



## SHORT COMMUNICATION

**A consideration of the correct calculation of thermodynamic parameters of adsorption**

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(Received 9 October 2007)

**Abstract:** The Langmuir and Freundlich isotherm equations have been widely used for interpreting various adsorption processes. There are, however, many serious mistakes in the literature in determination or calculation of thermodynamic parameters, especially in the determination of the change in the free energy of adsorption using Langmuir, Freundlich and Henry constants. Many authors used these constants for the determination of  $\Delta G$  expressed instead of dimensionless in some concentration units (for example:  $1 \text{ mol}^{-1}$ ,  $1 \text{ g}^{-1}$ ,  $1 \text{ ml mg}^{-1}$ , etc.).

**Keywords:** adsorption, thermodynamic parameters, correct calculation.

## INTRODUCTION

Sorption occurring at a liquid or gaseous phase/solid surface interface plays an important role in many processes.<sup>1,2</sup> The sorption is a general term that comprises adsorption processes which occur at a solid/solution interface, as well as those in which a solute (molecule or ion) penetrates the bulk of a sorbent phase. The sorption of solutes by a solid phase is based on forces acting between the sorbent and the sorbate. These forces can be classified as van der Waals, Coulomb and Lewis acid–base interactions and range over many orders of magnitude.

The sorption of various ions or molecules plays a significant role in a wide variety of natural, synthetic, inorganic, biological, and technological processes, and is also of major theoretical interest. There are many studies of adsorption from solution by various solid adsorbents.

Different adsorption mechanisms may be found by studying the dependence of adsorption on various variables (pH, concentration of solutes, ionic strengths, and the type and topology of surfaces), and by interpreting the parameters of the determined adsorption isotherms. Also, thermodynamic parameters of adsorption from solutions provide a great deal of information concerning the type and mechanism of the adsorption process.

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doi: 10.2298/JSC0712363M

The correct calculation of thermodynamic parameters, especially the change of the free energy of adsorption at a solid/liquid interface is the subject of this paper.

#### ADSORPTION ISOTHERM EQUATIONS AND THERMODYNAMIC PARAMETERS

There are several types of adsorption from solutions isotherms.<sup>3</sup> Langmuir and Freundlich isotherms are the most commonly used models, since they can be applied to a wide range of adsorbate concentrations. The general form of the Langmuir<sup>4</sup> equation for adsorption from solution is:

$$q_e = q_{\max} \frac{K_L c_e}{1 + K_L c_e} \quad (1)$$

where  $q_e$  is the amount of adsorbate adsorbed on the adsorbent at equilibrium ( $\text{mol g}^{-1}$ ),  $q_{\max}$  is the maximum adsorption capacity corresponding to a complete monolayer coverage on the adsorbent surface ( $\text{mol g}^{-1}$ ),  $K_L$  is the Langmuir constant ( $\text{dm}^3 \text{mol}^{-1}$ ), and  $c_e$  is the concentration of adsorbate at equilibrium ( $\text{mol dm}^{-3}$ ). The values of  $q_{\max}$  and  $K_L$  can be evaluated from the slope and the intercept of the linear form of the Langmuir equation:

$$\frac{c_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{c_e}{q_{\max}} \quad (2)$$

The Freundlich<sup>5</sup> equation is a semi-empirical one employed to describe heterogeneous systems:

$$q_e = K_F c_e^{1/n} \quad (3)$$

where  $K_F$  is the Freundlich constant ( $\text{dm}^3 \text{g}^{-1}$ ) and  $1/n$  is the heterogeneity factor. The value of  $K_F$  and  $n$  can be evaluated from the intercept of the slope of the linear form of the Freundlich equation:

$$\ln q_e = \ln K_F + (1/n) \ln c_e \quad (4)$$

The free energy change,  $\Delta G$ , of adsorption is given by:

$$\Delta G = -RT \ln K \quad (5)$$

where  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the temperature (K), and  $K$  is the equilibrium constant.

It is well known that the unit for  $\Delta G$  is  $\text{J mol}^{-1}$ . Since the unit for the term  $RT$  is also  $\text{J mol}^{-1}$ , the equilibrium constant  $K$  in Eq. (5) must be dimensionless.

Very often, the calculation of the free energy change of adsorption applying Eq. (5), as found in the literature, is erroneous. Namely, many authors when calculating  $\Delta G$  use numerical values for  $K$  given in various units ( $1 \text{ mol}^{-1}$ ,  $1 \text{ g}^{-1}$ ,  $\text{ml mg}^{-1}$ , *etc.*). As a consequence, the calculated values for the free energy change and the entropy change,  $\Delta S$ , of adsorption are incorrect. In order to obtain a correct value of  $\Delta G$ , the  $K$  value in Eq. (5) must be dimensionless.

If adsorption was investigated from an aqueous solution and if  $K$  is given in  $\text{dm}^3 \text{mol}^{-1}$ , then  $K$  can be easily recalculated as dimensionless by multiplying it

by 55.5 (number of moles of water per liter of solution). Accordingly, the correct  $\Delta G$  value can be obtained from:

$$\Delta G = -RT \ln (55.5K) \quad (6)$$

The term  $55.5K$  ( $\text{dm}^3 \text{mol}^{-1} \text{mol dm}^{-3}$ ) is dimensionless. In the case when  $K$  is given in  $\text{dm}^3 \text{g}^{-1}$ , similar to above,  $K$  can be easily recalculated to become dimensionless by multiplying it by 1000 ( $1 \text{ dm}^3 = 1000 \text{ ml}$  (or  $\text{g}$ , since the solution density is  $\approx 1 \text{ g ml}^{-1}$ )).

#### SOME RECENT LITERATURE DATA AND DISCUSSION

Some examples of erroneous calculations of  $\Delta G$  and  $\Delta S$  values of various adsorption processes found in the literature are given below.

Recently, Gardea-Torresdey and co-workers presented a detailed thermodynamic and isotherm study of the biosorption of Cd(II), Cr(III), and Cr(VI) by saltbush (*Atriplex conescens*) biomass.<sup>6</sup> In the Conclusions, the authors wrote, "The Gibbs free energy values show that, though the biosorption was spontaneous for Cr(III) and Cd(II), the adsorption of Cr(III) was privileged compared to that of Cd(II), and that the biosorption of Cr(VI) was non-spontaneous." The authors came to such an erroneous conclusion on the basis of the values of  $\Delta G$  calculated using Eq. (5). The biosorption equilibrium constants,  $K_c$ , for the binding data of Cd(II), Cr(III), and Cr(VI) by saltbush leaves biomass were calculated either from the intercept of the Khan and Singh plot<sup>7</sup> ( $\ln (q_e/C_e)$  versus  $q_e$ , Fig. 3 in Ref. 6) or from the slope of the  $q_e$  versus  $c_e$  curve (Eq. [6], and Fig. 4 in Ref. 6). The calculated  $K_c$  values, in both cases, are expressed in  $\text{l g}^{-1}$ . The calculated  $K_c$  values are presented in Table I (Table 2 in Ref. 6). Accordingly, the values of  $\Delta G$  (calculated using Eq. [5]) and  $K_c$  (expressed in  $\text{l g}^{-1}$ ), given in Table I are incorrect.

TABLE I. Thermodynamic parameters for biosorption of Cd(II), Cr(III) and Cr(VI) on saltbush biomass at  $24 \pm 2$  °C<sup>6</sup>

Metal	Khan and Singh		$q_e$ versus $c_e$ plot	
	$K_c / \text{l g}^{-1}$	$\Delta G / \text{kJ mol}^{-1}$	$K_c / \text{l g}^{-1}$	$\Delta G / \text{kJ mol}^{-1}$
Cd(II)	1.334	-0.7121	1.380	-0.7957
Cr(III)	3.934	-3.3837	13.522	-6.4340
Cr(VI)	0.095	5.8075	0.251	3.4160

By multiplying these  $K_c$  values by 1000, dimensionless  $K_c$  values were obtained (Table II) and these values were used to recalculate the  $\Delta G$  values, according to  $\Delta G = -RT \ln 1000K_c$ , also given in Table II. It is evident from the Table II that the recalculated  $\Delta G$  values are negative for all investigated metal ions. This indicates that the sorption of Cd(II), Cr(III) and Cr(VI) on saltbush biomass is a spontaneous process.

Similarly, erroneous calculations of  $\Delta G$  and  $\Delta S$  values of various ions/molecules on various sorbents were published recently.<sup>8-17</sup> As a consequence of such

incorrect calculations, many erroneous conclusions, very often contradictory to the experimentally obtained results, were drawn.

TABLE II. The recalculated  $K_c$  and  $\Delta G$  values for the biosorption of Cd(II), Cr(III) and Cr(VI) on saltbush biomass at  $24 \pm 2$  °C

Metal	Khan and Singh		$q_e$ versus $c_e$ plot	
	$K_c$	$\Delta G / \text{kJ mol}^{-1}$	$K_c$	$\Delta G / \text{kJ mol}^{-1}$
Cd(II)	1334	-17.77	1380	-17.85
Cr(III)	3934	-20.44	13522	-23.49
Cr(VI)	95	-11.24	251	13.64

In addition to these incorrect calculations, there are many erroneous methodical approaches in a large number of papers devoted to adsorption from solutions.

It is well known that the adsorption of metal ions is strongly dependent on the solution pH. Also, during the adsorption experiment there is a change in pH. For one adsorption isotherm, the solution pH should be constant. Also, the equilibrium solution pH, instead of initial one, should be given. The same is valid for adsorbate concentrations. Very often, some authors erroneously present the adsorbed amount of ions as a function of the initial instead of the equilibrium ion concentration. It is known that polyvalent metal ions hydrolyze in aqueous solutions. The degree of hydrolysis of a metal ion is affected by its type and concentration, solution pH, and temperature. Depending on these parameters, various hydrolytic species can exist in aqueous solutions. Very often, the authors neglect this phenomenon.

#### CONCLUSIONS

Several examples of various adsorption processes taken from the literature were examined. As shown, the calculated  $\Delta G$  and  $\Delta S$  values reported in these papers are incorrect. A correct calculation of the named thermodynamic parameters is suggested. Also, some serious mistakes made during adsorption experiments or interpretations of the obtained data are given. This paper can help all researchers working in the adsorption area, and especially those who may not be familiar with the subject.

*Acknowledgement:* The author is grateful to the Ministry of Science of the Republic of Serbia for financial support ( Project No. 142004).

#### ИЗВОД

#### НЕКА РАЗМАТРАЊА О ПРАВИЛНОМ ИЗРАЧУНАВАЊУ ТЕРМОДИНАМИЧКИХ ПАРАМЕТАРА ПРОЦЕСА АДОРПЦИЈЕ

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Ленгмирова и Фројндлихова адсорпциона изотерма широко се користе за интерпретацију различитих адсорпционих процеса. Међутим, постоје многе озбиљне грешке у литера-

тури при одређивању или израчунавању термодинамичких параметара, нарочито при израчунавању промене слободне енергије адсорпције из вредности Ленгмуирових, Фројндлихових и Хенријевих константи. Многи аутори користе бројчане вредности ових константи, за израчунавање  $\Delta G$ , изражене у неким концентрационим јединицама (нпр. у:  $\text{l mol}^{-1}$ ,  $\text{l g}^{-1}$ ,  $\text{ml mg}^{-1}$ , итд.) уместо као бездимензионе величине.

(Примљено 9. октобра 2007)

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