New physicochemical interpretations for Adsorption of Trichloroethylene on Activated Carbon: Steric and Energetic Interpretation using Statistical Physics Approach

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Abstract
Experimental adsorption isotherms of trichloroethylene (TCE) on activated carbon at four temperatures were analyzed theoretically by a double layer with one energy established through statistical physics approach. This model contains three parameters affecting the adsorption process i.e. the number of molecules per site \( n \), the monolayer adsorbed quantity \( Q_0 \) and the concentration at half- saturation \( c_{1/2} \). In this work, we propose a steric and energetic interpretation for the different adsorption isotherms of TCE on activated carbon. We calculate also the thermodynamic functions to characterize the adsorption process such as, entropy, free energy, and internal energy as function concentration. The different parameters and the thermodynamic functions were discussed with temperature.

Keywords: Adsorption Isotherm; Statistical Physics; Modeling; Trichloroethylene

1. Introduction
Groundwater contamination is a worldwide threat for environment and living beings and trichloroethylene (TCE) can be considered as one of the most dangerous and toxic organic pollutants[1]. TCE is present in groundwater with concentration as high as few ppm’s, as reported by the Environmental Protection Agency in U.S.A[1]. Several techniques have been proposed and attempted for the removal of pollutants[2–6]. Among these numerous methods of pollutants removal, it is now recognized that adsorption, using solid supports, is an effective and useful technique. It is well known that in literature there are many publications interested in wastewaters treatment, especially by means of the adsorption of pollutants onto numerous adsorbents. Conventional materials have been used with success. The challenge for adsorption is to promote non-conventional materials mainly in term of high adsorption capacity and low cost. Waters contaminated by organic chemicals can be treated essentially by adsorption on activated carbons which have a good pollutant removal capacity and a great versatility[7,8]. The knowledge of adsorption isotherms as well as of reliable adsorption models plays an important role in the analysis and design of adsorption systems. The performance of an adsorption treatment mainly depends on the thermodynamic aspects of solute-solvent-
sorbent interactions and on the transport phenomena involving the diffusive-convective transport within the porous media. The equilibrium conditions are the most significant limits for the application of a given sorbent. Despite the large industrial application of this technology, the study on the dynamics of the adsorption of single compounds on carbon surface has received limited attention, while extensive researches have been focused in the past decades on the adsorption phenomenology.

As a matter of fact, several authors have proposed empirical models for a phenomenological description of adsorption isotherms (Langmuir model, Freundlich model….). However, most of these models do not provide any indication about the adsorption mechanism and the isotherm formulations have no physical significance or relationship with the physico-chemical parameters involved in the adsorption process.

To understand and analyze the adsorption process of TCE on activated carbon, an approach of several isotherm models was developed in this work. It depends on the assumptions that are used to derive each model. However, all mathematical analyses of experimental adsorption data were found to be useful in characterizing and interpreting the adsorption process based on the magnitudes of the fitting parameters.

The main goal of the present paper is to give physical interpretations (steric and energetic interpretation) at microscopic level of TCE adsorption on activated carbon at four temperatures ranged from 283 to 323K. Our approach is based on a quantum statistical consideration of adsorption using a double layer model with one energy. We calculate also the thermodynamic functions to enrich our study as function temperature. In reference [1], this experimental study of the different adsorption isotherms is reported.

2. Double layer model with one energy formulation

The following statistical treatment here presented is applicable to both liquid and gas systems. As first approximation, the mutual interaction between the adsorbed molecules is neglected and their concentrations will be considered as relatively low. To apply statistical physics treatment, some assumptions will be considered. It is assumed that the adsorbate molecules are anchored onto receptor sites with the energy levels $\varepsilon_i$. Each receptor site can be empty or occupied. Adsorption involves an exchange of particles from free state to the adsorbed one. Its investigation cannot be performed without employing the grand canonical ensemble to take into account the particle number variation through the introduction of a variable chemical potential, $\mu$, in the adsorption process. The internal degree of freedom of the adsorbate molecules may be neglected in aqueous solution thereby allowing only the most important degree of freedom, i.e. the translational one, to be taken into account. This arises because the electronic degree of freedom cannot be excited thermally and the rotational degree of freedom is hampered in solution. The vibrational degree of freedom can be neglected in comparison with the translational one. According to these assumptions, the grand canonical partition function of one receptor site describing the microscopic states of a system following the physical situation in which this system is placed may be expressed as [9-13]:

$$Z_{gc} = \sum_{N_i} e^{-\beta(-\varepsilon_i - \mu)N_i}$$  \hspace{1cm} (1)

Where $-\varepsilon_i$ is the receptor site adsorption energy, $\mu$ is the chemical potential, $N_i$ is the receptor site occupation state and $\beta$ is defined as, $1/k_B T$ where $k_B$ is the Boltzmann constant and $T$ absolute temperature.

According to the Gibbs ensemble method, each macroscopic system may be represented as a large number of copies of equal volume. Each copy (subsystem) is statistically independent. To satisfy this requirement, the subsystem would ordinarily be a macroscopic, too. In this case surface effects, due to the influence of neighboring subsystems, become negligible. However, being evidently a microsystem, the receptor sites are
independent or may be still considered statistically independent. The total grand canonical partition related to $N_M$ receptor sites per surface unit, which we assume identical and independent, is written then[12-16]:

$$Z_{gc} = (z_{gc})^{N_M}$$

(2)

The average site occupation number can be written as[11,12,17]:

$$N_o = k_B T \frac{\partial \ln Z_{gc}}{\partial \mu}$$

(3)

We consider that a variable number of molecules are adsorbed onto $N_M$ receptor sites located on a unit mass of the adsorbent. In general the adsorption reaction of adsorbate molecules $(A)$ onto receptor sites $(S)$ should include a stoichiometric coefficient $(n)$, expressible as the following equation[11,12]:

$$nA+S \overset{\leftrightarrow}{\rightarrow} AS^n$$

(4)

The parameter $n$ is an average number, which can be an integer or not, greater or smaller than 1. If $n$ is greater than 1, it represents the number of molecules anchored on one site, according to multimolecular adsorption mechanism. If $n$ is less than 1, it would represent “the fraction of molecule per site” and a multianchorage adsorption mechanism can be hypothesized. In addition to its stoichiometric aspect, $n'=1/n$ represents the anchorage number of one molecule on an average number of receptor sites.

The total number of the adsorbed molecules is then written as[11,15,16]:

$$Q = nN_o$$

(5)

For this model, the adsorption is hypothesized to occur on two layers. First, we assume that the molecules are adsorbed with the same energy $-\varepsilon$. Occupancy status $N_i$ can assume the value 0 if the site is empty and the value 1 if the site is occupied by $n$ molecules and $2n$ if the site is occupied by two molecules. The grand canonical partition function for a single site is given by[14,18]:

$$z_{gc} = 1 + e^{\beta(\varepsilon+\mu)} + e^{2\beta(\varepsilon+\mu)}$$

(6)

Finally, the adsorbed quantity versus concentration is given by the following expression[12]:

$$Q = nN_M \frac{c}{c_{1/2}}^n + 2 \left( \frac{c}{c_{1/2}} \right)^{2n}$$

$$1 + \left( \frac{c}{c_{1/2}} \right)^n + \left( \frac{c}{c_{1/2}} \right)^{2n}$$

(7)

where, $n$ is the number of adsorbed molecule(s) per site, $N_M$ (mg g$^{-1}$) is the receptor site density and $c_{1/2}$ (µg L$^{-1}$) is the concentration at half saturation.

For solid–liquid systems, the parameter $c_{1/2}$ can be related to the molar adsorption energy $\Delta E^a$ (kJ mol$^{-1}$) as[11,12,15,16,18]:

$$c_{1/2} = c_s e^{-\Delta E^a / RT}$$

(8)

where, $c_s$ (mg L$^{-1}$) is the TCE solubility, $R$ is the ideal gas constant (kJ mol$^{-1}$ K$^{-1}$) and $T$ is the temperature (K).

The $N_M$ parameter can be related with the adsorbed quantity at saturation $Q_0$ (mg g$^{-1}$) by the equation:

$$Q_0 = nN_M N_{imax}$$

(9)

being, $N_{imax}$ the maximal number of adsorbed layers, in this model $N_{imax}$=2. The adsorbed quantity at saturation is an important factor which characterizes the adsorption system. It is about a steric parameter.
which gives us information on the adsorption capacity of the material. It is a very interesting parameter for the wastewaters depollution.

To understand this model, we present in figure 1 a simple illustration of the distribution of TCE molecules on activated carbon.

![Figure 1](image)

**Figure 1.** Distribution of the molecules adsorbed on a solid material according to a double layer model with one energy.

### 3. Results and Discussions

The nonlinear fit of the experimental data with the analytical models, allowed us to estimate the physicochemical parameters related to the adsorption process. The evolution of such parameters as a function of experimental conditions will be investigated in details to interpret and understand the physical process at molecular level. It follows that two interpretations, steric and energetic, are derived. We use a fitting computer program to simulate the experimental data using the double layer model with one energy.

The different adsorption isotherms were tested also by four statistical models such as, monolayer model with one energy, monolayer model with two energies, double layer model with one energy, and the double layer model with two energies. The mathematical fitting method utilized to contrast the experimental data versus the proposed model, was based on the Levenberg-Marquardt iterating algorithm using a multivariable non-linear regression program. The best fitting result is established once the residuals between the experimental and theoretical values by the model are minimized according to a determined level of confidence[19]. In our case, the level of confidence was set at 95%. Two figures of merit were used as indicators of the overall goodness-of-fit of the model to the data. The first is the multiple correlation coefficients squared, \( R^2 \) also known as the coefficient of determination which is a standardized measure of the goodness-of-fit. This coefficient is given by[20,21]:

\[
R^2 = 1 - \left( 1 - \frac{\sum_{i} (Q_{i,\text{exp}} - \bar{Q}_{\text{exp}})^2 - \sum_{i} (Q_{i,\text{exp}} - \bar{Q}_{i,\text{model}})^2}{\sum_{i} (Q_{i,\text{exp}} - \bar{Q}_{\text{exp}})^2} \right) \times \left( \frac{n_p - 1}{n_p - p} \right)
\]  

(10)

where \( Q_{i,\text{model}} \) is each value of \( Q \) predicted by the fitted model, \( Q_{i,\text{exp}} \) is each value of \( Q \) measured experimentally, \( \bar{Q}_{\text{exp}} \) is the average of \( Q \) experimentally measured, \( n_p \) is the number of experiments performed and \( p \) is the number of parameters of the fitted model.

The second is the residual root mean square error (RMSE) also called the estimated standard error of the regression which is a nonstandardized measure of the goodness-of-fit. If the model is correct and the parameter estimates unbiased, then approximately 95% of the estimated values should fall within \( \pm \)2 RMSE of their true values. For a number \( p \) of adjustable parameters the estimated standard error is given by[22]:

\[
\text{RMSE} = \sqrt{\frac{\sum_{i} (Q_{i,\text{exp}} - Q_{i,\text{model}})^2}{n_p - p}}
\]  

(11)
The ideal fitting is obtained when the value of $R^2$ is close to the unit. In Table 1, the coefficients of determination and the residual root mean square error for each model are reported.

Table 1. Values of coefficient of determination $R^2$ of each model

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Monolayer model with one energy</th>
<th>Monolayer model with two energies</th>
<th>Double layer model with one energy</th>
<th>Double layer model with two energies</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>0.984</td>
<td>0.986</td>
<td>0.996</td>
<td>0.991</td>
</tr>
<tr>
<td>293</td>
<td>0.980</td>
<td>0.981</td>
<td>0.996</td>
<td>0.984</td>
</tr>
<tr>
<td>308</td>
<td>0.976</td>
<td>0.977</td>
<td>0.998</td>
<td>0.978</td>
</tr>
<tr>
<td>323</td>
<td>0.971</td>
<td>0.975</td>
<td>0.997</td>
<td>0.978</td>
</tr>
</tbody>
</table>

We note in table 1, the double layer model with one energy presents high $R^2$ values. Allowing these criteria, the double layer model with one energy was preferred. This model is simple and provides a good description of the adsorption process of TCE on activated carbon. We give in figure 2 an illustration of the fitting by the selected model of adsorption isotherms of TCE on activated carbon at four temperatures (283, 293, 308, 323K).

![Figure 2](image-url)

**Figure 2.** Experimental data of adsorption isotherms of TCE fitted by a double layer model with one energy (the statistical model is illustrated by a red color).

The different parameters of this model are presented in table 2, obtained by numerical simulations at different temperatures.
Table 2. Fitted parameters obtained by simulation of the TCE adsorption on activated carbon using the double layer with one energy.

<table>
<thead>
<tr>
<th>Temperature (T(K))</th>
<th>Number of molecules per site</th>
<th>Monolayer quantity (mg/g)</th>
<th>Adsorbed quantity at half-saturation (µg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>0.64 ± 0.033</td>
<td>194 ± 10.21</td>
<td>6810 ± 358.42</td>
</tr>
<tr>
<td>293</td>
<td>0.73 ± 0.038</td>
<td>182 ± 9.57</td>
<td>6730 ± 354.21</td>
</tr>
<tr>
<td>308</td>
<td>0.87 ± 0.045</td>
<td>148 ± 7.78</td>
<td>5732 ± 301.68</td>
</tr>
<tr>
<td>323</td>
<td>0.94 ± 0.049</td>
<td>118 ± 6.21</td>
<td>4700 ± 247.36</td>
</tr>
</tbody>
</table>

The effect of temperature on the adsorption isotherm is of great importance. So, the temperature affects the physicochemical parameters which govern the adsorption process. Analysis of variance (ANOVA) revealed that the effect of temperature on adsorbed quantities was significant (p > 0.05). A detailed study of variation of the fitting parameters is included in the following.

3.1. Steric Interpretation

The adsorption reaction expresses that the parameter $n$ is a stoichiometric coefficient; it represents the number of molecules per site given in the expression of the model. It is also a steric coefficient which gives information on the position of the molecule at the adsorbent surface. In fact, the molecule of TCE has several manners of to be anchored on the receptor site according to its geometry and its angle of incidence with the adsorbent surface.

Depending on $n$ values two possible way of anchoring of the adsorbed molecules can be distinguished. In the first, when $n$ is lower than 1, the adsorbed molecules adopt a position parallel to the adsorbent surface[11,12]. In this case, we define the anchorage number $n' = 1/n$ which represents the number of sites occupied by one molecule. In the second case, when the number of molecules per site is superior to 1 (one receptor-site occupied by more than one molecule), the molecules are adsorbed in a perpendicular position to the adsorbent surface[11,12]. The number of molecules per site $n$ which is introduced in the model is an integer for the perpendicular position and a fractional one for the parallel position. In the adopted model, the result is an average value on the whole adsorption surface and, coherently, it is a decimal.

For example if $n = 0.87$, the value can be derived as weighted mean between $\frac{1}{2}$ and 1, which gives a number of anchorage $n'$ which varies between 0.5 and 1. The value of $n$ can be written as an average between two molecules with percentage having respectively an anchorage ($n' = 1$) and two anchorages ($n' = 1/n$). If we denote by $x$ the percentage of molecules with a single anchorage, the percentage of molecules having two anchorages is then $(1-x)$, so we can write $0.87 = x \cdot 1 + (1-x) \cdot 0.5$, which rules out that the 74% TCE are anchored with a single anchorage and 26% are anchored with two (parallel anchorage).

In the light of these results, it can be deduced that the anchorage of the TCE its size as well as its structure. The number of molecules per site varies slightly depending on the temperature from 283 to 308 K; hence the TCE maintains its position on the receptor sites of the activated carbon, independently on the temperature. In figure 3 the variation of the number of molecules per site versus temperature is reported.
Figure 3. Variation of the number of molecules per site versus temperature

When the temperature is further increased, the number of molecules increases, this means that the TCE molecules has the tendency to orient perpendicular on the activated carbon under the effect of thermal agitation. The second steric parameter is the monolayer adsorption quantity which depends on the number of molecules per site (n) and the density of receptor sites ($N_M$). This parameter is an important factor which characterizes the adsorption system and represents the ability of the surface of activated carbon to hold TCE molecules. It is a very interesting parameter for the industry as well as the wastewaters depollution. The estimated values of the monolayer adsorption quantity for TCE are varied between 118 to 194 mg/g, as shown in figure 4.

Figure 4. Variation of the monolayer adsorbed quantity versus temperature

As can be observed, the temperature has a significant effect on the adsorbed quantity. Indeed, the increase of temperature leads to the reduction of the adsorbed amount. The evolution of this parameter explains the exothermic nature of the adsorption of TCE by activated carbon as we will show in the calculation of adsorption energy. The third steric parameter is the density of receptors sites $N_M$. In figure 5 the variation density of receptors sites of versus temperature are reported. We note that the density of receptors sites decrease versus the temperature which can be explained by the fact that some receptors sites are note occupied. These results are in good agreement with the fact that the TCE molecule tends to orient perpendicularly on the adsorbent surface of activated carbon. In figure 5, the variation of the density of receptors sites versus temperature is reported.
3.2. Energetic interpretation

The energetic investigation is fundamental to study in deep the adsorption process. For this reason, we propose a subsequent study of some energy quantities characterizing the interactions between the adsorbed molecules and the activated carbon. The adsorption energy is calculated using the following relation[11,12]:

\[
- \Delta E^a = -RT \ln \left( \frac{c_s}{c_{1/2}} \right)
\]  

in which \(c_s = \text{g/L} \) is the solubility of TCE in water, assumed to be constant in the range of studied temperatures. \(c_{1/2} \) is the half-saturation concentration determined by model fitting. The adsorption energy of TCE adsorbed on activated carbon is presented in table 3 at different temperatures.

Table 3. Adsorption energy at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Adsorption energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>-11.73</td>
</tr>
<tr>
<td>293</td>
<td>-12.18</td>
</tr>
<tr>
<td>308</td>
<td>-13.21</td>
</tr>
<tr>
<td>323</td>
<td>-14.39</td>
</tr>
</tbody>
</table>

The type of interaction can be classified, to a certain extent, by the magnitude of the change in adsorption energy. Physical adsorption such as hydrogen bonding usually proves values <30 kJ.mol\(^{-1}\)[23,24]. Other physical sorption mechanisms such as van der Waals forces are usually 4–10 kJ.mol\(^{-1}\), hydrophobic bond forces about 5 kJ.mol\(^{-1}\), coordination exchange about 40 kJ mol\(^{-1}\) and dipole bond forces 2–29 kJ mol\(^{-1}\)[25]. On the other hand, chemical bond forces are usually >80 kJ mol\(^{-1}\)[23,25]. The values of adsorption energy obtained in this study show that binding between molecules and surface takes place through a physical adsorption such as hydrogen bonding interactions. It is obviously noticed from the values of adsorption energies that the TCE gives energy to the solvent to be adsorbed, i.e., it is about exothermic process. Furthermore, all adsorption energy values indicate that it is about physical adsorption and no dissociative adsorption took place. We note also that the adsorption energy increase in modulus versus the temperature which can be explained by the exothermic character of the adsorption process.
4. Thermodynamic functions

The investigation of the adsorption process using the grand canonical partition function is a powerful tool because it is often possible to write the grand canonical partition function as a product of independent contributions. Thus, a complicated problem can be simplified by solving several independent problems. According to the statistical physics treatment, thermodynamic properties can be evaluated to reinforce the interpretations of the adsorption systems. These thermodynamic functions are entropy, Gibbs free adsorption energy and internal energy. The information given by the entropy is very important in the characterization of the behavior of adsorbed molecules. This parameter is due to various arrangements of the adsorbed molecules at the surface. In general, any reaction for which the change in the Gibbs free adsorption energy \( G \) is negative should be favorable or spontaneous. Thus, its investigation is important to understand the physical adsorption process. The internal energy concept is an indispensable tool for the understanding of the physicochemical phenomena such as the case of adsorption process[18].

Starting from the definition of the grand potential \( J \) and using the grand canonical partition function \( Z_{GC} \), we can write[13,26-28]:

\[
J = -k_B T \ln Z_{GC} = E_a - \mu Q_a - TS_a
\]  

(17)

\[
J = -\frac{\partial}{\partial \beta} \ln Z_{GC} - T S_a
\]  

(18)

By equalizing these two expressions, it can be obtained:

\[
T S_a = -\frac{\partial}{\partial \beta} \ln Z_{GC} + k_B T \ln Z_{GC}
\]  

(19)

from which the expression of the entropy can be derived:

\[
S_a = -\frac{k_B}{\beta} \ln(Z_{GC}) + \ln(Z_{GC})
\]  

(20)

By introducing the expression of the grand canonical partition function, the expression of the entropy is then written:

\[
S_a = \frac{Q_a}{k_B n} \left[ \ln \left( 1 + \left( \frac{c}{c_{1/2}} \right)^n + \left( \frac{c}{c_{1/2}} \right)^{2n} \right) - \left( \frac{c}{c_{1/2}} \right)^n \ln \left( \frac{c}{c_{1/2}} \right)^n + \left( \frac{c}{c_{1/2}} \right)^{2n} \ln \left( \frac{c}{c_{1/2}} \right)^{2n} \right]
\]  

(21)

In figure 6 the evolution of the entropy as a function of equilibrium residual concentration and parametric with the temperature is reported.

![Figure 6](image)

**Figure 6.** Variation of the entropy versus concentration

The entropy has two different behaviors below and above the half-saturation value. Indeed, the entropy increases with the concentration before the half-saturation and decreases after this point. When the
concentration is lower than the value corresponding to the half-saturation, the molecule of TCE has various possibilities to choose a receptor site to be adsorbed and therefore the disorder increases at the surface with the concentration. After the half-saturation, the adsorbent molecule has low probability to choose adsorbent site since the surface tends toward the saturation and therefore tends toward the order. The entropy can reach zero when the saturation is reached [27]. Moreover, the entropy decreases with temperature, which explains that the amount adsorbed decreases. It is obvious that the entropy calculated and represented is the statistical and configurational entropy, which is related to the number of possible configurations \( \Omega \) to achieve the adsorption of \( Q \) molecules on \( N_M \) receptor sites. This entropy can be written as 
\[
S = k_B \ln \Omega \quad \text{in the case of the micro-canonical ensemble to describe the adsorption, in which all configurations are equiprobable with}
\]
\[
\Omega = \frac{Q_0!}{Q!(Q_0 - Q)!}. 
\]
Consequently, the following expression of the entropy can be derived [26,27]:
\[
S = k_B \left[ Q_0 \ln Q_0 - Q \ln Q - \left( Q_0 - Q \right) \ln \left( Q_0 - Q \right) \right] 
\]
(22a)

According to this expression, \( S \) has a maximum when \( Q = \frac{Q_0}{2} \) being the derivative expression
\[
\frac{\partial (S / k_B)}{\partial Q} = \ln Q + \ln (Q_0 - Q)
\]
(22b)

This configurational entropy is similar to the net integral entropy associated to the adsorption process. The net integral entropy describes the degree of disorder and randomness of motion of adsorbed molecules [29]. The free enthalpy described the spontaneity of the system. It is given by the following relation[15,18]:
\[
G = \mu Q 
\]
(23)

Where \( \mu \) is the chemical potential of adsorbed molecule, and \( Q \) is the adsorbed amount. The chemical potential is given by:
\[
\mu = k_B T \ln \left( \frac{c}{z_v} \right) 
\]
(24)

Where \( z_v \) is the translation partition function per unit of volume. The free enthalpy has the following expression:
\[
G = k_B T Q_0 \ln \left( \frac{c}{z_v} \right) \frac{\left( \frac{c}{c_{1/2}} \right)^n + 2 \left( \frac{c}{c_{12}} \right) \left( \frac{c}{c_{1/2}} \right)^{2n}}{1 + \left( \frac{c}{c_{1/2}} \right)^n + \left( \frac{c}{c_{1/2}} \right)^{2n}}
\]
(25)

In the figure 7, the free enthalpy as a function of TCE concentration and parametric with the temperature is reported. As the Fig 7 showed, the free enthalpy of the adsorption process of TCE on activated carbon at all temperatures was negative, indicating that the adsorption process was spontaneous in nature, and the free energy declines monotonically. In this case, higher isothermal work was required to pack more molecules into the cavity space than at the initial stages due to screened active sites. We also note that the increase in temperature leads an increase of the free energy; this means that the increase in temperature reduces the spontaneity of the system.
Figure 7. Variation of the free enthalpy versus concentration

The internal energy is given by [14,18]:

\[
\frac{E_{\text{int}}}{k_B} = -\frac{\partial \ln(Z_{ge})}{\partial \beta} + \frac{\mu}{\beta} \frac{\partial \ln(Z_{ge})}{\partial \mu}
\]

(26)

The expression of the internal energy is given by:

\[
E_{\text{int}} = k_B T \frac{Q_0}{n} \left[ \ln \left( \frac{c}{Z_v} \right) + 2 \left( \frac{c}{c_{1/2}} \right)^n + \frac{c}{c_{1/2}} \ln \left( \frac{c}{c_{1/2}} \right) + 2 \left( \frac{c}{c_{1/2}} \right)^{2n} + \frac{c}{c_{1/2}} \ln \left( \frac{c}{c_{1/2}} \right)^{2n} \right]
\]

(27)

The evolution of the internal energy is depicted in figure 8. The internal energy is negative, this confirms that the system evolves spontaneously since it releases of energy. We also note that an increase in temperature causes an increase in the internal energy in algebraic value following thermal collisions.

Figure 8. Variation of the internal energy versus concentration

5. Conclusion
In this work, the different adsorption isotherms of TCE on activated carbon were modeled and interpreted using the double layer model with one energy. The statistical model is thermodynamically consistent and the
physicochemical parameters intervening in the adsorption process are taken into account during the theoretical treatment. By application our model on the different adsorption isotherms, we have learned a lot of important information of the adsorption of TCE on activated carbon.

We distinguished that the TCE molecule has a parallel anchorage on the surface of the activated carbon, but this molecule tends towards a perpendicular anchorage under the thermal agitation. The evolution of the monolayer adsorbed quantity explains the exothermic nature of the adsorption of TCE on activated carbon. The adsorption energy was calculated from the energetic parameter $c_{1/2}$ that was deduced from the experimental isotherms by numerical simulation. The adsorption energy increases in modulus versus the temperature which can be explained by the exothermic character of the adsorption process. The study of the configurational entropy led to follow the disorder evolution at the adsorbent surface with the adsorbed quantity from the beginning of the adsorption process till the saturation. A thermodynamic analysis of free enthalpy and internal energy has been calculated showing that the system is spontaneous and liberate energy.

References


