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Some mistakes and misinterpretations in the analysis of thermodynamic adsorption data

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Highlights

- The assumptions underlying the Temkin isotherm model are discussed.
- Verifying the dimensional consistency of equations helps in avoiding mistakes.
- Calculated parameters should be always accompanied by their errors of estimate.
- The classical linear van't Hoff plot may lead to erroneous prediction of thermodynamic parameters.
- Comparing different graphical representations may help in assessing data reliability.
- The sign of $\Delta G°$ does not provide any information about the spontaneity of a process.
- The selected isotherm model must be consistent with the isosteric heat of adsorption trend.

Abstract

In this work, we discuss some results and statements recently published in the scientific adsorption literature. In particular, we focus on the thermodynamic aspects of the adsorption process, including dimensional inconsistency of fitted parameters, Temkin isotherm assumptions, inaccurate calculation of $\Delta H°$ and $\Delta S°$, parameter determination without providing the errors of estimate, mismatch between selected isotherm models and isosteric heat of adsorption, misleading interpretation of the spontaneity of a process, and interchangeability of ΔG and $\Delta G°$. A graphical method is proposed for assessing data reliability and applicability of the van't Hoff equation.

Keywords: Temkin isotherm; van't Hoff equation; standard Gibbs adsorption energy; adsorption spontaneity; dimensional consistency of equations; isosteric heat of adsorption

1. Introduction

Adsorption plays an important role in many natural and engineered processes, including protein-solid surface interaction [1–3], soil pollutants fate [4–6], heterogeneous catalysis [7,8], gas separation [9–11] and wastewater treatment [12,13]. For decades, this has attracted the attention of many researchers worldwide, resulting in the publication of a considerable number of adsorption studies, especially recently focused on the application of adsorptive removal of pollutants from aqueous solution. In recent years, a number of comment papers, reviews and research articles have been dedicated to discussing practical and conceptual errors found in the adsorption literature, with special emphasis on thermodynamic aspects. These critical papers have pointed out mistakes and inconsistencies in experimental procedures [14,15], thermodynamic parameters calculation [16–21], dimensional analysis [22] and theoretical formulations [23,24]. Notwithstanding these critical papers, recent research studies continue to interlink adsorption data and thermodynamics in inconsistent terms and ways. Thereby it is a matter of precise wording whether a statement is correct or wrong. As an example from the current literature, we consider a study on enthalpic and entropic selectivity in membrane filtration processes published in ES&T 2021 [25]. The authors used the water-membrane "*partition coefficient ... defined as the ratio of the diffusion rates forward and backward through the solution−membrane interface*". Obviously, this definition of the partition coefficient is wrong. It becomes correct when the term 'rates' is replaced by 'rate constants'. It is our intention to sensitize the experimentally oriented researcher to be aware of difficulties and pitfalls in this field.

In the present paper, we discuss some issues, apparently not yet sufficiently examined, arising from a critical analysis of recent published papers about the application of the Temkin isotherm and the van't Hoff equation, calculation of the isosteric heat of adsorption and interpretation of the spontaneity of adsorption processes.

2. Temkin isotherm

Although originally derived for analyzing gas–solid systems [26], the Temkin model can also be used in liquid–solid systems, provided that the assumptions underlying the model are satisfied. Unlike the simpler and more widely used Langmuir model [27,28], the Temkin model (expressed in the approximated form as Eq. (1)) considers that the adsorption enthalpy is not constant but varies linearly with the adsorbent surface coverage as a result of (i) adsorbate interactions or (ii) heterogeneity of adsorption sites [29]. The two cases lead to different analytical solutions of the Temkin model that will not be examined here; details of their derivation can be found elsewhere [26,29]. In the case of porous adsorbents, surface coverage can also be understood as the extent of pore filling. It should be noted that according to the Temkin theory, the change in the surface coverage not only affects the adsorption enthalpy but also the adsorption Gibbs energy and the thermodynamic adsorption equilibrium constant. In contrast, the adsorption entropy is assumed to be surface-coverage-independent.

Interestingly, if one restricts the adsorption domain to the middle range of surface coverage, the same approximated form of the Temkin isotherm is obtained for both the adsorbate interactions and surface heterogeneity cases [29]:

$$\theta_e = \frac{RT}{\delta\Delta H}\ln\left(K°_T \frac{C_e}{C°}\right) \tag{1}$$

The latter equation is valid for dilute solutions of a non-ionic compound. Here θ_e (unitless), R (J K^{-1} mol^{-1}) and T (K) are the adsorbent surface coverage fraction or extent of pore filling, the ideal gas constant and the temperature, respectively. The parameter $K°_T$ represents a *special case* of the generic Temkin thermodynamic adsorption equilibrium constant (see below); C_e and $C°$ are the solute concentrations in the equilibrated liquid phase and according to the selected standard state (both in mg L^{-1} or mol L^{-1}), respectively. The subscript *e* denotes the equilibrium state. According to IUPAC indications [30], $K°_T$ (like any other thermodynamic equilibrium constant) is a *dimensionless* quantity; its absolute value depends on the selected standard states of solute in the liquid and adsorbed state. The standard adsorbed state is implicitly defined by the concentration measure units used for expressing the adsorbent loading (amount of solute adsorbed per mass of adsorbent), for instance mg g^{-1} or mol g^{-1} [16]. It is worth noting that the meaning of both $\delta\Delta H$ (J mol^{-1}) and $K°_T$ varies depending on the type of adsorption scenario envisaged. In the case of adsorbate-adsorbate interactions, $\delta\Delta H$ represents the difference between the molar adsorption enthalpies at zero coverage and saturation, whereby $K°_T$ is the adsorption equilibrium constant at zero coverage. In case of surface heterogeneity, $\delta\Delta H$ is the difference between the smallest and the largest molar adsorption enthalpy of the sites, whereby $K°_T$ is the adsorption equilibrium constant associated with adsorbate binding to the strongest adsorption sites. The definition of $K°_T$ and the relations that connect $K°_T$ to the Gibbs energy, the adsorption enthalpy and the adsorption entropy, are given by the following equations [29]:

$$K°_T = \frac{\theta_e}{(1-\theta_e)\frac{C_e}{C°}} \tag{2}$$

$$K°_T = e^{-\frac{\Delta G°_0}{RT}} \tag{3}$$

$$\Delta G°_0 = \Delta H°_0 - T\Delta S° \tag{4}$$

Here $\Delta G°_0$ and $\Delta H°_0$ are the standard adsorption Gibbs energy and the standard adsorption enthalpy, respectively; the subscript “0” stands for zero coverage in the case of adsorbate-adsorbate interactions and for surface element $s = 0$ (associated with the largest adsorption enthalpy $\Delta H°_0$) in the case of surface heterogeneity, respectively. As previously stated, the thermodynamic parameter $\Delta S°$ represents the standard adsorption entropy, which is considered as being independent of θ and s.

Since in most cases the maximum adsorption capacity of the adsorbent, q_m (generally expressed as mg g^{-1} or mol g^{-1}), is not known *a priori*, Eq. (1) can be conveniently recasted in terms of the equilibrium adsorbent loading q_e (mg g^{-1} or mol g^{-1}), as:

$$q_e = q_m \frac{RT}{\delta\Delta H} \ln\left(K°_T \frac{C_e}{C°}\right) \tag{5}$$

where $\theta_\mathrm{e} = q_\mathrm{e}/q_\mathrm{m}$.

Due to its simplicity and to the fact that it can be rearranged in a linear form [22], Eq. (5) (or its linearized form) is widely used in the literature for describing the equilibrium of adsorption processes [31–34]. Considering the assumptions upon which the model relies, it is important to recall that Eq. (5) can only be expected to provide physically consistent results when all the fitted experimental data fall in the midrange of the adsorbent coverage.

As reported by Chu [22], even in most recently published works [32,35–37], a slightly different expression for approximating the Temkin isotherm is used in place of Eq. (5):

$$q_e = \frac{RT}{b_T}\ln(K_T C_e) \tag{6}$$

where $C°$ is missing and, for the sake of dimensional consistency, K_T (numerically equivalent to $K°_T$), is not dimensionless as $K°_T$ is but has the dimensions of the reciprocal of C_e: K_T and C_e are commonly expressed with units of L mg^{-1} or L mol^{-1} and mg L^{-1} or mol L^{-1}, respectively.

Comparison of Eq. (6) with Eq. (5) suggests that

$$b_T = \frac{\delta \Delta H}{q_m} \tag{7}$$

From Eq. (7) it may be deduced that b_T has to have units of (J mol^{-1}) × (mg g^{-1})$^{-1}$ or (J mol^{-1}) × (mol g^{-1})$^{-1}$. In contrast, in the works mentioned above [32,35–37], b_T has units of J mol^{-1} because it is erroneously considered an adsorption heat quantity. This mistake leads to dimensional inconsistency in Eq. (6) and to wrong estimation of the Temkin adsorption heat parameter, whose correct value is given by $\delta\Delta H$ (i.e. by $b_T \times q_m$, see Eq. (7)). It is important to remark that $\delta\Delta H$ is not an *absolute* adsorption enthalpy but rather a measure of the change in the adsorption enthalpy along the occupied adsorption sites or surface coverage (see Eq. (8)). The absolute adsorption enthalpy is implemented in the temperature dependence of the equilibrium constant K_T. Shamsudin et al. [35] investigated diclofenac (DCF) adsorption in water onto alginate/carbon films (AC-films) and applied Eq. (6) to the equilibrium adsorption data measured at various temperatures, obtaining the values of b_T reported in Table 1.

Table 1. Temkin parameters for the adsorption of DCF onto AC-films at various temperatures*

T (K)	b_T** (J mol^{-1}) × (mg g^{-1})$^{-1}$	K_T (L mg^{-1})
303	326.43	2.414
313	235.31	0.550
323	229.53	0.405
333	230.40	0.338
343	276.89	0.230

* Values of b_T and K_T as originally presented by Shamsudin et al. [35].

** Units of measure corrected by the present authors with respect to the incorrect original source (J mol^{-1}).

The format of data in Table 1 as well as in Table 2 is a typical example of unreasonable precision suggested by presenting 5 to 7 digits for calculated values. Actually, in most cases not more than three digits are significant. From these values of b_T, Shamsudin et al. inferred that "*the adsorption heat decreased linearly with surface coverage due to adsorbent-adsorbate interaction and it ranged from 229.5 to 326.4 J/mol*". We state that the procedure they used for determining the change in the adsorption heat with surface coverage is not correct. According to the Temkin theory, one should instead use Eq. (8) [29]:

$$\Delta H_\theta = \Delta H_0 + \delta\Delta H \cdot \theta \tag{8}$$

where ΔH_θ and ΔH_0 are the adsorption enthalpies at any θ and at zero coverage, respectively. It should be noted that, in Eq. (8), $\delta\Delta H$ is assumed to be *temperature-independent*.

The meaning of b_T was also misinterpreted by Araújo and co-workers [32]; in their work, the adsorption of Pb(II) onto lobeira fruit was erroneously classified as physiosorption on the basis of the "low value" reported for b_T (0.2 kJ mol^{-1}): again, we remark that the value of b_T (both when considered as $\delta\Delta H$ and $\delta\Delta H/q_m$) does not provide information on the magnitude of the adsorption heat.

A third mistake related to the application of the Temkin isotherm model can be found in Saxena et al. [37]. The authors used the Temkin isotherm for modelling the adsorption of methylene blue (MB) onto carbon nanotubes. A basic requirement for the correct application of the Temkin model, as for any other isotherm model, is that adsorption is fully reversible, i.e. the experimental data must refer to equilibrium conditions. However, the experiments of Saxena et al. showed that the adsorption of MB was largely irreversible. This means that the obtained adsorption data cannot be adequately described by an equilibrium isotherm, regardless of the applied model, rendering the analysis of the isotherm data inaccurate and any ensuing result unreliable.

3. Estimation of $\Delta H°$ and $\Delta S°$

It is very often found in adsorption studies that the estimates of $\Delta H°$ and $\Delta S°$ are invalidated by an erroneous calculation of the equilibrium adsorption constant. This issue has been exhaustively examined in previous reports [16,17,21,38–40] and hence does not require further elucidation here. In the present work, attention is focused on an issue related to the application of the well-known van’t Hoff equation in the following form [41]:

$$\ln K° = -\frac{\Delta H°}{R}\frac{1}{T} + \frac{\Delta S°}{R} \qquad (9)$$

where $K°$ is the generic thermodynamic adsorption equilibrium constant, and $\Delta H°$ (kJ mol^{-1}) and $\Delta S°$ (kJ K^{-1} mol^{-1}) are the standard adsorption enthalpy and the standard adsorption entropy, respectively. Assuming that neither $\Delta H°$ nor $\Delta S°$ vary appreciably with temperature, a plot of $\ln K°$ against $1/T$ (van’t Hoff plot) would produce a straight line from whose slope and intercept the values of $\Delta H°$ and $\Delta S°$, respectively, can be determined. The results of this procedure as presented by Ghosal and Gupta [42] are reported in Fig. 1 and Table 2.

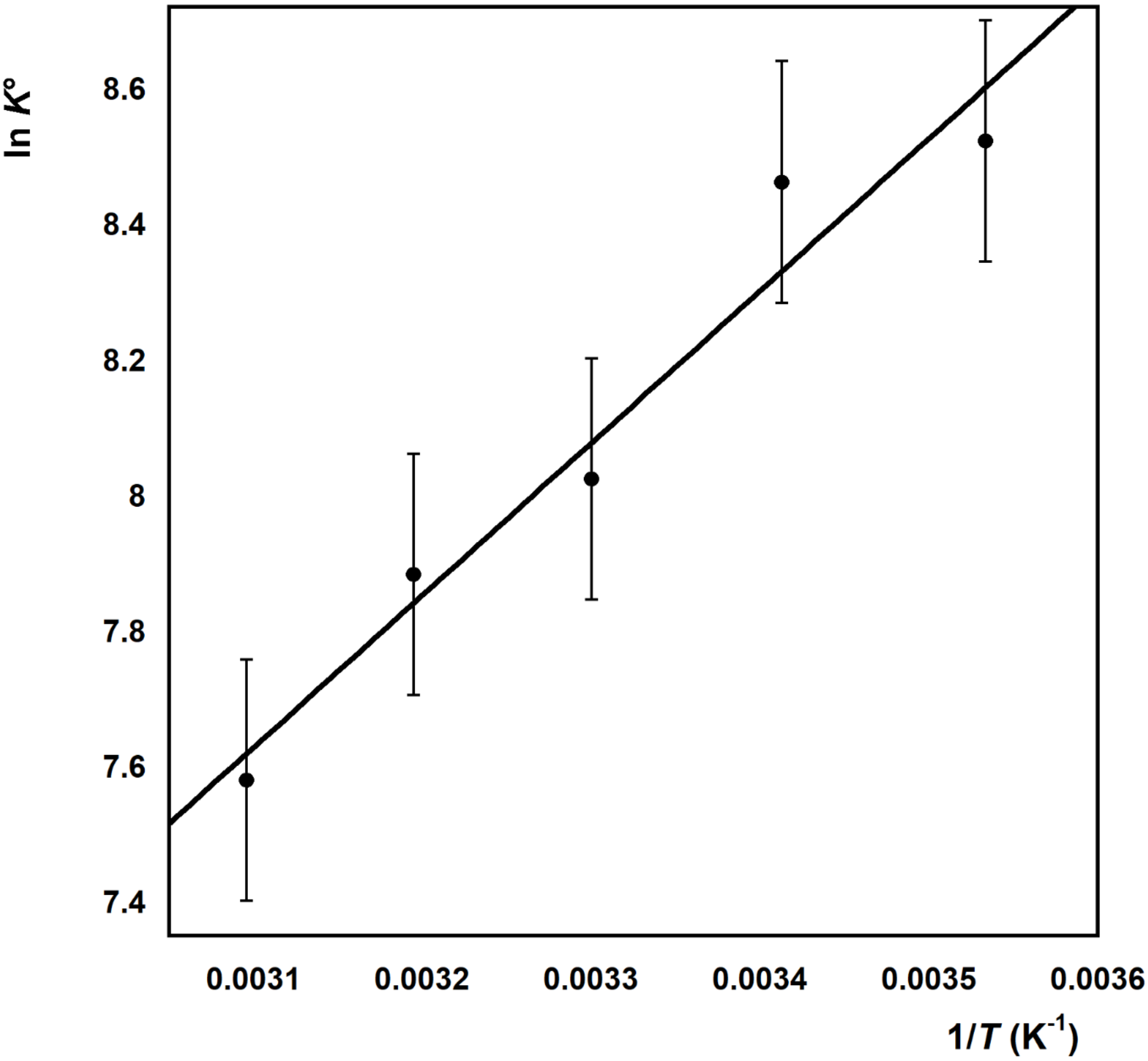


Fig. 1. Linear van’t Hoff plot using adsorption constants $K°$ (unitless) from the work of Ghosal and Gupta [42] (see also Table 2). Error bars represent the standard error (calculated by us) of the estimate of the model’s overall fit.

Table 2

Thermodynamic parameters for the adsorption of fluoride on an aluminum/olivine material*

T (K)	$K°$ (unitless)	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ K^{-1} mol^{-1})
283	5026.481*	-19 ± 2**	0.006 ± 0.008**
293	4730.845		
303	3051.498		
313	2651.44		
323	1957.408		

* Values of $K°$ as originally presented by Ghosal and Gupta [42].

** Errors ranges were calculated in the present work as standard error values of the parameters.

In their study, the authors investigated the thermodynamics of fluoride adsorption on an aluminum/olivine composite material. Based on the results shown in Fig. 1 and Table 2, Ghosal and Gupta claimed that "*the positive value of* $\Delta S°$ *reflected an affinity of the adsorbent on the fluoride ion along with the increase in the degree of freedom of the adsorbed species and the increase in randomness at the interface during the sorption process*". In our opinion, this statement is not supported by the data. It is worth noting that Ghosal and Gupta did not report the errors associated to the estimated parameters (unfortunately, a common practice in literature), thus providing no evidence of the reliability of their results. A logarithmic representation of the data, as in Eq. (9), might be misleading because it reduces the scattering for the eyes. Nevertheless, the error for $\Delta S°$ (as estimated and added by us in Table 2) is greater than the value of $\Delta S°$ itself, which clearly denotes a high degree of uncertainty regarding the absolute $\Delta S°$ value and even its sign. Thus from the above considerations, it becomes obvious that any speculation based upon the sign of $\Delta S°$ is pointless.

Ghosal and Gupta [41] present adsorption coefficients with 7 significant digits, which wrongly suggests an extremely high precision. Actually, these adsorption coefficients are derived from the Freundlich isotherm model, which yields K_F values in terms of (mg L^{-1}) × (L mg^{-1})$^{1/n}$. It is obvious that handling of ln K_F causes basic mathematical problems, and in particular that the value of $\Delta S°$ in Eq. (9) depends on the units of K_F. Hence, $\Delta S°$ calculated in this way has no real chemical meaning.

Shamsudin et al. [35] applied Eq. (9) for determining the thermodynamic parameters of diclofenac (DCF) adsorption onto alginate/carbon films (AC-films). The values of K_T used for the calculation were obtained from the Temkin model (Table 1); the results are displayed in Fig. 2A and Table 3. According to Table 3, the authors concluded that "*ΔS of DCF adsorption was −0.04 kJ/mol·K indicated that the randomness decreased at the solid-solution interface during the removal of this pollutant*". Similarly to Ghosal and Gupta [42], Shamsudin et al. did not report the errors on $\Delta H°$ and $\Delta S°$. In order to test the reliability of the fitting procedure via Eq. (9) and possibly obtain a better estimation of $\Delta H°$ and $\Delta S°$, Lima et al. [43] suggested the use of the non-linear form of the van't Hoff equation (Eq. (10)) because this provides parameters statistically more reliable than those from the regression according to the linear format:

$$K°_T = e^{\left(-\frac{\Delta H°}{R}\frac{1}{T}+\frac{\Delta S°}{R}\right)} \tag{10}$$

In the latter case, $K°_T$ is plotted as an exponential function of T for parameter determination by the non-linear regression method.

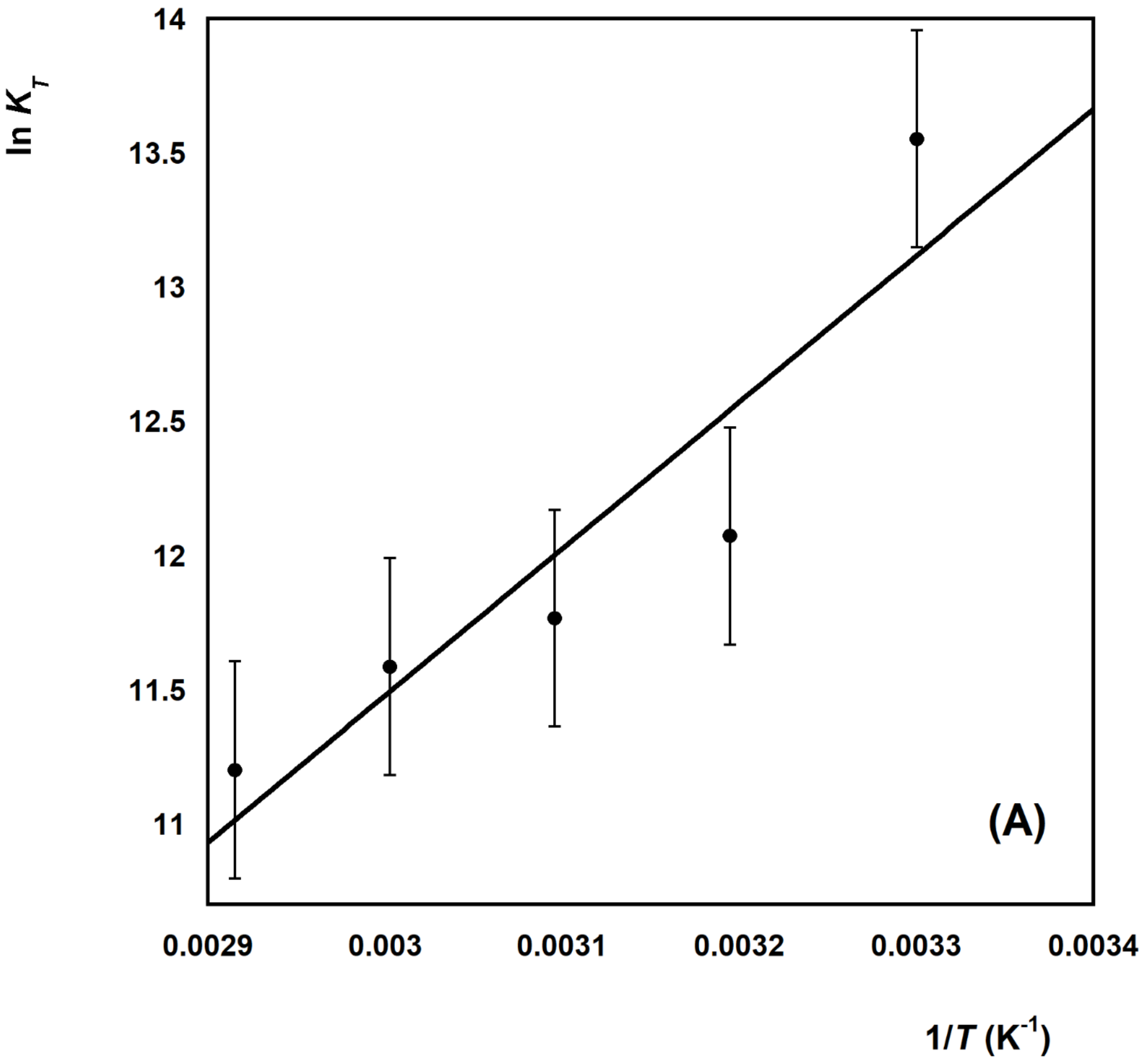
Alternatively, one can first calculate the standard adsorption Gibbs energy ($\Delta G°$) from Eq. (11), and then apply the Gibbs equation (Eq. (12)):

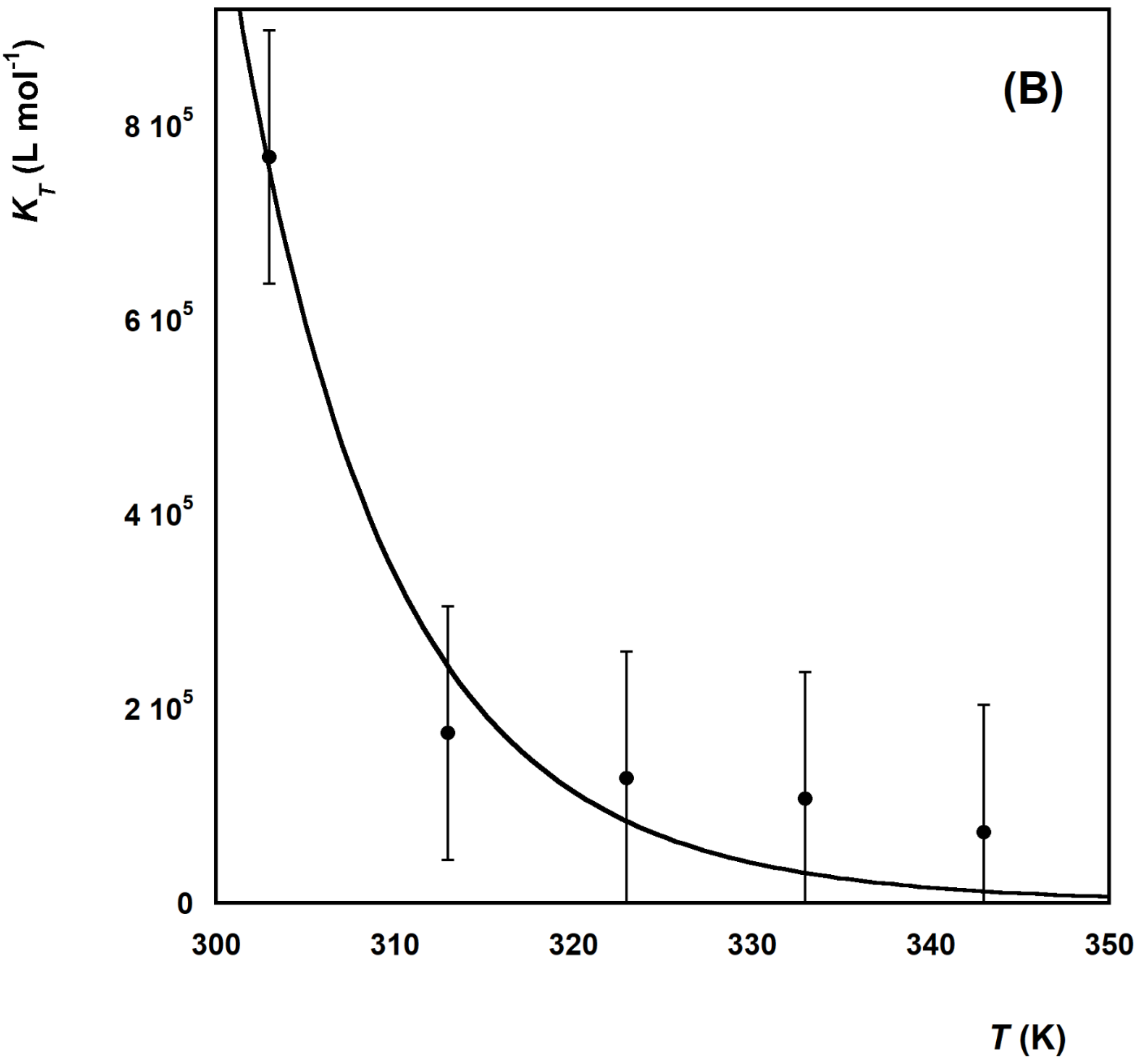
$$\Delta G° = -RT \ln K°_T \tag{11}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{12}$$

A plot of $\Delta G°$ against T should produce a straight line with intercept and slope equal to $\Delta H°$ and $-\Delta S°$, respectively.

In Figs. 2A-2C, the use of the three equations (Eqs. (9), (10), (12)) on the data set of Shamsudin et al. [35] is graphically compared; Table 3 reports the estimated values of $\Delta H°$ and $\Delta S°$, together with their associated standard errors.


ln K_T
14
13.5
13
12.5
12
11.5
11
0.0029
0.003
0.0031
0.0032
0.0033
0.0034
1/T (K^{-1})
(A)


(B)
K_T (L mol^{-1})
8 10^5
6 10^5
4 10^5
2 10^5
0
300
310
320
330
340
350
T (K)

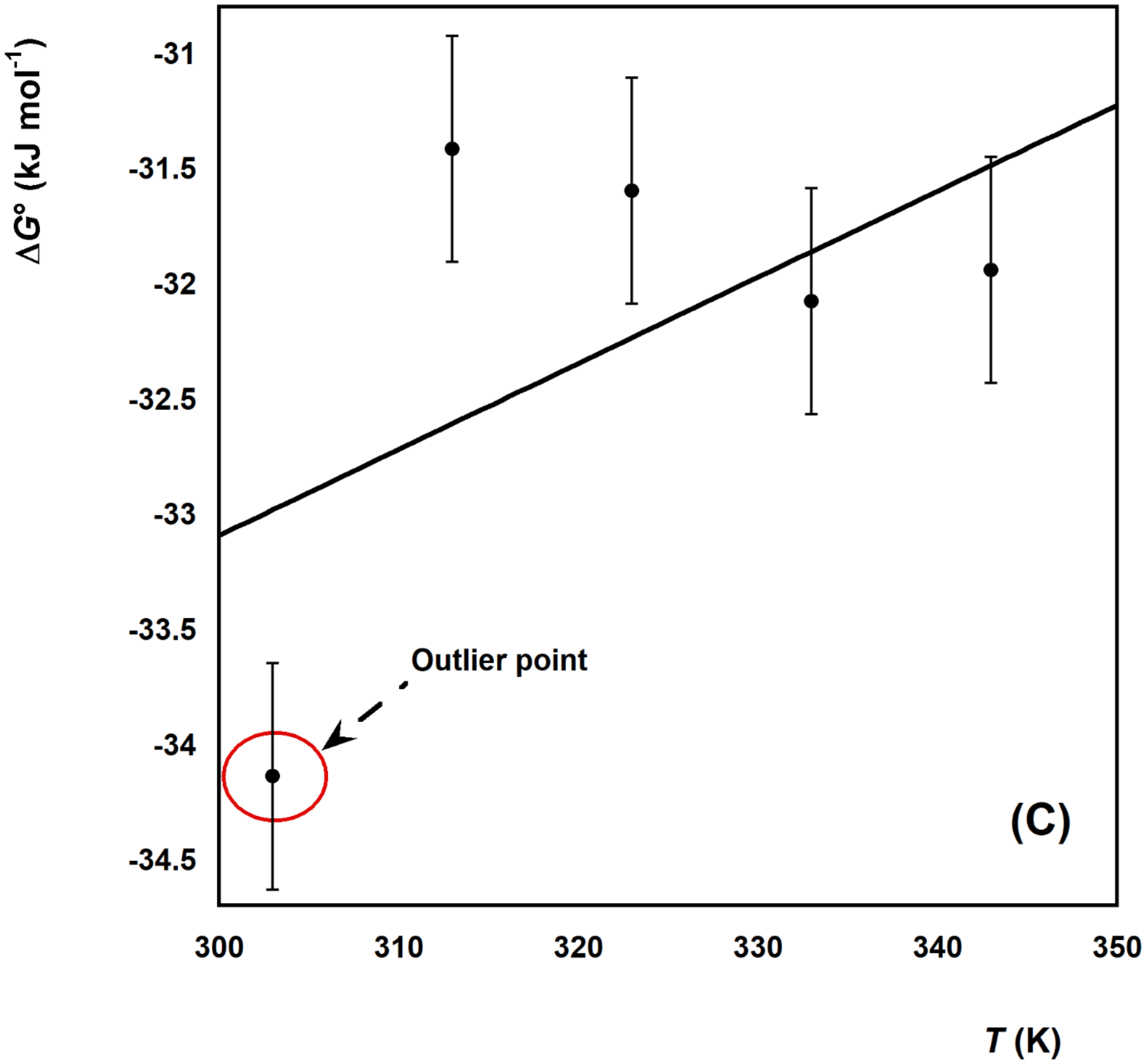


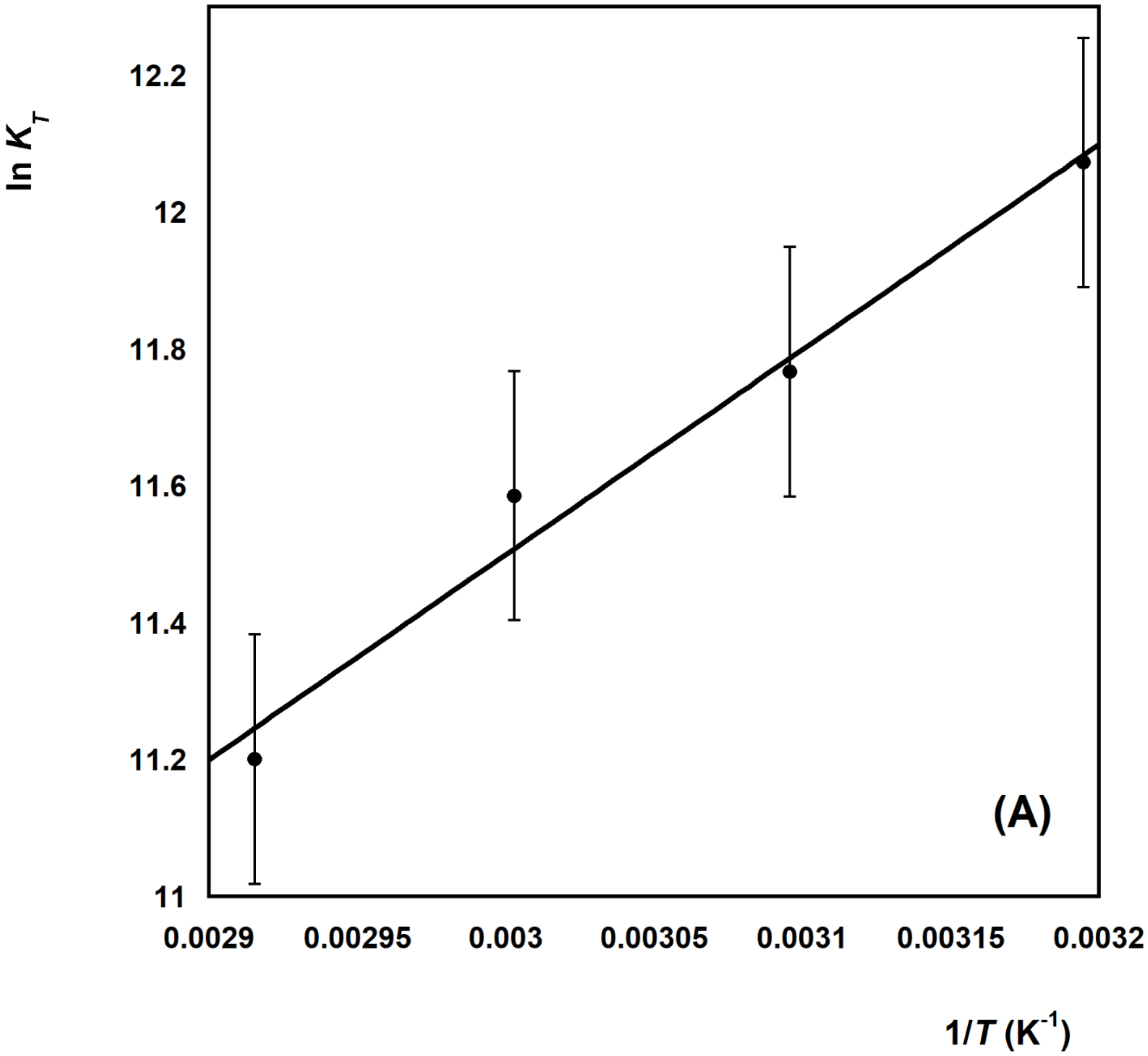
Fig. 2. Adsorption of DCF onto AC-films. Data taken from Shamsudin et al. [35]. Comparison between linear van't Hoff plot (A), non-linear van't Hoff plot (B) and Gibbs plot (C); full data set; solute standard state = 1 mol L^{-1}; K_T in part A and B should be dimensionless (i.e. $K°_T$), but is taken here in its original (erroneous) format (L mol^{-1}). Error bars represent the standard error (calculated by us) of the estimate of the model's overall fit.

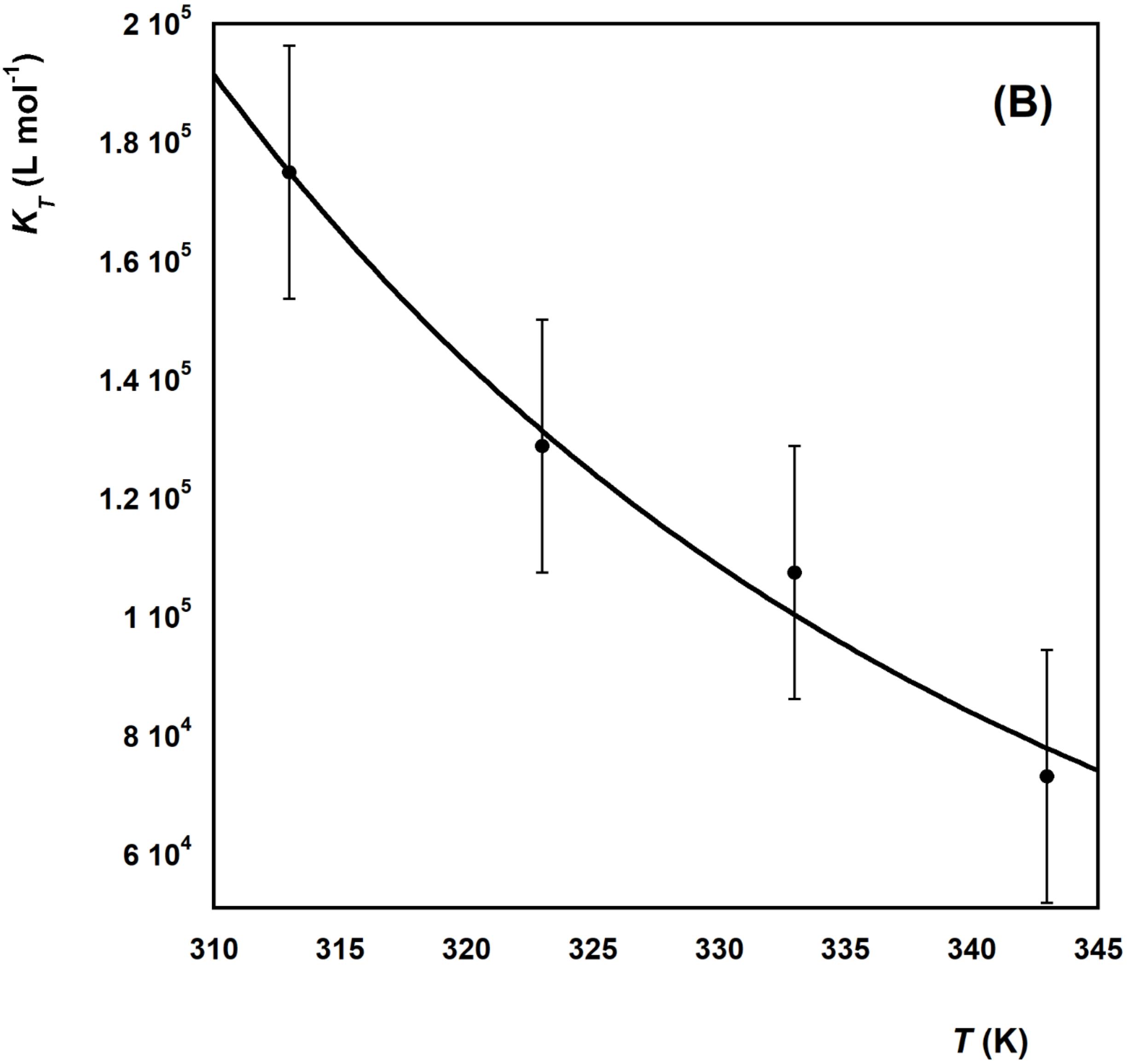
Table 3

Thermodynamic parameters for the adsorption of DFC onto AC-films as determined by various data treatment methods. Original adsorption data (K_T as f(T)) are taken from Shamsudin et al. [35]. Error intervals are the standard error values of the parameters.

	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ K^{-1} mol^{-1})
Full data set		
Linear van’t Hoff plot	(-5 ± 1) × 10	(-4 ± 3) × 10^{-2}
Non-linear van’t Hoff plot	(-9 ± 2) × 10	(-18 ± 7) × 10^{-2}
Gibbs plot	(-4 ± 1) × 10	(-4 ± 3) × 10^{-2}
Corrected data set		
Linear van’t Hoff plot	(-2.5 ± 0.3) × 10	(2 ± 1) × 10^{-2}
Non-linear van’t Hoff plot	(-2.4 ± 0.2) × 10	(2 ± 1) × 10^{-2}
Gibbs plot	(-2.5 ± 0.3) × 10	(2 ± 1) × 10^{-2}

Using the linearized equation (Eq. (9)), $\Delta H°$ and $\Delta S°$ were calculated as (–5 ± 1) × 10 kJ mol^{-1} and (−4 ± 3) × 10^{-2} kJ K^{-1} mol^{-1}, respectively. As expected, the error on $\Delta S°$ is particularly high (≈ 75%), denoting a high degree of uncertainty in the estimation of this parameter. Significantly different results are obtained with the non-linearized van’t Hoff equation (Eq. (10)). As regards the Gibbs equation (Eq. (12)), it is worth noting that it provides numerical results similar to those obtained with the linear model (see Table 3). However, its graphical representation in Fig. 2C clearly shows that the experimental data point at T = 303 K significantly deviates from the trend of the other points, likely biasing the fitting analysis and leading to incorrect estimation of $\Delta H°$ and $\Delta S°$. In order to improve the predictions of the thermodynamic parameters, Fig. 3 and Table 3 report the results of the curve-fitting procedures performed omitting the outlier data point.


ln K_T
12.2
12
11.8
11.6
11.4
11.2
11
0.0029
0.00295
0.003
0.00305
0.0031
0.00315
0.0032
1/T (K^{-1})
(A)


(B)
K_T (L mol^{-1})
2 10^5
1.8 10^5
1.6 10^5
1.4 10^5
1.2 10^5
1 10^5
8 10^4
6 10^4
310
315
320
325
330
335
340
345
T (K)

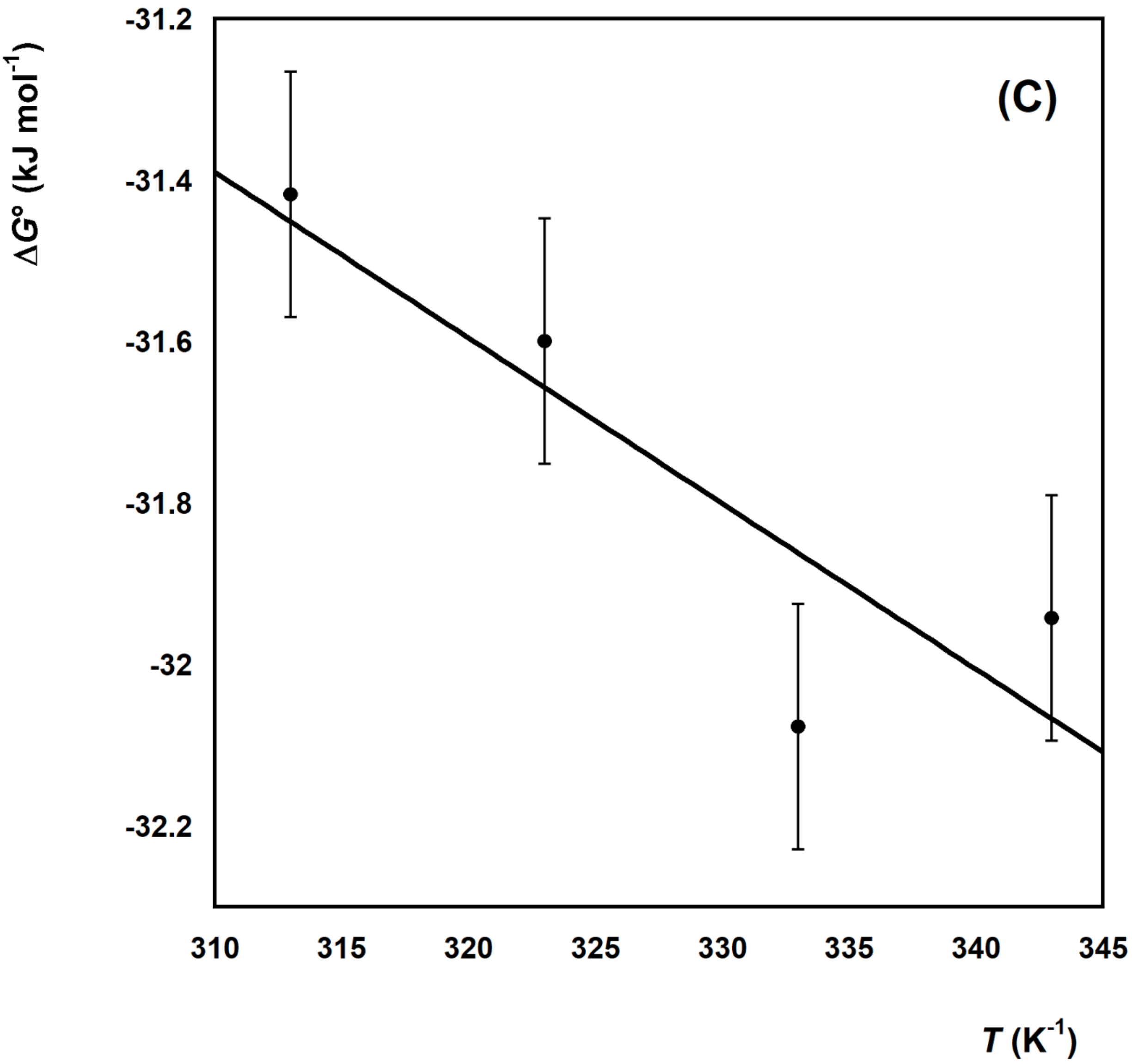


Fig. 3. Adsorption of DCF onto AC-films. Data taken from Shamsudin et al. [35]. Comparison between linear van't Hoff plot (A), non-linear van't Hoff plot (B) and Gibbs plot (C); corrected data set; solute standard state = 1 mol L^{-1}; K_T in part A and B should be dimensionless (i.e. $K°_T$), but is taken here in its original (erroneous) format (L mol^{-1}). Error bars represent the standard error (calculated by us) of the estimate of the model's overall fit.

As can be seen, the results indicate that the three models are more accurate for describing the data (and the errors for parameters) when the outlier point is not included, providing comparable values for both $\Delta H°$ and $\Delta S°$. Although at first sight the data scattering in Fig. 3C also appears to be large, this is due to the quite narrow scale of $\Delta G°$ on the ordinate. The comparison of data presentations in

Figs. 2 and 3 clearly shows that identification of outlier points is more difficult in the linear van't Hoff plot due to its logarithmic K_T scale.

4. Relationship between isotherm models and isosteric heat of adsorption

The suitability of an isotherm model for describing an adsorption process can be assessed by verifying whether the trend of the isosteric heat of adsorption is consistent with that envisaged by the isotherm model.

The isosteric heat of adsorption ($\Delta_{ist}H$) refers to a fixed surface coverage and represents the differential heat of adsorption at given adsorbate equilibrium concentration and temperature [16,44]. It can be determined by using the Clausius–Clapeyron equation [41]:

$$\Delta_{ist}H = -RT^2 \frac{\mathrm{d}\ln C_e}{\mathrm{d}T} = -\frac{RT^2}{C_e}\frac{\mathrm{d}C_e}{\mathrm{d}T} \tag{13}$$

The principle of isostericity dictates that the adsorbed amount at equilibrium q_e is constant; on the other hand, q_e depends on temperature and on liquid-phase concentration C_e. The correlation between q_e and C_e can be described by several isotherms, for example by the Langmuir isotherm model which can be expressed in terms of the thermodynamic Langmuir equilibrium constant $K°_L$ as:

$$q_e = \frac{q_m K°_L \frac{C_e}{C°}}{1 + K°_L \frac{C_e}{C°}} \tag{14}$$

and in the case of the non-dimensionless Langmuir equilibrium constant K_L as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{15}$$

where q_m is the monolayer maximum adsorption capacity. Here K_L has dimensions of the reciprocal of C_e. In the Langmuir model, it is assumed that the adsorption sites are energetically equivalent and that there are no intermolecular forces between adsorbate molecules [45]. Hence the adsorption enthalpy ($\Delta H°$) is constant over the whole range of adsorbent coverage. In the Appendix part we demonstrate mathematically that $\Delta_{ist}H = \Delta H°$. As expected, in the frame of the Langmuir model,

$\Delta_{ist}H$ is *constant* and equal to $\Delta H°$. Let us now examine how various literature studies apply this knowledge.

Chen et al. [46] studied the adsorption performance of a titanium/zirconium polymer (Ti/Zr-DBMD) for Pb(II) ions from aqueous solution. The authors affirmed that the adsorption of Pb(II) on Ti/Zr-DBMD "*conformed to the Langmuir isotherm model*". On the same data basis, they found that the isosteric heat of adsorption decreased (in absolute values) significantly with an increase of the adsorbent loading (see Fig. 4).

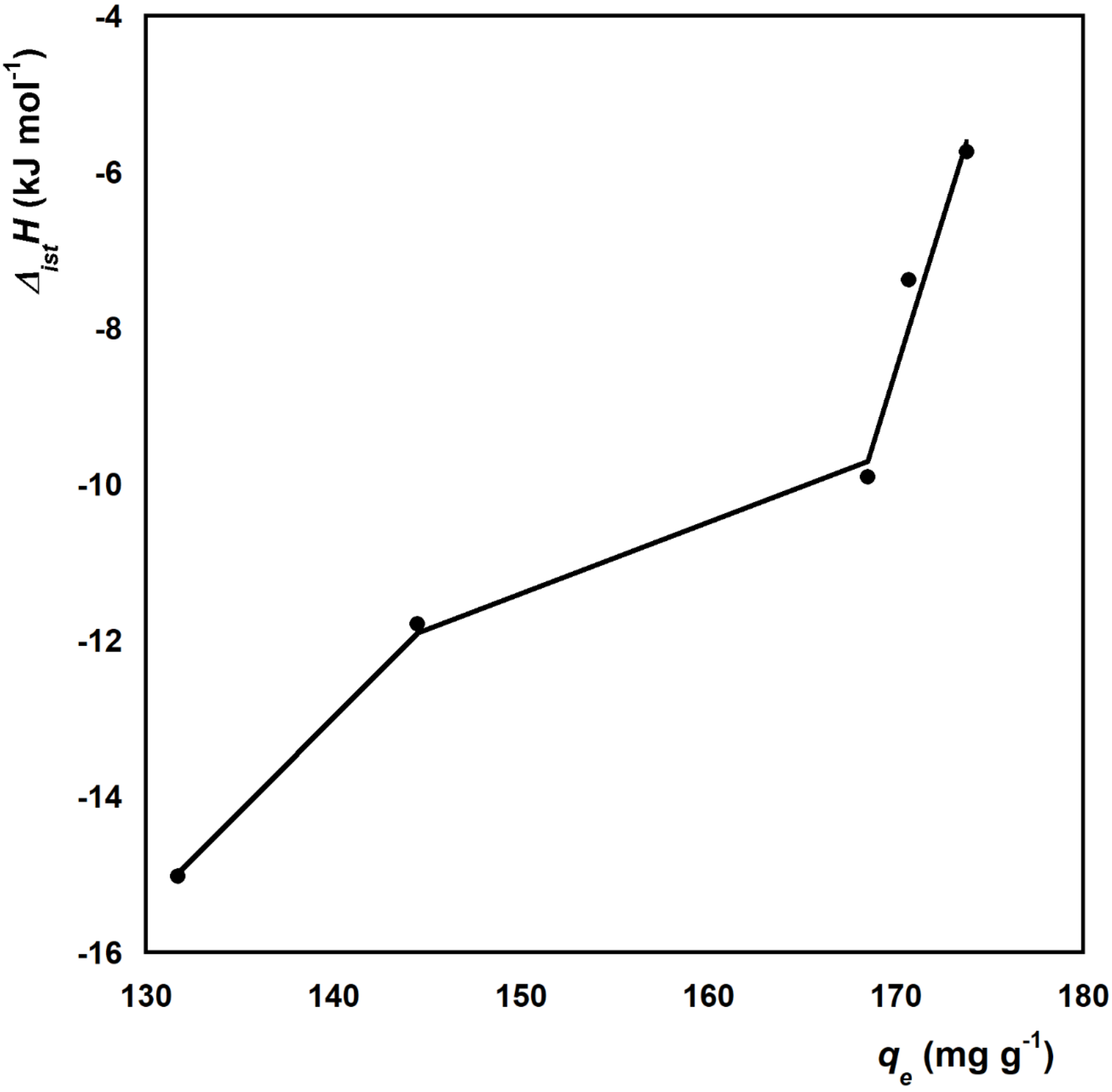


Fig. 4. Adsorption of Pb(II) ions onto a Ti/Zr-DBMD adsorbent: isosteric heat of adsorption as a function of the equilibrium adsorbent loading. Adapted from Chen et al. [46].

The latter finding clearly contradicts the Langmuir model assumption according to which, as we have shown above, the heat of adsorption is independent on the adsorbent surface coverage. This observation suggests that the Langmuir model is inadequate for describing the equilibrium of the Pb(II) adsorption onto Ti/Zr-DBMD. Apparently, the authors were not aware of the necessary correlation between the various constraints of the Langmuir adsorption model.

5. Sign of $\Delta G°$ and spontaneity of adsorption processes

A frequent and widespread mistake in adsorption studies is to determine the spontaneity of the process from the sign of $\Delta G°$, which is the *standard* free enthalpy of adsorption here.

Sentences still appearing in recent literature, such as: "*The ΔG° values for all the adsorption temperatures were obtained to be negative which indicates the spontaneous and feasible* CO_2 *adsorption process*" [36], or "*To determine the spontaneity of the adsorption process, thermodynamic studies were carried out.*" [47], "*…thermodynamic functions allowed to verify if the adsorption was favorable and spontaneous*" [35], or "*The fact that ΔG° was negative indicated that the adsorption of Pb(II) on Ti/Zr-DBMD was a spontaneous process*" [46], or "*It could be seen … that the values of ΔG° … were all negative at different temperatures, suggesting Pb(II) adsorption on both BMC and OMC was spontaneous*" [48], and similar statements in [49,50,53], are meaningless. It should be noted that if adsorption were not favorable and spontaneous, it would not take place under the given conditions at all.

This common mistake arises from the fact that $\Delta G°$ and ΔG are used interchangeably. ΔG is the change in free enthalpy due to adsorption of a dissolved solute under the experimental conditions under study. Usually it applies to the state of an initially 'clean' adsorbent. Unlike the sign of ΔG, the sign of $\Delta G°$ provides no information on the spontaneity of a process [16,17,51,52]. Simply stated: the driving force of an adsorption depends on the distance of the actual state (solute + adsorbent) from the equilibrium state. This means that any adsorption process proceeds spontaneously when starting with a clean adsorbent. Inspection of Eq. (11) suggests that the sign of $\Delta G°$ solely depends on the numerical value of $K°_T$ (or of any other equilibrium constant used for $\Delta G°$ calculation), which in turn varies with the *selected* standard conditions: for $0 < K°_T < 1$, we get $\Delta G° > 0$ whereas for $K°_T > 1$ it follows that $\Delta G° < 0$. As an example, in the study of Shamsudin et al. [35], the selected standard condition for the solute was 1 mol L^{-1} (implicitly defined by the concentration measure units used by the authors for expressing the solute concentration in the liquid phase), which gives $K°_T$ values >1 and therefore $\Delta G° < 0$ (Table 4). Based on the observation that the calculated $\Delta G°$ were negative (see the third column in Table 4), the authors erroneously inferred that "*DCF adsorption on AC-films was spontaneous*". However, by using 1 mg L^{-1} as the standard state for the solute, we get $K°_T < 1$ and hence, $\Delta G° > 0$ for four of the five temperatures tested (see the fifth column in Table 4). The negative value at 303 K has already been identified as an outlier (see above). Simply stated: the driving force for adsorption is higher when the adsorbent comes into contact with 1 mol L^{-1} of solute concentration compared to 1 mg L^{-1}.

Table 4
Adsorption of DCF onto AC-films. Data adapted from Shamsudin et al. [35]. Values of $\Delta G°$ are calculated using two different solute standard conditions.

T (K)	$K°_T$ (Solute standard condition = 1 mol L^{-1})	$\Delta G°$ (kJ mol^{-1}; solute standard condition = 1 mol L^{-1})	$K°_T$ (Solute standard condition = 1 mg L^{-1})	$\Delta G°$ (kJ mol^{-1}; solute standard condition = 1 mg L^{-1})
303	7.68×10^5	-34.1	2.414	-2.2
313	1.75×10^5	-31.4	0.550	1.6
323	1.29×10^5	-31.6	0.405	2.4
333	1.075×10^5	-32.1	0.338	3.0
343	0.732×10^5	-31.9	0.230	4.2

This does not imply that the adsorption process with low DCF concentrations, e.g. 1 mg L^{-1}, becomes non-spontaneous. A change in the standard state (that is, a change in the units of measure) cannot affect the direction of the process because the actual activities (or concentrations) of reactants and products (hence the reaction quotient and ΔG, *not* $\Delta G°$) remain the same.

6. Adsorption from different phases

Finally we want to point to another aspect when interpreting thermodynamic parameters such as ΔG_{ads}, ΔH_{ads}, and ΔS_{ads} for adsorption in condensed media, e.g. in water. In contrast to adsorption from the gas phase, in condensed media these parameters reflect changes of molecular interactions in both the solid *and* the liquid phases. Solutes, adsorbates and adsorbents are all subjects of solvation. This makes the chemical meaning of such terms more complex.

Conclusions

Adsorption is one of the most relevant processes in water treatment techniques and for catalysis in aqueous systems. This role is reflected by a large number of experimental and theoretical adsorption studies published in the pertinent literature. Correct data treatment and interpretation is essential for their further application. The present contribution points to a number of pitfalls and misinterpretations frequently found in adsorption studies, in particular when adsorption data are interpreted in terms of thermodynamic parameters. Only selected examples are presented here: this is by no means an exhaustive analysis of the literature.

Most of the considerations in this article concern basic knowledge in physical chemistry rather than sophisticated science. Regrettably, obvious methodical or conceptual errors, as exemplarily stressed for adsorption phenomena in this paper, appear frequently in the literature. Inconsistency of units, for example, is not “merely” a formal error but invalidates the entire output. These publications are written by established scientists, pass careful reviewer checks and are finally published in well-respected journals. There, they affect understanding of the subject-matter (e.g. adsorption phenomena) and style of writing (e.g. number of digits for data presentation) in the scientific community, in particular for the younger scientists. Significant methodical errors should not remain undisputed but should be remediated in a timely manner in the respective journals. Although this kind of scientific self-healing is sometimes perceived as irritating, it is essential in order to preserve and protect the chain of logical deduction.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix

Relationship between adsorption isotherm models and isosteric heat of adsorption

The isosteric heat of adsorption ($\Delta_{\mathrm{ist}}H$) refers to a fixed surface coverage and represents the differential heat of adsorption at given adsorbate equilibrium concentration and temperature. It can be determined by using the Clausius–Clapeyron equation:

$$\Delta_{ist}H = -RT^2 \frac{\mathrm{d}\ln C_e}{\mathrm{d}T} \tag{A1}$$

or

$$\Delta_{ist}H = -\frac{RT^2}{C_e}\frac{\mathrm{d}C_e}{\mathrm{d}T} \tag{A2}$$

The principle of isostericity dictates that the adsorbed amount at equilibrium q_e is constant; on the other hand, q_e depends on temperature and solute's liquid-phase concentration. It follows that an infinitesimal change in q_e is given by

$$\mathrm{d}q_e = \left(\frac{\partial q_e}{\partial T}\right)_{C_e} \mathrm{d}T + \left(\frac{\partial q_e}{\partial C_e}\right)_T \mathrm{d}C_e = 0 \tag{A3}$$

which yields

$$-\frac{\left(\frac{\partial q_e}{\partial T}\right)_{C_e}}{\left(\frac{\partial q_e}{\partial C_e}\right)_T} = \frac{\mathrm{d}C_e}{\mathrm{d}T} \qquad \text{(A4)}$$

Substitution of Eq. (A4) into Eq. (A2) leads to

$$\Delta_{ist}H = \frac{RT^2}{C_e}\frac{\left(\frac{\partial q_e}{\partial T}\right)_{C_e}}{\left(\frac{\partial q_e}{\partial C_e}\right)_T} \qquad \text{(A5)}$$

It should be noted that the values of the partial derivatives of q_e with respect to T and C_e in Eq. (A5) are model-dependent. As an example, let us consider the Langmuir model: in this case it is assumed that the adsorption sites are energetically equivalent and that there are no intermolecular forces between adsorbate molecules. Hence, the adsorption enthalpy ($\Delta H°$) is constant over the whole range of adsorbent coverage. The Langmuir isotherm is given by

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \qquad \text{(A6)}$$

where q_m and K_L are the monolayer maximum adsorption capacity and the Langmuir equilibrium constant, respectively.

By substituting Eq. (A6) into Eq. (A5) and solving the derivatives of q_e with respect to T and C_e, one obtains

$$\Delta_{ist}H = \frac{RT^2}{K_L}\frac{\partial K_L}{\partial T} \qquad \text{(A7)}$$

The explicit dependence of K_L on T can be obtained by combining Eqs. (11) and (12) from the main part:

$$K_\mathrm{L} = e^{\frac{\Delta S°}{R}} e^{-\frac{\Delta H°}{RT}} \qquad \text{(A8)}$$

By substituting Eq. (A8) into Eq. (A7) and solving, under the assumption that both $\Delta H°$ and $\Delta S°$ are temperature-independent, we finally get:

$$\Delta_{ist}H = \Delta H° \qquad \text{(A9)}$$

As expected, according to the Langmuir model, $\Delta_\mathrm{ist}H$ is *constant* and equal to $\Delta H°$.

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