

## A CRITICAL ASSESSMENT OF THE CALCULATION AND ANALYSIS OF THERMODYNAMIC PARAMETERS FROM ADSORPTION DATA

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### INTRODUCTION

Adsorption can be considered as a vital process of successful technologies like for example, those used for the removal of heavy metal ions, synthetic dye molecules and toxic chemicals from aqueous solution [1]. Moreover, adsorption of an organic molecule on a metal surface is the key mechanistic step that can inhibit corrosion through the building of a barrier that restricts access of aggressive species from the environment to the metal surface [2]. In particular, of great current interest are the so-called green corrosion inhibitors that decrease the corrosion rates to the desired level with minimal environmental impact [3].

Derivation of the adsorption isotherm is the most convenient way to study quantitatively the adsorbed layer of an organic corrosion inhibitor. Thermodynamic parameters of solute adsorption from aqueous solutions provide a great deal of information concerning the type and mechanism of the adsorption process [4]. Unfortunately, calculation of thermodynamic parameters from adsorption data as well as its analysis are very often vitiated, as we discuss here, based on a large number of published works. At least three aspects require clarification to ensure correct data derivation and interpretation.

Firstly, the thermodynamic equilibrium constant of adsorption  $K_{eq}$  is a dimensionless magnitude. On the other hand, its related constant as derived from adsorption isotherm data, the adsorption constant  $K_a$ , has units of  $(\text{mol/l})^{-1}$ . Clearly, these two values are not the same and prior to obtaining the change in the standard free energy of adsorption  $\Delta G^\circ_{ad}$  from  $K_a$  a careful evaluation of the valid adsorption isotherm must be made, i.e. under which conditions of the adsorbate (charge and concentration) and which type of isotherm render  $K_a$  equivalent to  $K_{eq}$ .

A second aspect usually disregarded is that it is  $\Delta G$  rather than  $\Delta G^\circ$  what serves as a criterion for spontaneous change at constant temperature and pressure. Moreover, while the considered adsorption equilibrium carried out under standard conditions is characterized by a *single value* of  $\Delta G^\circ_{ad}$ , this adsorption process can have an infinite number of  $\Delta G_{ad}$  values, reflecting the infinite possible compositions between the extreme states, that is to say, the organic molecules in solution that will be adsorbed (initial state) and the already adsorbed organic molecules at the surface (final state). Consequently, a feasible way to circumvent this difficulty in the analysis is required.

Finally, adsorption involves attracting molecules of the inhibitor to the metal surface. Thus, energy is released and adsorption is normally exothermic. For an adsorption process the enthalpic change  $\Delta H_{ad}$  is negative, while the entropic change  $\Delta S_{ad}$  is mostly also negative since adsorbed molecules lose their translation freedom when they get attached to the metal surface. Absolute values of  $\Delta H_{ad}$  indicate whether physical adsorption or chemisorption takes place. However, published data often consider these values for  $\Delta G_{ad}^{\circ}$  instead.

Proper analysis of thermodynamic parameters obtained from adsorption data is a basic requirement for the characterization and optimization of an adsorption-dependent process like the action of organic corrosion inhibitors. Thus, this work aims at presenting a critical assessment of typical flawed examples from the literature together with alternative good practice to be considered, for preference.

## DISCUSSION

The usual case in the works from the literature corresponds to an adsorption process where the mutual interaction of inhibitor is negligible and the interaction with the metal substrate is independent of the coverage  $\theta$ . In this case, the Langmuir isotherm applies, which can be expressed as in equation (1).

$$\frac{C}{\theta} = \frac{1}{K_a} + C \quad (1)$$

where  $C$  is the concentration of the inhibitor.

$\theta$  is calculated from the measured corrosion rates for the inhibited system at different concentrations of the inhibitor.  $C \theta^{-1}$  vs.  $C$  plots at different temperatures  $T$  are used to derive  $K_a$  values. Finally,  $\Delta G_{ad}^{\circ}$  vs.  $T$ , associated with  $K_a$  can be derived according to equation (2), under the assumption that the thermodynamic equilibrium constant  $K_{eq}$  is the same as the adsorption constant  $K_a$ .

$$\Delta G_{ad}^{\circ} = -RT \ln(K_{eq}) \quad (2)$$

It can be easily shown that for a dilute solution of charged adsorbates or for a solution of uncharged adsorbates at any concentration,  $K_{eq}$  can be reasonably approximated by  $K_a$  [5]. Therefore, using the Langmuir adsorption constant to obtain  $\Delta G^{\circ}(T)$  and subsequently to derive  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  for the adsorption process is satisfactory. However, this approach is inadequate for other adsorption isotherm equations or distribution constants.

In actual fact, for the conditions stated above and considering the relationship between the activity and the molar concentration of the adsorbate, equation (2) can be written as in equation (3).

$$\Delta G_{ad}^0 = -RT \ln[K_a (1 \text{ mol L}^{-1})] \quad (3)$$

where  $K_a$  in units of  $(\text{L mol}^{-1})$  is multiplied by the molar concentration of the standard reference solution, here  $1 \text{ mol L}^{-1}$ .

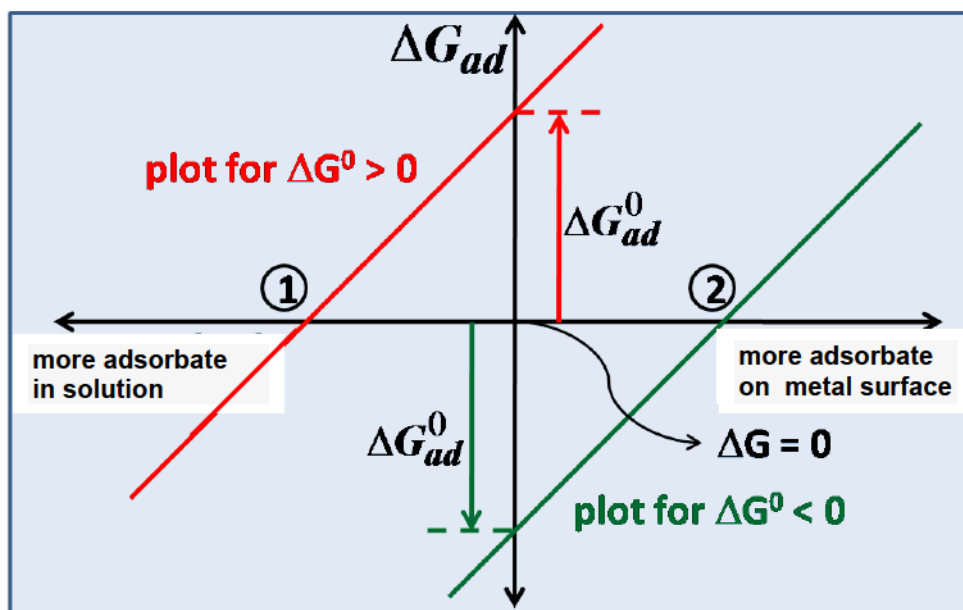
In expression (3) that links  $K_a$  with  $\Delta G_{ad}^0$ , the factor 55.5 (the water molar concentration) is commonly included in the argument of the logarithmic term to correct for the cratic contribution to the free energy of inhibitor adsorption on the metal [6]. The term “cratic” is widely used for the translational contribution to the free energy of an association process. In principle, the correction factor 55.5 is considered by some authors to generate values that agree well with experimental data, even though this term has not been derived from first principles statistical mechanics as a translational contribution [7]. Some authors even consider that the “cratic correction” is inadequate to remove the contribution of translational motion from standard free energies and entropies of chemical reactions of association [8]. Moreover, it was suggested that the factor 55.5 in units of  $\text{mol H}_2\text{O} / \text{L H}_2\text{O}$  is required to cancel units with  $K_a$  in equation (3) [9]. Simple observation of equation (3) shows this is an erroneous concept. Also, for  $K_a$  derived from adsorption data in units of  $(\text{L g}^{-1})$  the factor 55.5 is expected to be substituted with the factor  $1000 \text{ g H}_2\text{O} / \text{L H}_2\text{O}$  to meet the units of  $K_a$ . Strictly speaking, for  $K_a$  obtained in units of  $(\text{L g}^{-1})$  correction of its value using the molecular weight of the inhibitor must be made prior to using equation (3).

Another common erroneous statement is that adsorption is spontaneous if  $\Delta G_{ads}^0 < 0$ . However, whether (at a given composition) the adsorption process spontaneously proceeds to the formation of adsorbed inhibitor instead of desorption of these species, depends on the sign of  $\Delta G_{ad}$  at that composition, instead of the sign of  $\Delta G_{ads}^0$  [10].

As clearly depicted in Figure 1, for very large negative values of  $\Delta G_{ad}^0$  the adsorption process will be spontaneous and virtually complete under most reasonable sets of the system composition, but not for all of them. Put in other words, the larger the negative values of  $\Delta G_{ad}^0$  are, the closer to the limit of unit coverage, the equilibrium condition ( $\Delta G_{ad} = 0$ ) results. See point ② in Figure 1. The opposite is true for large positive values of  $\Delta G_{ad}^0$ . See point ① in Figure 1. Thus,  $\Delta G_{ad}^0$  can only be used to get a rough idea of whether the adsorption process is possibly complete in a preferred direction but does not indicate whether physical adsorption or chemisorption takes place, as usually claimed in the works from the literature.

In essence, the process is spontaneous when there is adsorption and inhibition. In this respect, it would not be necessary a thermodynamic calculation to prove this. The very observation that the inhibition occurs shows that the adsorption is a spontaneous process. Nonetheless,  $\Delta G_{ad}$  vs.  $T$  values are still required to derive enthalpy and entropy changes that allow to know whether physical adsorption or chemisorption takes place, as discussed in the following.





**Figure 1.** Semi-logarithmic plots of  $\Delta G_{ad}$  as a function of the relative concentrations of inhibitor molecules in solution and adsorbed on the metal surface during the progress of the adsorption process and given by  $\ln Q$  (see equation (4)). Red line for  $\Delta G^{\circ}_{ad} > 0$ , green line for  $\Delta G^{\circ}_{ad} < 0$ . [Adapted from Stephen Lower, Simon Fraser University, chem1 virtual textbook]

As already indicated in the introduction adsorption is normally exothermic. Furthermore, physical adsorption involves weak forces of attraction and less heat evolves whereas chemical adsorption, involving strong forces of attraction, is related to a higher flow of heat released from the system. For the adsorption process  $\Delta H_{ad}$  is negative, while  $\Delta S_{ad}$  is also negative as described above. Bearing in mind that  $\Delta G_{ad} = \Delta H_{ad} - T\Delta S_{ad}$  adsorption will spontaneously occur if  $\Delta H_{ad} > T\Delta S_{ad}$ .

$\Delta G_{ad}$  values can be calculated according to the following relationship [11]:

$$\Delta G_{ad} = \Delta G^{\circ}_{ad} + RT \ln Q \quad (4)$$

where  $Q$  is the activity quotient.

$Q$  can be calculated considering the following formal expression

$$Q = \theta / [(1-\theta) C] \quad (5)$$

Thus, for a fixed global composition  $Q = 1$  results  $\Delta G_{ad} = \Delta G^{\circ}_{ad}$  and

$$\theta = C / (1 + C) \quad (6)$$

Since the mechanism of corrosion protection by inhibitors acting through adsorption on the metal surface from a solution contain the inhibitive substance in millimolar or even smaller concentrations only [12,13]  $C \ll 1$  and introducing this condition into equation (6) results  $\theta \cong C$ . This condition is met almost at the beginning of the process, with a composition of nearly all the inhibitor species in solution. Consequently, adsorption enthalpy and entropy changes can be derived from  $\Delta G_{ad}(Q=1)$  values and correlated with the initial stages of the adsorption of the inhibitor. Plotting  $\Delta G_{ad}(Q=1)$  vs T a straight line can be obtained. From the corresponding y-intercept and slope of this line,  $\Delta H_{ad}(Q=1)$  and  $\Delta S_{ad}(Q=1)$  can be derived. Physical adsorption is characterised by small enthalpy changes, rarely less than  $-25 \text{ kJmol}^{-1}$ , whereas chemisorption usually exhibits much more negative values below  $-40 \text{ kJmol}^{-1}$  [10].

## CONCLUSIONS

Adsorption data are used to calculate important thermodynamic quantities. These parameters, in turn, are critical design variables that allow to estimate the performance and predict the mechanism of corrosion control by an adsorption inhibitor. The widespread approach to calculate and analyze thermodynamic parameters derived from adsorption data was examined. In this regard, crucially flawed aspects were detected and alternative good practice was presented. The Langmuir adsorption constant in units of  $\text{L mol}^{-1}$  can be considered equivalent to the thermodynamic equilibrium constant in order to calculate the change in standard free energy of adsorption. When a cratic correction factor is used only the factor 55.5 is valid.  $\Delta G_{ad}^{\circ}$  values can be merely used to get a rough idea of whether the adsorption process is possibly complete in a preferred direction but never to judge whether physical adsorption or chemisorption takes place. With that aim,  $\Delta H_{ad}$  can be calculated for a system composition related to a low surface coverage.

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