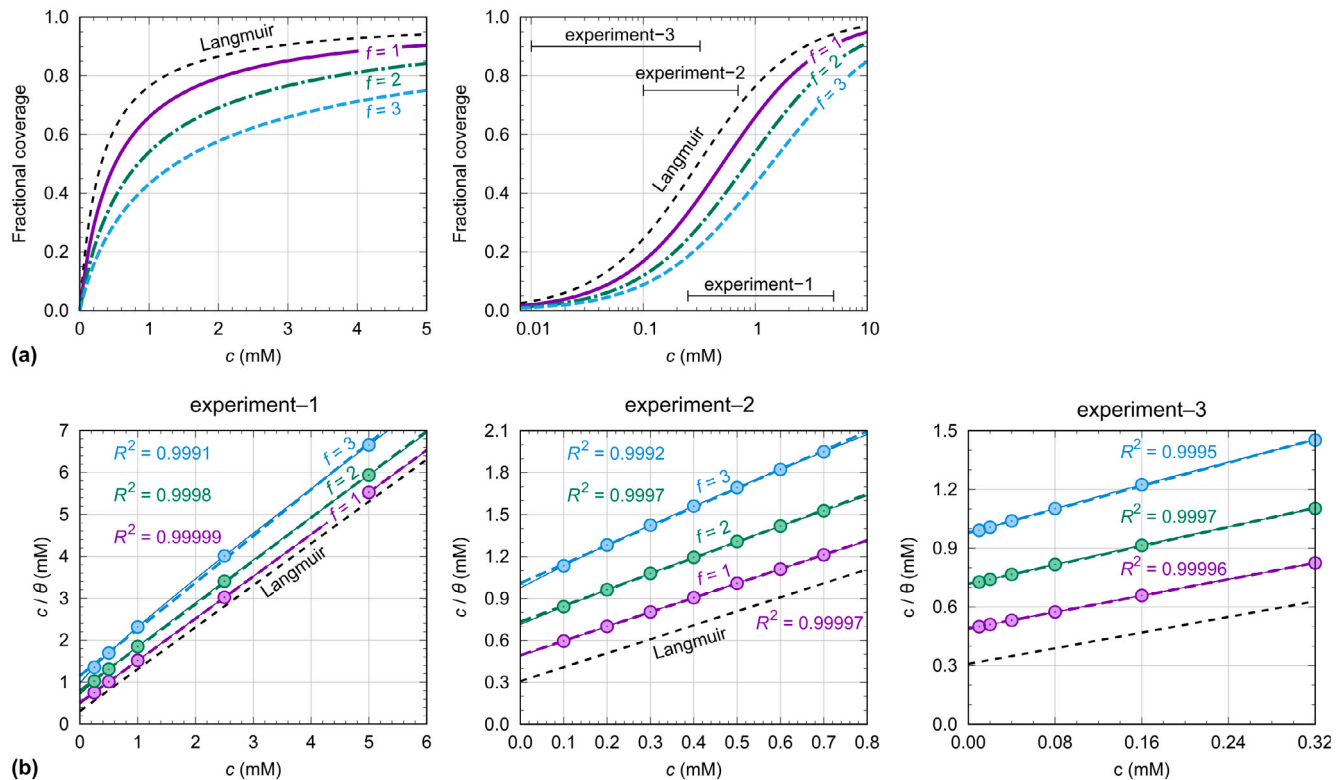


Fig. 7. Analogous to Fig. 5, but for the Temkin isotherms with  $f = 1, 2$ , and  $3$  for the equilibrium constant  $K$  corresponding to  $\Delta G_{\text{ads}}^{\circ} = -30$  kJ/mol at  $T = 298.15$  K.

isotherm is used to generate the  $(c, c/\theta)$  data points at specific concentrations. Concentrations are the highest for the virtual experiment-1 and the lowest for the virtual experiment-3. The specific concentrations are the following:

- (i) Experiment-1:  $c = 0.25, 0.5, 1, 2.5, 5$  mM.
- (ii) Experiment-2:  $c = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7$  mM.
- (iii) Experiment-3:  $c = 0.01, 0.02, 0.04, 0.08, 0.16, 0.32$  mM.

The equilibrium constant  $K$ , used in these experiments, was calculated with Eq. (3) by using  $\Delta G_{\text{ads}}^{\circ} = -30$  kJ/mol and  $T = 298.15$  K. The value of  $-30$  kJ/mol was chosen because it corresponds to the order of magnitude of many reported  $\Delta G_{\text{ads}}^{\circ}$  values in the corrosion inhibition literature and is in between the threshold values of  $-20$  and  $-40$  kJ/mol that are often used to distinguish between physisorption and chemisorption. Note that this 20/40 rule was criticized recently [3] by arguing that it is not a reliable criterion to distinguish between the two adsorption modes.

The results of these virtual experiments are shown in Figs. 5, 6, and 7 for the Frumkin, Flory–Huggins, and Temkin isotherms, respectively, whereas Table 3 summarizes the most important results. It is evident from these figures that the linear Eq. (4) is able to almost perfectly fit the “experiments”, with coefficients of determination being close to 1, i.e.,  $R^2 > 0.99$ . The only exception is the attractive Frumkin isotherm at the lowest considered coverage range (experiment-3), where  $R^2 = 0.35$  and the Frumkin isotherm differs significantly from the fitted line.

These results demonstrate that Eq. (4) is an effective equation that can describe various adsorption models. This finding explains why so many studies find that it is able to fit their experimental data. However, in many of them, the slope deviates from 1, yet the Langmuir model is claimed, which is incorrect because any significant deviation from the slope of 1 indicates a non-Langmuir adsorption model. Furthermore, notice from Table 3 that only linear regression of the attractive Frumkin isotherm at lower coverages (experiments 2 and 3) results in a slope less than 1, confirming the theoretical analysis of Section 2.

Other important findings, based on the current results, are: (i) the higher the concentrations used in fitting, the closer the slope is to 1. This is not only the result of the fitting but a general behavior of Type-I isotherms. Note in Table 3 that the true slopes at  $c = 0$  deviate considerably from 1, whereas at  $c = 1$  M, the majority of them are already very close to 1. Conversely, (ii) lower concentrations are better for spotting deviations from the slope of 1 and linearity. For the latter, not only small concentrations but also a wide-enough range of concentrations should be considered. (iii) According to numeric considerations, lower concentrations predict more accurate standard adsorption Gibbs energies (note that, for virtual experiment-1,  $\Delta G_{\text{ads}}^{\text{fit}}$  are the farthest from the actual  $\Delta G_{\text{ads}}^{\circ}$  of  $-30$  kJ/mol, whereas for virtual experiment-3, they are the most accurate). Indeed, the standard adsorption Gibbs energies, predicted with the linear regression, are quite accurate for the experiment-3, deviating by 0.2 kJ/mol or less from the true value (error below 1%), except for the attractive Frumkin isotherm, where the linear regression performs the worst, the error is 0.4 kJ/mol (or slightly above 1%). In contrast, for higher concentrations (virtual experiments 2 and 3), the errors are up to about 10%. However, lower concentrations can be more problematic experimentally because it is likely more difficult to determine accurate coverages due to higher experimental uncertainties at lower concentrations. Lower concentrations also require longer times for adsorption because the mass flux of molecules from bulk solution at concentration  $c$  to the surface is proportional to  $c/t^{1/2}$ , where  $t$  is the time [30]. Hence, the time needed to reach an equilibrium/steady-state coverage scales as  $t \propto c^{-2}$ , implying that, for example, a 10-times lower concentration requires a 100-times longer time to reach the equilibrium surface coverage. This aspect, therefore, needs to be considered in experiments because one must ensure that equilibrium/steady-state has been achieved before measuring the coverage to be used in the analysis.

Note that for the Temkin isotherm, the estimated standard adsorption Gibbs energies  $\Delta G_{\text{ads}}^{\text{fit}}$  were also corrected with Eq. (27) to correspond to  $\Delta G_{\text{ads}}^{\circ}$  (written in parentheses in Table 3) to yield a more direct comparison to the reference value of  $\Delta G_{\text{ads}}^{\circ} = -30$  kJ/mol. As explained in the Section 2.3 and Appendix E,  $\Delta G_{\text{ads}}^{\text{fit}}$  represents the actual heterogeneous surface and  $\Delta G_{\text{ads}}^{\circ}$  the most reactive surface patch.

Table 3 confirms the inferences put forward in the analysis section: for attractive (repulsive) Frumkin isotherms, the linear regression underestimates (overestimates) the intercepts, resulting in too high (low) equilibrium constants and too exergonic (endergonic) standard adsorption Gibbs energies. Also for Flory–Huggins and Temkin isotherms, the intercepts are slightly overestimated, resulting in slightly too endergonic standard adsorption Gibbs energies. Despite these systematic errors, current results firmly demonstrate that the three considered isotherms can be fitted quite well with the linear Eq. (4), resulting in accurate estimates of standard adsorption Gibbs energies. Table 3, therefore, empirically confirms the usability of Eq. (4) and provides strong support to the theoretically inferred claim in Section 2.2 that Eq. (4) is superior to Villamil Eq. (5). The latter equation gives higher adsorption equilibrium constants (for  $m > 1$ ) and, correspondingly, slightly more exergonic standard adsorption Gibbs energies, i.e.:

$$\Delta G_{\text{ads}}^{\text{fit, Villamil}} = \Delta G_{\text{ads}}^{\text{fit}} - RT \ln m. \quad (28)$$

At room temperature, the  $RT \ln m$  term is 1.7, 2.7, 3.4, and 4.0 kJ/mol for  $m = 2, 3, 4$ , and 5, respectively. Hence, for low values of  $m$ , these differences are moderate, which can be attributed to the logarithmic dependence of  $\Delta G_{\text{ads}}^{\circ}$  on the equilibrium constant. Due to moderate differences, it is possible that in some cases, the Villamil equation may provide more accurate estimates of  $\Delta G_{\text{ads}}^{\circ}$  due to error cancellation. However, such cases are serendipitous.

Real cases are most likely more complicated than the three considered isotherms. Yet still, based on current results, we can infer that the linear Eq. (4) is an effective and usable equation to estimate standard adsorption Gibbs energy, provided that the experimentally determined coverages are reliable and correspond to equilibrium/steady-state. The latter is an entirely different issue, and the usual practice, where inhibition efficiency is used as an estimate of the surface coverage, was recently criticized by Lindsay et al. [19].

#### 4. Conclusions

In this paper, we scrutinized whether the approach used in corrosion inhibition literature to estimate standard adsorption Gibbs energy is physically reasonable. This approach involves the linear regression of the  $c/\theta = 1/K + mc$  equation instead of the Langmuir  $c/\theta = 1/K + c$  isotherm. With the former equation, both the slope  $m$  and the intercept  $1/K$  are fitted. In contrast, the Langmuir isotherm requires a slope of 1. Herein, a theoretical basis for the  $c/\theta = 1/K + mc$  equation was established. It was demonstrated that the equation is very effective for describing various adsorption models, which explains why so many studies find that the equation is able to fit their experimental data. The equation can provide relatively accurate estimates for standard adsorption Gibbs energy, provided surface coverages were reliably determined experimentally and correspond to equilibrium/steady-state. The latter is particularly important for lower inhibitor concentrations in a solution that require considerably longer times to achieve equilibrium/steady-state coverage. It is also worth mentioning that the usual practice, where inhibition efficiency is used as an estimate of the surface coverage, was recently criticized [19].

When the  $c/\theta = 1/K + mc$  equation is used for linear regression of experimental data, any significant deviation from the slope of 1 implies non-Langmuir adsorption due to inter-adsorbate interactions, multi-site adsorption, or surface heterogeneity. Among these three causes, only attractive inter-adsorbate interactions lead to a slope of less than 1. For multi-site adsorption, it was shown that the slope  $m$  does not



correspond to the number of displaced water molecules  $n$  (or to the number of sites an inhibitor molecule adsorbs to), thus refuting the usual inference in the literature, which claims that  $m = n$ . In contrast,  $m$  can be significantly smaller than  $n$ .

It was further shown that for Type-I isotherms for which the saturation coverage is normalized to 1,  $c/\theta$  eventually becomes linearly proportional to  $c$  with the slope of 1 at high concentrations. In contrast, at very low concentrations, the slope can deviate considerably from 1 and depends on the adsorption isotherm type. This implies that when non-Langmuir adsorption is fitted with the linear  $c/\theta = 1/K + mc$  equation, the slope  $m$  depends on the concentration range used for fitting. In particular, the higher the concentrations, the closer the slope is to 1. Conversely, lower concentrations are better for spotting deviations from the slope of 1 and linearity. For the latter, also a wide-enough range of concentrations should be used. According to numeric considerations, linear regression performed at lower concentrations also predict more accurate standard adsorption Gibbs energies (here, low concentrations imply concentrations corresponding to low surface coverages). However, lower concentrations are likely more problematic experimentally, leading to larger errors in coverage determinations. For the Frumkin, Flory–Huggins, and Temkin isotherms, it was also shown to what adsorbate standard states the so-estimated standard adsorption Gibbs energies correspond.

## 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 data used by the manuscript are contained within it, whereas the scripts used to generate the graphs and results will be made available on request.

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## Appendix A. Langmuir isotherm: the “ideal” case

### A.1. Gas phase

In the gas phase, plain molecular adsorption can be written as:



where  $\text{Mol}_{(\text{g})}$ ,  $\square$ , and  $\text{Mol}_{(\text{ad})}$  stand for a molecule in the gas phase, free adsorption site, and adsorbed molecule, respectively. With a thermodynamic approach, the Langmuir adsorption isotherm can be straightforwardly derived by treating adsorption sites as quasi-chemical species. The fundamental premise of the Langmuir adsorption model is the absence of intermolecular interactions,<sup>5</sup> hence the activities of species

<sup>5</sup> Other assumptions of the Langmuir adsorption model are that all adsorption sites are equivalent, only up to one molecule is adsorbed onto an adsorption site, and the maximum coverage is a single monolayer.

in reaction (A.1) can be replaced with mole and site fractions. Hence, the adsorption equilibrium constant can be written as:

$$K_{\text{ads}} = \frac{[\text{Mol}_{(\text{ad})}]}{[\text{Mol}_{(\text{g})}][\square]} = \frac{\theta}{x_{\text{Mol}}(1 - \theta)}, \quad (\text{A.2})$$

where  $\theta$  is the fractional molecular coverage,  $(1 - \theta)$  is the site fraction of free adsorption sites, and  $x_{\text{Mol}}$  is the molecular mole fraction in the gas phase that can be expressed with respect to a standard pressure  $p^\circ$  as  $x_{\text{Mol}} = p/p^\circ$ , where  $p$  is the molecular partial pressure. Hence:

$$K_{\text{ads}} = \frac{p^\circ \theta}{p(1 - \theta)} \quad (\text{A.3})$$

Usually, the Langmuir isotherm is written as:

$$K = \frac{\theta}{p(1 - \theta)}, \quad \text{hence: } K_{\text{ads}} = p^\circ K. \quad (\text{A.4})$$

If  $p^\circ$  is set to 1 bar,  $K_{\text{ads}}$  and  $K$  are numerically equivalent, but  $K$  has the unit of  $\text{bar}^{-1}$ , whereas  $K_{\text{ads}}$  is unitless.

At non-equilibrium pressure  $p$  and coverage  $\theta$ , the Gibbs energy of adsorption ( $\Delta G_{\text{ads}}$ ) can be written as [31]:

$$\Delta G_{\text{ads}} = \Delta G_{\text{ads}}^\circ + RT \ln \frac{\theta}{1 - \theta} - RT \ln \frac{p}{p^\circ}, \quad (\text{A.5})$$

where  $\Delta G_{\text{ads}}^\circ$  is the standard adsorption Gibbs energy. This equation implies that a convenient choice for the adsorbate standard state is  $\theta^\circ = 0.5$  because the logarithmic term vanishes, i.e., plugging  $\theta = 0.5$  and  $p = p^\circ$  into Eq. (A.5) leads to  $\Delta G_{\text{ads}} = \Delta G_{\text{ads}}^\circ$ .

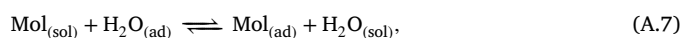
### A.2. Aqueous phase

If the adsorption of solvated molecular species on a sample immersed into a solution is considered as a plain adsorption reaction (10), which is analogous to reaction (A.1), the aqueous-phase adsorption can be treated analogously to the gas-phase adsorption by replacing the partial pressure  $p$  with molecular molar concentration  $c$ . Hence, Eq. (A.4) can be rewritten as:

$$K = \frac{\theta}{c(1 - \theta)}, \quad (\text{A.6})$$

where  $K$  has a unit of  $\text{M}^{-1}$ . A reasonable choice for the standard states is  $c^\circ = 1 \text{ M}$  and  $\theta^\circ = 0.5$ .

In contrast, if aqueous-phase molecular adsorption is considered as substitutional adsorption:



then the adsorption equilibrium constant is:

$$K_{\text{ads}} = \frac{[\text{Mol}_{(\text{ad})}][\text{H}_2\text{O}_{(\text{sol})}]}{[\text{Mol}_{(\text{sol})}][\text{H}_2\text{O}_{(\text{ad})}]} = \frac{\theta x_{\text{H}_2\text{O}}}{x_{\text{Mol}}(1 - \theta)}. \quad (\text{A.8})$$

Mole fractions in a solution can be expressed as:

$$x_{\text{H}_2\text{O}} = \frac{c_{\text{H}_2\text{O}}}{c_{\text{H}_2\text{O}} + c} \quad \text{and} \quad x_{\text{Mol}} = \frac{c}{c_{\text{H}_2\text{O}} + c}, \quad (\text{A.9})$$

so that their ratio is:

$$\frac{x_{\text{H}_2\text{O}}}{x_{\text{Mol}}} = \frac{c_{\text{H}_2\text{O}}}{c}. \quad (\text{A.10})$$

Hence, Eq. (A.8) can be rewritten as:

$$K_{\text{ads}} = \frac{\theta c_{\text{H}_2\text{O}}}{c(1 - \theta)} = c_{\text{H}_2\text{O}} K, \quad (\text{A.11})$$

where  $K$  is defined by Eq. (A.6). The molarity of pure water at 25 °C is  $c_{\text{H}_2\text{O}} = 55.34 \text{ M}$ , although the value of 55.5 M is often used instead. The latter value corresponds to the density of water of 1 kg/L, but the correct density at 25 °C is 0.997048 kg/L [1].

The fundamental thermodynamic relation between the standard adsorption Gibbs energy and equilibrium constant is:

$$K_{\text{ads}} = \exp\left(-\frac{\Delta G_{\text{ads}}^\circ}{RT}\right). \quad (\text{A.12})$$

However, usually the constant  $K$  is utilized instead of  $K_{\text{ads}}$ , which implies:

$$K = \frac{1}{c_{\text{H}_2\text{O}}} \exp\left(-\frac{\Delta G_{\text{ads}}^{\circ}}{RT}\right). \quad (\text{A.13})$$

The standard Gibbs energy of adsorption is, therefore:

$$\begin{aligned} \Delta G_{\text{ads}}^{\circ} &= -RT \ln K_{\text{ads}} \\ &= -RT \ln [K \cdot (1 \text{ M})] - RT \ln \frac{c_{\text{H}_2\text{O}}}{1 \text{ M}} \\ &= -RT \ln [K \cdot (1 \text{ M})] - 10 \text{ kJ/mol} \quad \text{at } T = 298.15 \text{ K}, \end{aligned} \quad (\text{A.14})$$

where 1 M is used to make the logarithmic terms unitless (1 M can be seen as a standard state concentration,  $c^{\circ}$ ). Hence, for the same adsorbate at room temperature, the standard adsorption Gibbs energy of the substitutional reaction (A.7) is 10 kJ/mol more exergonic than that of the plain reaction (10). Therefore, it matters how the adsorption reaction is defined.

As for the convenient standard states, in addition to the coverage of 0.5 discussed above, there is another choice, based on the chemical potentials of involved species [31,32], which, for the ideal case, can be written as:

$$\mu_{\text{Mol(ads)}} = \mu_{\text{Mol(ads)}}^{\circ} + RT \ln \theta_{\text{Mol}}, \quad (\text{A.15})$$

$$\mu_{\text{H}_2\text{O(ads)}} = \mu_{\text{H}_2\text{O(ads)}}^{\circ} + RT \ln \theta_{\text{H}_2\text{O}}, \quad (\text{A.16})$$

$$\mu_{\text{Mol(sol)}} = \mu_{\text{Mol(sol)}}^{\circ} + RT \ln x_{\text{Mol}}, \quad (\text{A.17})$$

$$\mu_{\text{H}_2\text{O(sol)}} = \mu_{\text{H}_2\text{O(sol)}}^{\circ} + RT \ln x_{\text{H}_2\text{O}}, \quad (\text{A.18})$$

These equations suggest unit fractional coverages ( $\theta_{\text{Mol}}^{\circ} = \theta_{\text{H}_2\text{O}}^{\circ} = 1$ ) and unit mole fractions ( $x_{\text{Mol}} = x_{\text{H}_2\text{O}} = 1$ ) as convenient standard states.<sup>6</sup>

Based on Eqs. (A.15)–(A.18), the adsorption Gibbs energy can be written as:

$$\begin{aligned} \Delta G_{\text{ads}} &= \mu_{\text{products}} - \mu_{\text{reactants}} \\ &= \mu_{\text{Mol(ads)}} + \mu_{\text{H}_2\text{O(sol)}} - (\mu_{\text{Mol(sol)}} + \mu_{\text{H}_2\text{O(ads)}}) \\ &= \mu_{\text{Mol(ads)}} - \mu_{\text{H}_2\text{O(ads)}} - (\mu_{\text{Mol(sol)}} - \mu_{\text{H}_2\text{O(sol)}}) \\ &= \Delta G_{\text{ads}}^{\circ} + RT \ln \frac{\theta_{\text{Mol}}}{\theta_{\text{H}_2\text{O}}} - RT \ln \frac{x_{\text{Mol}}}{x_{\text{H}_2\text{O}}}, \end{aligned} \quad (\text{A.19})$$

where:

$$\Delta G_{\text{ads}}^{\circ} = \mu_{\text{Mol(ads)}}^{\circ} + \mu_{\text{H}_2\text{O(sol)}}^{\circ} - (\mu_{\text{Mol(sol)}}^{\circ} + \mu_{\text{H}_2\text{O(ads)}}^{\circ}). \quad (\text{A.20})$$

The two logarithmic terms in Eq. (A.19) vanish when  $\theta_{\text{Mol}} = \theta_{\text{H}_2\text{O}}$  and  $x_{\text{Mol}} = x_{\text{H}_2\text{O}}$ ; in such a case  $\Delta G_{\text{ads}}$  becomes  $\Delta G_{\text{ads}}^{\circ}$ . Hence, in the ideal case, the requirement for a reasonable choice of standard states is that reactant  $\text{H}_2\text{O}_{(\text{ad})}$  and product  $\text{Mol}_{(\text{ad})}$  are considered at the same coverages, and reactant  $\text{Mol}_{(\text{sol})}$  and product  $\text{H}_2\text{O}_{(\text{sol})}$  at the same concentrations, i.e.,  $\theta_{\text{Mol}} = \theta_{\text{H}_2\text{O}}$  and  $x_{\text{Mol}} = x_{\text{H}_2\text{O}}$ . It is worth observing that  $\theta = 0.5$  in Eq. (A.5) is equivalent to  $\theta_{\text{Mol}} = \theta_{\text{H}_2\text{O}}$  in Eq. (A.19).

## Appendix B. Standard states: some considerations

In non-ideal cases, the chemical potentials of species, involved in the substitutional adsorption reaction (A.7), can be written as:

$$\mu_{\text{Mol(ads)}} = \mu_{\text{Mol(ads)}}^{\circ} + RT \ln a_{\text{Mol(ads)}}, \quad (\text{B.1})$$

$$\mu_{\text{H}_2\text{O(ads)}} = \mu_{\text{H}_2\text{O(ads)}}^{\circ} + RT \ln a_{\text{H}_2\text{O(ads)}}, \quad (\text{B.2})$$

$$\mu_{\text{Mol(sol)}} = \mu_{\text{Mol(sol)}}^{\circ} + RT \ln a_{\text{Mol(sol)}}, \quad (\text{B.3})$$

$$\mu_{\text{H}_2\text{O(sol)}} = \mu_{\text{H}_2\text{O(sol)}}^{\circ} + RT \ln a_{\text{H}_2\text{O(sol)}}, \quad (\text{B.4})$$

<sup>6</sup> Instead of  $x_{\text{Mol}} = x_{\text{H}_2\text{O}} = 1$ , also  $c_{\text{Mol}} = c_{\text{H}_2\text{O}} = 1 \text{ M}$  can be chosen (it gives the same  $\Delta G_{\text{ads}}^{\circ}$  result in the ideal case).

where  $a_i$  stands for the activity of the species  $i$ . Obviously, these equations imply that for standard states,  $a_i = 1$ .<sup>7</sup> Based on the above equations, the adsorption Gibbs energy can be written as (cf. Eq. (A.19)):

$$\Delta G_{\text{ads}} = \Delta G_{\text{ads}}^{\circ} + RT \ln \frac{a_{\text{Mol(ads)}}}{a_{\text{H}_2\text{O(ads)}}} - RT \ln \frac{a_{\text{Mol(sol)}}}{a_{\text{H}_2\text{O(sol)}}}. \quad (\text{B.5})$$

This equation corresponds to a case where a molecule replaces a single water molecule during adsorption, reaction (A.7). The case where a molecule replaces several water molecules is considered in Appendix D.

Eq. (B.5) suggests that, for the substitutional adsorption, it is convenient to require  $a_{\text{Mol(ads)}} = a_{\text{H}_2\text{O(ads)}}$  and  $a_{\text{Mol(sol)}} = a_{\text{H}_2\text{O(sol)}}$  for standard states (in the case where a molecule replaces  $n$  adsorbed water molecules, the corresponding conditions are  $a_{\text{Mol(ads)}} = a_{\text{H}_2\text{O(ads)}}^n$  and  $a_{\text{Mol(sol)}} = a_{\text{H}_2\text{O(sol)}}^n$ ). Note that, by definition,  $a_i = 1$  for any choice of a standard state because the choice affects the value of  $\mu_i^{\circ}$  instead. In this sense, the  $a_{\text{Mol(ads)}} = a_{\text{H}_2\text{O(ads)}}$  and  $a_{\text{Mol(sol)}} = a_{\text{H}_2\text{O(sol)}}$  conditions correspond to choices that leave  $\Delta G_{\text{ads}}^{\circ}$  invariant.

If the *unsymmetrical* reference system [33] is chosen for the chemical potentials in the bulk solution,<sup>8</sup> then, for dilute solutions, activities can be approximated by concentrations:

$$\text{for } x_{\text{Mol}} \rightarrow 0: \quad \frac{a_{\text{Mol(sol)}}}{a_{\text{H}_2\text{O(sol)}}} \approx \frac{x_{\text{Mol}}}{x_{\text{H}_2\text{O}}} = \frac{c}{c_{\text{H}_2\text{O}}}. \quad (\text{B.6})$$

Consequently, the adsorption equilibrium constant can be written as (cf. Eq. (A.11)):

$$K_{\text{ads}} = \frac{a_{\text{Mol(ads)}} c_{\text{H}_2\text{O}}}{a_{\text{H}_2\text{O(ads)}} c} = c_{\text{H}_2\text{O}} K, \quad \text{hence: } Kc = \frac{a_{\text{Mol(ads)}}}{a_{\text{H}_2\text{O(ads)}}}. \quad (\text{B.7})$$

Note that according to Eq. (6), isotherms can be written in the  $Kc = f(\theta)$  form, where  $f(\theta)$  stands for a “function-of-coverage”. Hence:

$$Kc = \frac{a_{\text{Mol(ads)}}}{a_{\text{H}_2\text{O(ads)}}} = f(\theta), \quad (\text{B.8})$$

where  $\theta \equiv \theta_{\text{Mol}}$  and, for a given adsorption configuration,  $\theta_{\text{H}_2\text{O}} = 1 - \theta$ . With aid of Eqs. (B.6) and (B.8), the adsorption Gibbs energy of Eq. (B.5) can be written as:

$$\Delta G_{\text{ads}} = \Delta G_{\text{ads}}^{\circ} + RT \ln f(\theta) - RT \ln \frac{x_{\text{Mol}}}{x_{\text{H}_2\text{O}}}. \quad (\text{B.9})$$

This equation is analogous to Eq. (7) for plain adsorption.

If instead of activities, coverages are used, Eq. (B.9) becomes:

$$\begin{aligned} \Delta G_{\text{ads}} &= \Delta G_{\text{ads}}^{\circ} + RT \ln \frac{\gamma_{\text{Mol(ads)}} \theta_{\text{Mol}}}{\gamma_{\text{H}_2\text{O(ads)}} \theta_{\text{H}_2\text{O}}} - RT \ln \frac{x_{\text{Mol}}}{x_{\text{H}_2\text{O}}}, \\ &= \Delta G_{\text{ads}}^{\oplus} + RT \ln \frac{\theta_{\text{Mol}}}{\theta_{\text{H}_2\text{O}}} - RT \ln \frac{x_{\text{Mol}}}{x_{\text{H}_2\text{O}}}, \end{aligned} \quad (\text{B.10})$$

where  $\gamma_i$  is the activity coefficient of the adsorbed species  $i$ , and<sup>9</sup>:

$$\Delta G_{\text{ads}}^{\oplus} = \Delta G_{\text{ads}}^{\circ} + RT \ln \frac{\gamma_{\text{Mol(ads)}}}{\gamma_{\text{H}_2\text{O(ads)}}}. \quad (\text{B.11})$$

In the ideal case, all activity coefficients are 1 and  $\Delta G_{\text{ads}}^{\oplus} = \Delta G_{\text{ads}}^{\circ}$ , but for non-ideal cases,  $\Delta G_{\text{ads}}^{\oplus}$  depends on the chosen surface coverage even for  $\theta_{\text{Mol}} = \theta_{\text{H}_2\text{O}}$ . Hence, in the following, we will use four choices for the standard states:

<sup>7</sup> This condition does not yet determine standard states because activities are defined as fugacity ratios,  $a_i = f_i/f_i^{\circ}$ , where  $f_i^{\circ}$  is the fugacity of the standard state, which can be chosen according to convenience. A given choice of the standard state thus determines  $f_i^{\circ}$  and  $\mu_i^{\circ}$ .

<sup>8</sup> In the *unsymmetrical* reference system, the standard state for a solvent corresponds to a pure solvent, and the standard state for a solute to a hypothetical ideal solution having  $x_{\text{Mol}} = 1$ . Consequently, for dilute solutions ( $x_{\text{Mol}} \rightarrow 0$ ), where the solvent follows Raoult's law and the solute follows Henry's law, the activity coefficients are  $\gamma_{\text{H}_2\text{O(sol)}} \rightarrow 1$  and  $\gamma_{\text{Mol(sol)}} \rightarrow 1$ . Hence, activities can be replaced with concentrations [33,34].

<sup>9</sup> If also the non-ideality of a solution is taken into account,  $\Delta G_{\text{ads}}^{\oplus}$  is:

$$\Delta G_{\text{ads}}^{\oplus} = \Delta G_{\text{ads}}^{\circ} + RT \ln \frac{\gamma_{\text{Mol(ads)}}}{\gamma_{\text{H}_2\text{O(ads)}}} - RT \ln \frac{\gamma_{\text{Mol(sol)}}}{\gamma_{\text{H}_2\text{O(sol)}}}.$$

1. Coverages corresponding to  $f(\theta) = 1$  (or, equivalently,  $a_{\text{Mol(ad)}} = a_{\text{H}_2\text{O(ad)}}$ ), for which the first logarithmic term in Eq. (B.9) vanishes. These coverages depend on the adsorption model. Such standard states are labeled by the  $\ominus$  superscript, i.e.,  $\theta_{\text{Mol}}^{\ominus}$  and  $\theta_{\text{H}_2\text{O}}^{\ominus}$ . The corresponding standard adsorption Gibbs energy is labeled by  $\Delta G_{\text{ads}}^{\ominus}$ .
2. An exceedingly small coverage,  $\theta \rightarrow 0$ . This standard state is labeled by the  $(0)$  superscript. The corresponding labels are:  $\theta_{\text{Mol}}^{(0)}$ ,  $\theta_{\text{H}_2\text{O}}^{(0)}$ , and  $\Delta G_{\text{ads}}^{(0)}$ . Note that for  $\theta_i = 0$ , the corresponding chemical potential is  $\mu_{i(\text{ad})} = -\infty$ ; however, these infinities cancel for  $\Delta G_{\text{ads}}^{(0)}$ . Nevertheless, to have definite values of  $\mu_i^{(0)}$ , extra low coverage can be chosen for all adsorbed species, e.g.,  $\theta_i^{(0)} = 10^{-6}$ .
3. Coverage of one-half,  $\theta = 0.5$ . The corresponding labels are:  $\theta_{\text{Mol}}^{(1/2)}$ ,  $\theta_{\text{H}_2\text{O}}^{(1/2)}$ , and  $\Delta G_{\text{ads}}^{(1/2)}$ .
4. Full monolayer coverage,  $\theta = 1$ . The corresponding labels are:  $\theta_{\text{Mol}}^{(1)}$ ,  $\theta_{\text{H}_2\text{O}}^{(1)}$ , and  $\Delta G_{\text{ads}}^{(1)}$ .

Note that for the ideal (Langmuir) case,  $\Delta G_{\text{ads}}^{\ominus} = \Delta G_{\text{ads}}^{(0)} = \Delta G_{\text{ads}}^{(1/2)} = \Delta G_{\text{ads}}^{(1)}$ , i.e., the standard adsorption Gibbs energy is independent on the chosen standard state  $\theta_{\text{Mol}} = \theta_{\text{H}_2\text{O}}$  coverage. In contrast, for non-ideal cases, standard adsorption Gibbs energy depends on the chosen standard state  $\theta_{\text{Mol}} = \theta_{\text{H}_2\text{O}}$  coverage as explained above.

### Appendix C. Frumkin isotherm: lateral interactions

The Frumkin isotherm [21] takes into account lateral interactions between adsorbed molecules and can be written as [22]<sup>10</sup>:

$$Kc = \frac{\theta}{1-\theta} \exp(2w\theta). \quad (\text{C.1})$$

where  $w$  is a unitless parameter describing lateral interactions between adsorbed molecules ( $w < 0$  for attractive interactions, and  $w > 0$  for repulsive interactions), expressed with the magnitude of the  $RT$  units, i.e.:

$$w = \frac{\varepsilon_{\text{lat}}}{RT}, \quad (\text{C.2})$$

where  $\varepsilon_{\text{lat}}$  is a measure of lateral intermolecular energy.

For substitutional adsorption reaction (A.7), only lateral interactions between  $\text{Mol}_{(\text{ad})}$  species are considered herein, whereas, for water molecules, they are neglected. Hence,  $w$  can be seen as describing effective lateral interactions, i.e., the difference in the lateral interactions between  $\text{Mol}_{(\text{ad})}$  and  $\text{H}_2\text{O}_{(\text{ad})}$ . The chemical potentials of adsorbed species can thus be written as (cf. Eqs. (B.1) and (B.2)):

$$\mu_{\text{Mol(ad)}} = \mu_{\text{Mol(ad)}}^{\ominus} + k_B T \ln \theta_{\text{Mol}} + 2\varepsilon_{\text{lat}} \theta_{\text{Mol}}, \quad (\text{C.3})$$

$$\mu_{\text{H}_2\text{O(ad)}} = \mu_{\text{H}_2\text{O(ad)}}^{\ominus} + k_B T \ln \theta_{\text{H}_2\text{O}}, \quad (\text{C.4})$$

and consequently:

$$\mu_{\text{Mol(ad)}} - \mu_{\text{H}_2\text{O(ad)}} = \mu_{\text{Mol(ad)}}^{\ominus} - \mu_{\text{H}_2\text{O(ad)}}^{\ominus} + k_B T \ln \frac{\theta_{\text{Mol}}}{\theta_{\text{H}_2\text{O}}} + 2\varepsilon_{\text{lat}} \theta_{\text{Mol}}, \quad (\text{C.5})$$

which leads to:

$$\Delta G_{\text{ads}} = \Delta G_{\text{ads}}^{\ominus} + RT \ln \frac{\theta_{\text{Mol}}}{\theta_{\text{H}_2\text{O}}} + 2\varepsilon_{\text{lat}} \theta_{\text{Mol}} + \text{s.t.}, \quad (\text{C.6})$$

where “s.t.” stands for *solution term*. It pertains to species in the solution and is irrelevant to the discussion below. According to Eqs. (C.3) and (C.4), *natural* choices for the standard states are  $\theta_{\text{H}_2\text{O}} = 1$  and a coverage of  $\text{Mol}_{(\text{ad})}$  at which  $\ln \theta_{\text{Mol}} + 2w\theta_{\text{Mol}} = 0$ . The latter is inconvenient because it depends on the value of  $w$ . A more convenient

<sup>10</sup> Note that the exponential term is often written with the minus sign as  $\exp(-2w\theta)$  or even without the factor 2 as  $\exp(-w\theta)$ ; for the emergence of factor 2, see, for example, Ref. [35]. Here, we use  $\exp(2w\theta)$  so that  $w$  follows the standard thermodynamic sign convention (i.e.,  $w < 0$  for attraction).

choice is the “ideal  $\theta_{\text{Mol}} = 1$ ” [32]; the “ideal  $\theta_{\text{Mol}} = 1$ ” is a hypothetical state with  $\theta_{\text{Mol}} = 1$  and infinite distances between adsorbed molecules so that  $w = 0$ .

Another convenient choice is based on Eq. (C.5), where the logarithmic term vanishes for  $\theta_{\text{Mol}} = \theta_{\text{H}_2\text{O}}$ . Hence, the standard state coverages can be chosen as  $\theta_{\text{Mol}} = \theta_{\text{H}_2\text{O}} \ll 1$ , where the lateral interactions are negligible,  $w \rightarrow 0$ . In this case, chemical potentials are:

$$\mu_{\text{Mol(ad)}}^{(0)} = \mu_{\text{Mol(ad)}}^{\ominus} + k_B T \ln \theta_{\text{Mol}}^{(0)}, \quad (\text{C.7})$$

$$\mu_{\text{H}_2\text{O(ad)}}^{(0)} = \mu_{\text{H}_2\text{O(ad)}}^{\ominus} + k_B T \ln \theta_{\text{H}_2\text{O}}^{(0)}, \quad (\text{C.8})$$

and the corresponding standard adsorption Gibbs energy is:

$$\Delta G_{\text{ads}}^{(0)} = \Delta G_{\text{ads}}^{\ominus}. \quad (\text{C.9})$$

If one chooses the true  $\theta_{\text{Mol}} = 1$  and  $\theta_{\text{H}_2\text{O}} = 1$  as the standard states, then the corresponding chemical potentials are (cf. Eq. (C.3)):

$$\mu_{\text{Mol(ad)}}^{(1)} = \mu_{\text{Mol(ad)}}^{\ominus} + 2\varepsilon_{\text{lat}} \quad \text{and} \quad \mu_{\text{H}_2\text{O(ad)}}^{(1)} = \mu_{\text{H}_2\text{O(ad)}}^{\ominus}, \quad (\text{C.10})$$

resulting in the following standard adsorption Gibbs energy:

$$\Delta G_{\text{ads}}^{(1)} = \Delta G_{\text{ads}}^{\ominus} + 2\varepsilon_{\text{lat}}. \quad (\text{C.11})$$

Hence, even if  $\theta_{\text{H}_2\text{O}} = \theta_{\text{Mol}}$  is chosen for the standard states, the standard adsorption Gibbs energy depends on the coverage (or, alternatively, on how much the lateral interactions are plugged in). The “average” standard adsorption Gibbs energy for  $\theta_{\text{Mol}} = \theta_{\text{H}_2\text{O}}$  choices can be calculated as:

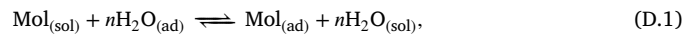
$$\langle \Delta G_{\text{ads}}^{\theta} \rangle = \Delta G_{\text{ads}}^{\ominus} + \int_0^1 2\varepsilon_{\text{lat}} \theta d\theta = \Delta G_{\text{ads}}^{\ominus} + \varepsilon_{\text{lat}}, \quad (\text{C.12})$$

which corresponds to the value of standard adsorption Gibbs energy for the  $\theta_{\text{Mol}} = \theta_{\text{H}_2\text{O}} = 0.5$  standard states (cf. Eq. (C.6)):

$$\Delta G_{\text{ads}}^{(1/2)} = \Delta G_{\text{ads}}^{\ominus} + \varepsilon_{\text{lat}} = \langle \Delta G_{\text{ads}}^{\theta} \rangle. \quad (\text{C.13})$$

### Appendix D. Flory–Huggins type isotherms: accounting for molecular size

The Flory–Huggins isotherm [22] describes substitutional adsorption and takes into account molecular size. Hence, adsorption is considered by the following reaction:



which implies that a molecule  $\text{Mol}$  replaces  $n$  water molecules during adsorption. There are several variants of the Flory–Huggins isotherm, but the one derived by statistical mechanics was given by Dhar et al. [26]<sup>11</sup>:

$$Kc = \frac{\theta}{(1-\theta)^n} \exp(1-n). \quad (\text{D.2})$$

<sup>11</sup> If, instead of the mole-fraction statistics, a site-fraction statistics is used for the bulk solution phase, the Dhar–Flory–Huggins isotherm is [26]:

$$Kc = \frac{\theta}{n(1-\theta)^n} \exp(1-n).$$

As for other isotherm variants, for example, Parsons [36] used the following form of the Flory–Huggins isotherm:

$$Kc = \frac{\theta}{n(1-\theta)^n},$$

which is equivalent to the multisite Langmuir adsorption isotherm derived by statistical mechanics by Nitta et al. [37]. This isotherm can also be derived by a quasi-thermodynamic approach from reaction (D.1) by using the site-fractions for the bulk solution phase [26]. If, instead, mole fractions are used for the bulk solution, the isotherm reads:

$$Kc = \frac{\theta}{(1-\theta)^n}.$$

Standard adsorption Gibbs energies derived from various variants of the Flory–Huggins isotherm differ by a constant that depends on  $n$  only, hence they can be interconverted.

Statistical-mechanics considerations reveal that for the Dhar–Flory–Huggins model, the chemical potentials of the adsorbed species can be written as [31]:

$$\mu_{\text{Mol(ad)}} = \mu_{\text{Mol(ad)}}^{\circ} + RT \ln \theta_{\text{Mol}} + RT(1 - \theta_{\text{Mol}})(1 - n), \quad (\text{D.3})$$

$$\mu_{\text{H}_2\text{O(ad)}} = \mu_{\text{H}_2\text{O(ad)}}^{\circ} + RT \ln \theta_{\text{H}_2\text{O}} + RT(1 - \theta_{\text{H}_2\text{O}})(1 - n^{-1}). \quad (\text{D.4})$$

Convenient standard states for adsorbed species are therefore  $\theta_{\text{Mol}} = 1$  and  $\theta_{\text{H}_2\text{O}} = 1$  because with this choice only the first terms on the right side of Eqs. (D.3) and (D.4) survive, i.e.:

$$\mu_{\text{Mol(ad)}}^{(1)} = \mu_{\text{Mol(ad)}}^{\circ} \quad \text{and} \quad \mu_{\text{H}_2\text{O(ad)}}^{(1)} = \mu_{\text{H}_2\text{O(ad)}}^{\circ}. \quad (\text{D.5})$$

Hence:

$$\Delta G_{\text{ads}}^{(1)} = \Delta G_{\text{ads}}^{\circ}. \quad (\text{D.6})$$

For the purpose of this manuscript—i.e., approximating various isotherms on the  $c/\theta$  vs.  $c$  plot with a linear regression—a simpler variant of the Flory–Huggins type isotherm is more convenient, i.e.:

$$Kc = \frac{\theta}{(1 - \theta)^n}. \quad (\text{D.7})$$

The corresponding chemical potentials are:

$$\mu_{\text{Mol(ad)}} = \mu_{\text{Mol(ad)}}^{\circ} + RT \ln \theta_{\text{Mol}}, \quad (\text{D.8})$$

$$\mu_{\text{H}_2\text{O(ad)}} = \mu_{\text{H}_2\text{O(ad)}}^{\circ} + RT \ln \theta_{\text{H}_2\text{O}}. \quad (\text{D.9})$$

Hence, also for this simpler variant,  $\theta_{\text{Mol}} = 1$  and  $\theta_{\text{H}_2\text{O}} = 1$  are convenient adsorbate standard states, yielding  $\Delta G_{\text{ads}}^{(1)} = \Delta G_{\text{ads}}^{\circ}$ . From Eqs. (D.8) and (D.9), the difference in chemical potentials between  $\text{Mol}_{(\text{ad})}$  and  $n\text{H}_2\text{O}_{(\text{ad})}$  is<sup>12</sup>:

$$\mu_{\text{Mol(ad)}} - n\mu_{\text{H}_2\text{O(ad)}} = \mu_{\text{Mol(ad)}}^{\circ} - n\mu_{\text{H}_2\text{O(ad)}}^{\circ} + RT \ln \frac{\theta_{\text{Mol}}}{(\theta_{\text{H}_2\text{O}})^n}. \quad (\text{D.10})$$

Based on this equation and using the  $\theta_{\text{H}_2\text{O}} = 1 - \theta_{\text{Mol}}$  relation, the adsorption Gibbs energy can be written as:

$$\Delta G_{\text{ads}} = \Delta G_{\text{ads}}^{\circ} + RT \ln \frac{\theta_{\text{Mol}}}{(1 - \theta_{\text{Mol}})^n} + \text{s.t.}, \quad (\text{D.11})$$

which is equivalent to the Flory–Huggins type isotherm of Eq. (D.7), where  $\theta \equiv \theta_{\text{Mol}}$ .

Eqs. (D.10) and (D.11) suggest another choice for the standard states of  $\text{Mol}_{(\text{ad})}$  and  $\text{H}_2\text{O}_{(\text{ad})}$ . This choice corresponds to the coverage of  $\text{Mol}_{(\text{ad})}$  such that  $\theta_{\text{Mol}} = (1 - \theta_{\text{Mol}})^n$  and  $\theta_{\text{H}_2\text{O}} = 1 - \theta_{\text{Mol}}$ . However, this choice is inconvenient because the corresponding standard state coverages depend on  $n$  and the two standard state coverages are not equivalent for  $n > 1$ , i.e.,  $\theta_{\text{Mol}} \neq \theta_{\text{H}_2\text{O}}$ . In contrast, for  $n = 1$ , this choice corresponds to  $\theta_{\text{H}_2\text{O}}^{(1/2)} = \theta_{\text{Mol}}^{(1/2)} = 0.5$  standard states.

#### D.1. Comparison between the Dhar and the simpler Flory–Huggins type isotherm

The difference between the Dhar–Flory–Huggins isotherm of Eq. (D.2) and the simpler Flory–Huggins type isotherm of Eq. (D.7) is in the factor  $\exp(1 - n)$ . The simpler variant corresponds to the plain thermodynamic consideration of substitution reaction (D.1). However, a Mol molecule does not substitute arbitrary  $n$  water molecules during adsorption. It replaces water molecules from  $n$  contiguous adsorption sites, and the statistical-mechanics derivation accounts for the proper statistics [26], resulting in the factor  $\exp(1 - n)$ .

<sup>12</sup> Eq. (D.10) reveals that for  $n > 1$ ,  $\theta_{\text{Mol}}^{(0)}$  and  $\theta_{\text{H}_2\text{O}}^{(0)}$  are useless as standard states because the  $\ln[\theta_{\text{Mol}}^{(0)}/(\theta_{\text{H}_2\text{O}}^{(0)})^n]$  term diverges. As for the  $\theta_{\text{Mol}}^{(1/2)}$  and  $\theta_{\text{H}_2\text{O}}^{(1/2)}$  standard states, the corresponding standard adsorption Gibbs energy can be derived from Eq. (D.10) and is:

$$\Delta G_{\text{ads}}^{(1/2)} = \Delta G_{\text{ads}}^{\circ} + (n - 1)RT \ln 2.$$

As explained in Section 2.2, the  $c/\theta$  intercept and slope at  $c = 0$  of the simpler Flory–Huggins type isotherm of Eq. (D.7) are given by the relation:

$$\left(\frac{c}{\theta}\right)_{\theta \rightarrow 0} = \frac{1}{K} + nc \Rightarrow \text{intercept} = \frac{1}{K}, \quad \text{slope} = n. \quad (\text{D.12})$$

In contrast, the corresponding relation for the Dhar–Flory–Huggins isotherm at  $c = 0$  is:

$$\left(\frac{c}{\theta}\right)_{\theta \rightarrow 0} = \frac{\exp(1 - n)}{K_{\text{DFH}}} + nc, \quad \text{hence:} \\ \text{intercept} = \frac{\exp(1 - n)}{K_{\text{DFH}}}, \quad \text{slope} = n, \quad (\text{D.13})$$

which implies that the intercept  $\neq K_{\text{DFH}}^{-1}$  (the subscript DFH, standing for Dhar–Flory–Huggins, is used to distinguish this equilibrium constant from that of the simpler Flory–Huggins type isotherm). However, when Dhar–Flory–Huggins isotherm is fitted with Eq. (4), which is of the  $c/\theta = 1/K_{\text{fit}}^{\text{DFH}} + mc$  form, the intercept is interpreted as the inverse of the equilibrium constant. The relation between  $K_{\text{DFH}}$  and fitted  $K_{\text{fit}}$  is therefore:

$$K_{\text{fit}}^{\text{DFH}} = \frac{K_{\text{DFH}}}{\exp(1 - n)}. \quad (\text{D.14})$$

By expressing  $K_{\text{DFH}}$  with the Dhar–Flory–Huggins isotherm, Eq. (D.2), we get

$$K_{\text{fit}}^{\text{DFH}} = \frac{\frac{\theta}{c(1 - \theta)^n} \exp(1 - n)}{\exp(1 - n)} = \frac{\theta}{c(1 - \theta)^n}. \quad (\text{D.15})$$

Hence,  $K_{\text{fit}}^{\text{DFH}}$  is equivalent to the adsorption equilibrium constant of the simpler Flory–Huggins type isotherm of Eq. (D.7). This is the reason that we used the simpler variant in Sections 2 and 3. The standard adsorption Gibbs energies corresponding to the adsorption equilibrium constants  $K_{\text{fit}}^{\text{DFH}}$  and  $K_{\text{DFH}}$  are related by:

$$\Delta G_{\text{ads}}^{\text{fit-DFH}} = \Delta G_{\text{ads}}^{\circ \text{DFH}} + RT(1 - n). \quad (\text{D.16})$$

#### Appendix E. Temkin isotherm: surface heterogeneity

The Temkin adsorption isotherm [23] accounts for surface heterogeneity, and in its complete form, it is usually written as [22,23]:

$$\theta = \frac{1}{f} \ln \frac{1 + Kc}{1 + Kce^{-f}}, \quad \text{where } f > 0, \quad (\text{E.1})$$

which can be rearranged to:

$$Kc = \frac{e^{f\theta} - 1}{1 - e^{f(\theta - 1)}}, \quad (\text{E.2})$$

where  $f$  is the unitless parameter, named *nonuniformity exponent* [23], that “measures” the surface heterogeneity and is expressed with the magnitude of the  $RT$  units as:

$$f = \frac{|\varepsilon_{\text{het}}|}{RT}. \quad (\text{E.3})$$

So defined  $f$  is positive (cf. Eq. (E.1)). In the following, we assume for convenience that:

$$\varepsilon_{\text{het}} \equiv |\varepsilon_{\text{het}}|, \quad \text{hence } \varepsilon_{\text{het}} > 0. \quad (\text{E.4})$$

In the Temkin adsorption model, the magnitude of  $\varepsilon_{\text{het}}$  is the difference in adsorption energy between the least reactive and the most reactive patches on the surface (or the least and the most reactive surface sites), i.e., the adsorption energy of the most reactive patch is  $\varepsilon_{0,\text{ads}}$  and on the least reactive patch, it is  $\varepsilon_{1,\text{ads}} = \varepsilon_{0,\text{ads}} + \varepsilon_{\text{het}}$ . On other surface patches, adsorption energies vary linearly from  $\varepsilon_{0,\text{ads}}$  to  $\varepsilon_{1,\text{ads}}$  [22].

It is straightforward to show that for  $f = 0$ , the Temkin isotherm reduces to the Langmuir isotherm. In particular, by linearizing the exponential terms we obtain:

$$\lim_{f \rightarrow 0} \frac{e^{f\theta} - 1}{1 - e^{f(\theta - 1)}} = \frac{f\theta}{1 - (1 + f\theta)(1 - f)} = \frac{f\theta}{f(1 - \theta)} = \frac{\theta}{(1 - \theta)}, \quad (\text{E.5})$$



which is equivalent to the Langmuir isotherm (note that in going from the second to the third equality, the quadratic  $f^2\theta$  term was neglected).

For substitutional adsorption reaction (A.7), let us assume, similarly as done above for the Frumkin model, that the Temkin model pertains only to the Mol species, whereas water molecules behave ideally (i.e., they display the same adsorption energy on all surface patches). Hence,  $f$  can be seen as an effective heterogeneity measure that quantifies the difference in surface reactivity toward Mol and  $\text{H}_2\text{O}$ . Correspondingly, the chemical potentials of adsorbed species can be written as:

$$\mu_{\text{Mol(ad)}} = \mu_{\text{Mol(ad)}}^\circ + RT \ln a_{\text{Mol(ad)}}, \quad (\text{E.6})$$

$$\mu_{\text{H}_2\text{O(ad)}} = \mu_{\text{H}_2\text{O(ad)}}^\circ + RT \ln \theta_{\text{H}_2\text{O}}, \quad (\text{E.7})$$

where the activity  $a_{\text{Mol(ad)}}$  can be found as follows. According to Eq. (B.8),  $Kc = a_{\text{Mol(ad)}}/a_{\text{H}_2\text{O(ad)}}$  that in the current case is:

$$Kc = \frac{e^{f\theta_{\text{Mol}}} - 1}{1 - e^{f(\theta_{\text{Mol}} - 1)}} = \frac{a_{\text{Mol(ad)}}}{\theta_{\text{H}_2\text{O}}}. \quad (\text{E.8})$$

By using the  $\theta_{\text{H}_2\text{O}} = 1 - \theta_{\text{Mol}}$  relation, we arrive at:

$$a_{\text{Mol(ad)}} = (1 - \theta_{\text{Mol}}) \frac{e^{f\theta_{\text{Mol}}} - 1}{1 - e^{f(\theta_{\text{Mol}} - 1)}}, \quad (\text{E.9})$$

so that the chemical potential of  $\text{Mol}_{(\text{ad})}$  can be written as:

$$\mu_{\text{Mol(ad)}} = \mu_{\text{Mol(ad)}}^\circ + RT \ln \frac{(1 - \theta_{\text{Mol}})(e^{f\theta_{\text{Mol}}} - 1)}{1 - e^{f(\theta_{\text{Mol}} - 1)}}. \quad (\text{E.10})$$

The standard state for  $\text{Mol}_{(\text{ad})}$  thus corresponds to coverage at which the logarithmic term vanishes. This coverage depends on the value of  $f$ , which is inconvenient.

To obtain a standard state that is independent of the value of  $f$ , recall that, for substitutional adsorption, a convenient choice for the standard states is  $\theta_{\text{Mol}} = \theta_{\text{H}_2\text{O}}$ . One option is therefore to use “ideal”  $\theta_{\text{Mol}} = 1$  and  $\theta_{\text{H}_2\text{O}} = 1$  as the standard states. The “ideal”  $\theta_{\text{Mol}} = 1$  corresponds to a hypothetical state, where all patches on the surface display the same reactivity as the most reactive patch; this corresponds to  $f = 0$ . In this case,  $\mu_{\text{Mol(ad)}}$  can be obtained by using the equality of Eq. (E.5) in Eq. (E.10):

$$\begin{aligned} \mu_{\text{Mol(ad)}} &= \mu_{\text{Mol(ad)}}^\circ + RT \ln \frac{(1 - \theta_{\text{Mol}})\theta_{\text{Mol}}}{1 - \theta_{\text{Mol}}} \quad (\text{for } f = 0) \\ &= \mu_{\text{Mol(ad)}}^\circ + RT \ln \theta_{\text{Mol}}. \end{aligned} \quad (\text{E.11})$$

Another option is to use  $\theta_{\text{Mol}}^{(0)}$  and  $\theta_{\text{H}_2\text{O}}^{(0)}$  as the standard state coverages.

At exceedingly small coverage, the logarithmic term of Eq. (E.10) can be written as:

$$\begin{aligned} \lim_{\theta_{\text{Mol}} \rightarrow 0} \ln \frac{(1 - \theta_{\text{Mol}})(e^{f\theta_{\text{Mol}}} - 1)}{1 - e^{f(\theta_{\text{Mol}} - 1)}} &= \ln \frac{f\theta_{\text{Mol}}^{(0)}}{1 - e^{-f}} \\ &= \ln \frac{f}{1 - e^{-f}} + \ln \theta_{\text{Mol}}^{(0)}, \end{aligned} \quad (\text{E.12})$$

Hence, the expressions for chemical potentials at exceedingly small coverages are:

$$\mu_{\text{Mol(ad)}}^{(0)} = \mu_{\text{Mol(ad)}}^\circ + RT \ln \frac{f}{1 - e^{-f}} + RT \ln \theta_{\text{Mol}}^{(0)}, \quad (\text{E.13})$$

$$\mu_{\text{H}_2\text{O(ad)}}^{(0)} = \mu_{\text{H}_2\text{O(ad)}}^\circ + RT \ln \theta_{\text{H}_2\text{O}}^{(0)}, \quad (\text{E.14})$$

resulting in the following expression for  $\Delta G_{\text{ads}}^{(0)}$ :

$$\Delta G_{\text{ads}}^{(0)} = \Delta G_{\text{ads}}^\circ + RT \ln \frac{f}{1 - e^{-f}}. \quad (\text{E.15})$$

If  $K^{(0)}$  is defined to correspond to  $\Delta G_{\text{ads}}^{(0)}$  as:

$$K^{(0)} = \exp \left( - \frac{\Delta G_{\text{ads}}^{(0)}}{RT} \right), \quad (\text{E.16})$$

then the relation between  $K^{(0)}$  and  $K$  is:

$$K^{(0)} = K \frac{1 - e^{-f}}{f}. \quad (\text{E.17})$$

It should be noted that  $K^{(0)}$  corresponds to the mean reactivity of the surface displaying Temkin heterogeneity, where the adsorption energy varies linearly from the most reactive to the least reactive surface patch [22], i.e.:

$$\varepsilon_{i,\text{ads}} = \varepsilon_{0,\text{ads}} + s_i f RT \quad \text{and} \quad K_i = K e^{-s_i f}, \quad \text{where } s_i \in [0, 1]. \quad (\text{E.18})$$

This implies that  $K$  corresponds to the most reactive surface patch with  $s = 0$ . In contrast, for the least reactive surface patch,  $s = 1$  and its equilibrium constant is  $K e^{-f}$ .

The equilibrium constant corresponding to the mean surface reactivity is:

$$\langle K_i \rangle = K \int_0^1 e^{-s_i f} ds_i = K \frac{1 - e^{-f}}{f} = K^{(0)}, \quad (\text{E.19})$$

which is equivalent to  $K_{\text{fit}}$  of Eq. (26), that is, to the equilibrium constant corresponding to the inverse of the intercept on the  $c/\theta$  vs.  $c$  plot.

If instead of “ideal  $\theta_{\text{Mol}} = 1$ ”, true  $\theta_{\text{Mol}} = 1$  and  $\theta_{\text{H}_2\text{O}} = 1$  are chosen for the standard states, then<sup>13</sup>:

$$\begin{aligned} \mu_{\text{Mol(ad)}}^{(1)} &= \mu_{\text{Mol(ad)}}^\circ + RT \ln \frac{(1 - \theta_{\text{Mol}}^{(1)})(e^{f\theta_{\text{Mol}}^{(1)}} - 1)}{1 - e^{f(\theta_{\text{Mol}}^{(1)} - 1)}} \\ &= \mu_{\text{Mol(ad)}}^\circ + RT \ln \frac{e^f - 1}{f} \end{aligned} \quad (\text{E.20})$$

and

$$\mu_{\text{H}_2\text{O}}^{(1)} = \mu_{\text{H}_2\text{O(ad)}}^\circ + RT \ln \theta_{\text{H}_2\text{O}}^{(1)} = \mu_{\text{H}_2\text{O(ad)}}^\circ, \quad (\text{E.21})$$

which leads to:

$$\Delta G_{\text{ads}}^{(1)} = \Delta G_{\text{ads}}^\circ + RT \ln \frac{e^f - 1}{f}. \quad (\text{E.22})$$

At  $\theta_{\text{Mol}}^{(1/2)} = \theta_{\text{H}_2\text{O}}^{(1/2)} = 0.5$ , the corresponding standard adsorption Gibbs energy is:

$$\begin{aligned} \Delta G_{\text{ads}}^{(1/2)} &= \Delta G_{\text{ads}}^\circ + RT \ln \frac{e^{f/2} - 1}{1 - e^{-f/2}} = \Delta G_{\text{ads}}^\circ + RT \frac{f}{2} \\ &= \Delta G_{\text{ads}}^\circ + \frac{\varepsilon_{\text{het}}}{2}. \end{aligned} \quad (\text{E.23})$$

Eqs. (E.15), (E.22), and (E.23) imply that the standard adsorption Gibbs energy of the Temkin model depends on the coverage even for the  $\theta_{\text{Mol}} = \theta_{\text{H}_2\text{O}}$  choice of the standard states. This is due to surface heterogeneity, i.e., at very low coverage, molecules are mainly adsorbed at the most reactive surface patch. As the coverage increases, other less reactive patches are also being populated.

The “average” standard adsorption Gibbs energy for  $\theta_{\text{Mol}} = \theta_{\text{H}_2\text{O}}$  choices can be calculated as:

$$\begin{aligned} \langle \Delta G_{\text{ads}}^{(\theta)} \rangle &= \Delta G_{\text{ads}}^\circ + RT \int_0^1 \ln \frac{e^{f\theta} - 1}{1 - e^{f(\theta - 1)}} d\theta \\ &= \Delta G_{\text{ads}}^\circ + RT \frac{f}{2} = \Delta G_{\text{ads}}^\circ + \frac{\varepsilon_{\text{het}}}{2} = \Delta G_{\text{ads}}^{(1/2)}. \end{aligned} \quad (\text{E.24})$$

Hence, the same  $\langle \Delta G_{\text{ads}}^{(\theta)} \rangle = \Delta G_{\text{ads}}^{(1/2)}$  relation holds as for the Frumkin isotherm, cf. Eq. (C.13). It is also worth noting that:

$$\begin{aligned} \frac{1}{2} (\Delta G_{\text{ads}}^{(0)} + \Delta G_{\text{ads}}^{(1)}) &= \Delta G_{\text{ads}}^\circ + \frac{RT}{2} \left( \ln \frac{f}{1 - e^{-f}} + \ln \frac{e^f - 1}{f} \right) \\ &= \Delta G_{\text{ads}}^\circ + \frac{RT}{2} f = \Delta G_{\text{ads}}^{(1/2)}. \end{aligned} \quad (\text{E.25})$$

## Appendix F. Proof that for the Flory–Huggins type isotherm, $c/\theta \approx c$ at very high $c$

<sup>13</sup> Note that  $\lim_{\theta \rightarrow 1} \frac{(1 - \theta)(e^{f\theta} - 1)}{1 - e^{f(\theta - 1)}} = \frac{(1 - \theta)(e^f - 1)}{1 - (1 + f(\theta - 1))} = \frac{e^f - 1}{f}$ .

Here is a demonstration that the slope of the  $c/\theta$  vs.  $c$  curve of the Flory–Huggins adsorption isotherm should eventually approach the value of 1. Let us first expand the  $(1 - \theta)^n$  as a binomial series:

$$(1 - \theta)^n = 1 + \sum_{i=1}^n (-1)^i \binom{n}{i} \theta^i = 1 + \theta \sum_{i=1}^n (-1)^i \binom{n}{i} \theta^{i-1}. \quad (\text{F.1})$$

The Flory–Huggins type isotherm, Eq. (19), can now be written as:

$$Kc \left( 1 + \theta \sum_{i=1}^n (-1)^i \binom{n}{i} \theta^{i-1} \right) = \theta \quad (\text{F.2})$$

Dividing both sides by  $K\theta$  and rearranging, we get:

$$\frac{c}{\theta} = \frac{1}{K} - c \sum_{i=1}^n (-1)^i \binom{n}{i} \theta^{i-1} \quad (\text{F.3})$$

For  $\theta \rightarrow 1$ ,  $\theta^{i-1} \approx 1$ . Hence:

$$\frac{c}{\theta} \approx \frac{1}{K} - c \sum_{i=1}^n (-1)^i \binom{n}{i}. \quad (\text{F.4})$$

Note that  $\sum_{i=1}^n (-1)^i \binom{n}{i} = -1$ .<sup>14</sup> Hence, we finally get:

$$\frac{c}{\theta} \approx \frac{1}{K} + c. \quad (\text{F.5})$$

## Appendix G. Technical details

Graphs were plotted with Gnuplot [38] and their post-processing was done with the Inkscape software [39]. Gnuplot was also used for fitting. Derivation of equations was facilitated with WolframAlpha [40].

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<sup>14</sup> Let us illustrate this empirically for several values of  $n$ :

$$n = 2 : \sum_{i=1}^n (-1)^i \binom{n}{i} = -2 + 1 = -1,$$

$$n = 3 : \sum_{i=1}^n (-1)^i \binom{n}{i} = -3 + 3 - 1 = -1,$$

$$n = 4 : \sum_{i=1}^n (-1)^i \binom{n}{i} = -4 + 6 - 4 + 1 = -1,$$

$$n = 5 : \sum_{i=1}^n (-1)^i \binom{n}{i} = -5 + 10 - 10 + 5 - 1 = -1.$$

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