Retention of progesterone by four carbonaceous materials: study of the adsorption kinetics

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Abstract

The process by which progesterone in an ethanol solution is retained by four carbonaceous materials involves a reversible mechanism that conforms to a kinetic equation of unity partial order in both the progesterone concentration in solution, the coverage fraction ($\theta$) of the adsorbing surface and $(1 - \theta)$. Over the temperature range 10–40 °C, the specific rate constant varies from $5.29 \times 10^{-4}$ to $44.85 \times 10^{-4}$ s$^{-1}$. The formation of the activated species involved in the adsorption process is an endothermal, exoentropic step. The rate of the adsorption–desorption process is primarily determined by diffusion of progesterone molecules in the pores of the sorbent.

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1. Introduction

A physico-chemical knowledge of solid surfaces is interesting both for purely scientific reasons and for their practical implications. A number of processes including adsorption [1,2], ion exchange [1] and catalysis [3–5] possess technological interest. In the past 30 years, such processes have found uses in pharmacology and the pharmaceutical industry [6–8].

Ever since the concept of modified-release pharmaceutical forms was established [9], a large number of active principles have been administered in such forms. Also, theoretical studies on such systems and their preparation have substantially grown in number and variety.

Prolonged-release forms with a physically or chemically based action (viz. matrix systems and poorly soluble complexes such as ion-exchange resins, respectively), are very frequently encountered in the literature [10–18] and in pharmaceutical practice. On the other hand, forms involving a physico-chemical interaction with active sites on
a solid surface are uncommon; this function can be served, among others, by carbonaceous materials such as carbon black and activated carbon.

A proper study of the behaviour of the solid-drug system must deal with its kinetic, equilibrium and thermodynamic aspects, in relation to both the action of the drug in biological fluids and the previous preparation of solid-drug systems when a long-acting oral solid pharmaceutical form is to be developed.

In any of the above-described cases, studies are usually restricted to the behaviour of a solid–liquid system and, in relation to physical and/or chemical retention-release (adsorption–desorption and ion exchange), to those occurring at the solid–liquid interface.

This paper reports the kinetic results of the study of a system consisting of four carbon black and progesterone in an ethanol solution, from which an adsorbate (in the pharmaceutical sense of this word) might be obtained that could theoretically be used as the starting material for the preparation of long-acting oral solid pharmaceutical forms.

2. Material and methods

One gram of carbon black, henceforward referred to as HAF-V3, ISAF-V6, BP-880 and BP-1300, was used as sorbent. These carbonaceous materials had previously been thoroughly characterised [19]. The adsorbate employed was pregn-4-en-3,20-dione (progesterone), supplied in analytical-reagent grade by Guinama (Valencia, Spain) and dissolved in pro-analysis ethanol from Panreac (Barcelona, Spain). A volume of 250 ml of solution was used in each experiment.

A 500 ml Pyrex Erlenmeyer flask furnished with a stopper and an inlet for sample collection was used. The system was thermostated and stirred at 200 rpm on Gallenkamp stirrer throughout each experiment.

The concentration of the solution in contact with the solid was determined by using a spectrophotometric method to measure the absorption of light of \( \lambda = 241 \text{ nm} \) at preset time intervals.

3. Results

Two different experiment batches were conducted. In the first, a temperature of 20 °C and four progesterone solutions of known concentration, \( C \), were used; the results obtained are shown as \( C \) versus \( t \) isotherms in Fig. 1. The second experiment series, which involved the use of a 5 \times \( 10^{-5} \) M progesterone solution, was performed at 10, 20, 30 and 40 °C; the results are shown in Fig. 2.

4. Discussion

4.1. Kinetic equation. Specific rate and thermodynamic activation functions

4.1.1. First experiment series

The experiments of the first series were conducted in such a way as to facilitate the determination of the partial orders of the overall retention process in the adsorbate concentration in solution \( (C) \), the fraction of free (adsorbate-accessible) sorbent active sites \((1-\theta)\) and that of sites occupied by adsorbate (progesterone) molecules \((\theta)\). Of these three variables, only \( C \) could be determined in a direct manner, \( \theta \) and \((1-\theta)\) being calculated from it. Consequently, only the partial order of the process in \( C \) could be directly determined from the experimental results; those in \( \theta \) and \((1-\theta)\) were obtained by fitting the experimental results to the equations for previously reported models. The results obtained in the experiments are shown in Fig. 1.

The overall process by which an adsorbable solute \( A \) in solution is retained by a solid sorbent \( S \) can be formulated as follows:

\[
S(s) + A(\text{dis.}) \rightleftharpoons S - A(s)
\]  

the kinetic equation for which is

\[
-\frac{d[A]}{dt} = -\frac{dC}{dt} = k_1 \cdot C^{n_1} \cdot (1-\theta)^{n_2} - k_2 \cdot \theta^{n_3}
\]  

\( n_1 \) in the previous equation was determined using the so-called “differential method” [20,21], based on which \( \theta = 0 \) and \((1-\theta) = 1 \) at \( t = 0 \) and any
value of \( n_2 \) and \( n_3 \). Therefore, equation 2 simplifies to

\[
\left( \frac{-dC}{dt} \right)_0 = k_1 \cdot C_0^n
\]

where \( n = n_1 \), so \( n = 1 \).

The goodness of the \( n_1 \) value thus determined was assessed and the most likely values for \( n_2 \) and \( n_3 \) were determined using the so-called integral method [22], which compares experimental results with those provided by an iterative procedure involving application of the equation resulting from integration of Eq. (2) at different \( n_2 \) and \( n_3 \) values, and \( n_1 = 1 \). The best results were obtained with \( n_1 = n_2 = n_3 = 1 \), at which Eq. (2) can be rewritten as

\[
\frac{-dC}{dt} = k_1 \cdot C \cdot (1 - \theta) - k_2 \cdot \theta
\]

From this it follows that, at equilibrium,

\[
k_1 \cdot C_e \cdot (1 - \theta) = k_2 \cdot \theta
\]

where \( C_e \) denotes the progesterone concentration at equilibrium \((t \geq t_e)\).

If, on the other hand, one assumes \( \theta = 1 \) at equilibrium, then

\[
\theta = \frac{C_0 - C}{C_0 - C_e}
\]

\[
1 - \theta = \frac{C - C_e}{C_0 - C_e}
\]

Substitution of Eqs. (5)–(7) into Eq. (4), and rearrangement, yields [23]
\[
\frac{-dC}{dt} = \frac{k_1}{C_0 - C_e} \cdot (C^2 - 2 \cdot C_e \cdot C + C_e^2)
\]

Integration of Eq. (8) between 0 and \( t \) (\( t \) values), and from \( C_0 \) to \( C \), yields

\[
C = \frac{C_0 + k_1 \cdot C_e \cdot t}{1 + k_1 \cdot t}
\]  \( \text{(10)} \)

Fitting to Eq. (10) provided the results shown as a solid line in Figs. 1 and 2. The goodness of such fittings suggests that the process takes place in a reversible manner.

4.1.2. Second experiment series

The second series of experiments was intended to provide information about the equilibrium time \( (t_e) \), specific rates of adsorption \( (k_1) \), thermodynamic activation functions for the adsorption process and the factors determining the adsorption kinetics.

The experiments provided the results shown in Fig. 2. As can be seen, in all cases, isotherms \( C \) versus \( t \) intersect, probably due to the influence of
two factors; firstly, adsorption specific rate increases as temperature does whereas simultaneously the adsorbed amount at equilibrium time decreases with increasing temperature. This suggests that the adsorption process is exothermic— which is confirmed by the equilibrium isotherms, \( n^* \) versus \((C/C_0)\)—, probably as a result of a marked contribution of adsorbate diffusion through sorbent pores to the adsorption process.

The isotherms of Fig. 2 were used to calculate the parameters described in the following sections, which were in turn employed to derive the information described in each.

4.1.2.1. Equilibrium time. Equilibrium was considered to have been reached when at least two consecutive measurements were constant. Table 1 lists the adsorption–desorption equilibrium times obtained. Such values increase as \( S_{BET} \) and porosity do and as temperature decreases.

4.1.2.2. Specific rate constant \((k_1)\) and thermodynamic activation functions. The rate constant values thus calculated, \( k_1 \), were used to derive the thermodynamic activation functions for the process. To this end, the following equation, based on Eyring’s theory of the transition state [24] was employed:

\[
k = \frac{R \cdot T}{N \cdot h} \cdot e^{\frac{\Delta S^*}{R} + \frac{\Delta H^*}{R \cdot T}}
\]

from which it follows that

\[
\ln \frac{k}{T} = \ln \frac{R}{N \cdot h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{R} \cdot \frac{1}{T}
\]

Based on Eq. (12), the \( k_1 \) values in Table 2 were used to construct a \( \ln (k_1/T) \) versus \((1/T)\) plot. Analytical fitting of the data to the corresponding regression line allowed us to determine the \( \Delta H^* \) and \( \Delta S^* \) values listed in Table 3, which also includes \( \Delta G^* \) values (calculated from the expression \( \Delta G^* = \Delta H^* - T \cdot \Delta S^* \)).

From the results of Table 3 it follows that, as usual, the formation of the activated species involved in the adsorption process is an endothermic, exoentropic step, \( \Delta H^* \) decreasing with increasing \( S_{BET} \); because \( \Delta S^* < 0 \), the progesterone molecule in the activated species possesses fewer degrees of freedom than in solution (where it is in solvated form). On the other hand, the likelihood of the activated species being formed decreases with increasing temperature.

4.2. The potential influence of diffusion on the kinetics of the adsorption–desorption process

4.2.1. Retention rate expressed as \( d\theta/dt \).

Consequences

The rate equation for process 1 can be formulated indifferently either as in Eq. (4) or as follows:

\[
\frac{d\theta}{dt} = k_1' \cdot C \cdot (1 - \theta) - k_2 \cdot \theta
\]

which is related to Eq. (4) via

\[
\frac{d\theta}{dt} = \frac{1}{C_0 - C_c} \cdot \left( \frac{-dC}{dt} \right)
\]

an expression that is the derivative of Eq. (6) with respect to \( t \). Substitution of Eq. (4) into Eq. (14) yields

\[
\frac{d\theta}{dt} = \frac{1}{C_0 - C_c} \cdot [k_1 \cdot C \cdot (1 - \theta) - k_2 \cdot \theta]
\]

Substituting \( k_1 \cdot \theta \) in Eq. (15) by its value in Eq.
and rearranging yields:

\[
\frac{d\theta}{1 - \theta} = \frac{k_1}{C_0 - C_e} \cdot (C - C_e) \cdot dt
\]

(16)

of which from 0 to \( \theta \) and from 0 to \( t \) yields:

\[
\frac{1}{\theta} = 1 + \frac{1}{k_1} \cdot \frac{1}{t}
\]

(17)

Equation 10 is solved for \((C - C_e)\). This is substituted into Eq. (16), subsequent integration derivation of which yields:

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**Table 2**

Specific adsorption rate \((k_1)\), and calculated initial \((C_0)\) and equilibrium \((C_e)\) concentrations

<table>
<thead>
<tr>
<th>Adsorbent ((S_{BET}, \text{m}^2 \text{g}^{-1}))</th>
<th>(T (^\circ\text{C}))</th>
<th>(k_1 \cdot 10^4 \text{ (s}^{-1}))</th>
<th>(C_0 \cdot 10^5 \text{ (mol l}^{-1}))</th>
<th>(C_e \cdot 10^5 \text{ (mol l}^{-1}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAF-V3 (73)</td>
<td>10</td>
<td>7.0</td>
<td>4.9</td>
<td>3.6</td>
<td>0.9989</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>17</td>
<td>4.9</td>
<td>3.7</td>
<td>0.9974</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>26</td>
<td>4.9</td>
<td>3.8</td>
<td>0.9996</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>45</td>
<td>4.9</td>
<td>3.8</td>
<td>0.9964</td>
</tr>
<tr>
<td>ISAF-V6 (101)</td>
<td>10</td>
<td>5.3</td>
<td>4.7</td>
<td>2.4</td>
<td>0.9909</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>7.5</td>
<td>4.7</td>
<td>2.3</td>
<td>0.9969</td>
</tr>
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<td></td>
<td>30</td>
<td>12</td>
<td>4.7</td>
<td>2.5</td>
<td>0.9978</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>19</td>
<td>4.7</td>
<td>2.7</td>
<td>0.9982</td>
</tr>
<tr>
<td>BP-880 (232)</td>
<td>10</td>
<td>12</td>
<td>5.1</td>
<td>1.0</td>
<td>0.9980</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>19</td>
<td>5.1</td>
<td>1.1</td>
<td>0.9976</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>25</td>
<td>5.0</td>
<td>1.2</td>
<td>0.9989</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>32</td>
<td>5.1</td>
<td>1.4</td>
<td>0.9956</td>
</tr>
<tr>
<td>BP-1300 (548)</td>
<td>10</td>
<td>23</td>
<td>9.6</td>
<td>0.7</td>
<td>0.9994</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>33</td>
<td>9.8</td>
<td>1.0</td>
<td>0.9981</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>37</td>
<td>9.7</td>
<td>0.8</td>
<td>0.9989</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>42</td>
<td>9.7</td>
<td>0.8</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

---

**Table 3**

Thermodynamic activation functions of the adsorption process

<table>
<thead>
<tr>
<th>Adsorbent ((S_{BET}, \text{m}^2 \text{g}^{-1}))</th>
<th>(T (^\circ\text{C}))</th>
<th>(\Delta H^* \text{ (kJ mol}^{-1}))</th>
<th>(\Delta S^* \text{ (kJ mol}^{-1}))</th>
<th>(\Delta G^* \text{ (kJ mol}^{-1}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAF-V3 (73)</td>
<td>10</td>
<td>44.02</td>
<td>-0.11</td>
<td>74.63</td>
<td>0.9785</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>75.71</td>
<td>7.80</td>
<td>77.88</td>
<td>0.9919</td>
</tr>
<tr>
<td>ISAF-V6 (101)</td>
<td>10</td>
<td>31.85</td>
<td>-0.15</td>
<td>75.64</td>
<td>0.9919</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>77.18</td>
<td>78.73</td>
<td>80.28</td>
<td>0.9919</td>
</tr>
<tr>
<td>BP-880 (232)</td>
<td>10</td>
<td>24.76</td>
<td>-0.17</td>
<td>73.55</td>
<td>0.9730</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>75.27</td>
<td>76.99</td>
<td>78.72</td>
<td>0.9730</td>
</tr>
<tr>
<td>BP-1300 (548)</td>
<td>10</td>
<td>14.02</td>
<td>-0.20</td>
<td>73.95</td>
<td>0.9242</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>75.99</td>
<td>78.04</td>
<td>78.04</td>
<td>0.9242</td>
</tr>
</tbody>
</table>
The first of the previous portions—when present—fits the equation of Bangham \[32,33\], which can be formulated indifferently as

$$\ln \frac{1}{1 - \theta} = k_b \cdot t^m$$

(19)

or

$$\theta = k_b \cdot t^m$$

(20)

based on which

$$\frac{d\theta}{1 - \theta} = m \cdot k_b \cdot t^{m-1} \cdot dt$$

(21)

According to Bangham, when exponent \(m\) equals 0.5, the adsorption of further molecules inevitably entails their diffusion to the inside of the solid. However, Aharoni \[34\] suggests that, in practice, the process can be assumed to be essentially diffusive in nature at \(0.65 < m < 0.70\). Values of \(m\) below 0.5 are frequently encountered in chemisorption processes. Because the Bangham equation takes account of the influence of diffusion on the kinetics of the retention process, it should be considered in studying experimental results as adsorption processes always involve some diffusion—which is clearly apparent from Fig. 3.

In fact, Fig. 4 clearly reveals that, whether or not experimental \((\theta, t)\) data exhibit the above-described deviation at short times, at least the values obtained at the shorter times could be fitted to the Bangham equation; this would allow one to calculate \(m\), which, according to Aharoni \[28\], would provide a clue as to whether adsorption would take place essentially in a non-porous solid or—because it would occur in a porous one—it would be determined largely by diffusion. The second—seemingly straight—portion in the curve conforms to the empirical equation of Elovich

$$\frac{1}{(d\theta/dt)} = \frac{1 + 2 \cdot k_1 \cdot t + k_1^2 \cdot t^2}{k_1}$$

$$= \frac{1}{k_1} + 2 \cdot t + k_1 \cdot t^2$$

(18)

**Equation 18** allows one to draw two significant conclusions, namely:

- A plot of \([1/(d\theta/dt)]\) versus \(t\) will be a curve of second order in \(t\) the intercept and the slope of the last portion (long times) of which will increase and decrease, respectively, with increasing \(k_1\).

- At very small \(k_1\) values, the intercept of the previous plot will be very high (especially at very short times) and the influence of the product \(k_1 \cdot t^2\) will result in the points seemingly defining a straight line.

Based on these conclusions, the portion of the \([1/(d\theta/dt)]\) versus \(t\) plot at short times may occasionally be assimilated to a straight line; at long times, however, the plot clearly corresponds to a second-order potential function. Therefore, the \([1/(d\theta/dt)]\) versus \(t\) plot for reversible adsorption processes conforming to Eq. (13) occasionally consists of a “roughly straight” initial portion followed by an exponential (second-order polynomial) one. However, if virtually all active sites on the sorbent surface are free—which is the case at very short times—and exhibit a high affinity for the adsorbate, then retention rate \((d\theta/dt)\) may be anomalously high and \([1/(d\theta/dt)]\) anomalously low, giving rise to a negative deviation (with respect to a straight line) the magnitude of which will increase with increasing \(t\). Occasionally, the—usually short—portion close to the inflection (intersect) point between the initial branch (the upper limit of the deviation) and that corresponding to strict fulfilment of Eq. (18) might seem a straight line, so the \([1/(d\theta/dt)]\) versus \(t\) plot would apparently consist of up to three distinct portions, namely: an initial segment concave with respect to the \(x\)-axis, a straight segment and a convex one. These portions coincide with those hypothesised by Aharoni and co-workers \[25–31\] for the \([1/(d\theta/dt)]\) versus \(t\) plot corresponding to a highly complex process.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Interface</th>
<th>Outer solid surface</th>
<th>Inner pore surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>(t=0)</td>
<td>(C=C_0)</td>
<td>(C=C_0)</td>
<td>(\theta=0)</td>
</tr>
<tr>
<td>(t=t)</td>
<td>(C=C)</td>
<td>(C&lt;C_0)</td>
<td>(\theta&gt;0)</td>
</tr>
</tbody>
</table>

Fig. 3. Diffusion steps in a process involving adsorption alone.
\[ \theta = A + \frac{1}{b} \cdot \ln(t_0 + t) \]  

(22)

where \( A, b \) and \( t_0 \) are three constants the last of which corresponds to a negative value of \( t \) where the rate constant has an infinite value.

According to Aharoni [25], the Elovich equation usually holds for the results of processes involving the chemisorption of an adsorbate on a sorbent with a heterogeneous surface. According to other authors, however, the Elovich equation cannot be applied unless other processes preceding those which obey such an equation are considered; in the light of this assertion, Taylor and Thon [38] assumed the presence of a so-called pre-Elovich process of infinite rate starting and ending at \( t = 0 \).

Also, Aharoni and Tompkins [37] assumed the presence of pre-Elovich adsorption at an infinite rate that gradually evolved to an Elovich process. The previous two hypotheses are intended to account for the fact that the \( \theta \) versus \( \ln(t_0 + t) \) plot exhibits a convex deviation at the beginning of the process; physico-chemically, however, the previous assumptions (viz. an infinite rate) should be taken with caution. It should be borne in mind that the Elovich equation, in all its forms, is an empirical equation of limited validity—as admitted by Aharoni [34] in the above-mentioned review—intended as an approximate substitute for Eq. (17) over an interval of relatively low values of \( t \); in the absence of segment 1, \( 0 < t < t_p \); in its presence, \( t_1 < t < t_p \). To our minds, segment 2 suggests that the process develops consistently with the Langmuir equation and that it should be fitted to Eq. (17) (together with the data obtained and the longer times) rather than to Eq. (22).

Segment 3 can be assumed to appear when the retention process takes place in an irreversible manner, in conformance with the kinetic requirements that lead to the Langmuir equation; under these conditions, the rate equation is given by Eq.
and the relationship between \([1/(dθ/dt)]\) and time by Eq. (18).

Based on the foregoing, the results of Fig. 2 were used to calculate the corresponding \(θ\), \((1/θ)\) and \([1/(dθ/dt)]\) values, which were employed to construct Figs. 4–6.

As can be seen from Fig. 4, the rate constant increases with increasing temperature; the fact that all \((θ, t)\) curves converge at \(θ = 1\) is a result of using \(θ_c = (C_0 - C_e)/(C_0 - C_v) = 1\) in every single experiment. Based on Eq. (17), a plot of \(1/θ\) versus \(1/t\) (Fig. 5) should consist of straight lines the slopes of which will increase with increasing temperature; this can be assumed to indicate that adsorption takes place in a reversible manner and conforms to the Langmuir equation. For carbon black HAF-V3, ISAF-V6 and BP-880 the expected behaviour is observed. With BP-1300 (a solid with more developed microporous texture), some of the points obtained at the shorter times (especially at \(T = 10^\circ\)C) exhibit a negative deviation from the straight line observed at the longer times; such points could be studied in the light of the Bangham equation in order to derive complementary information. The shapes of the lines in Fig. 6 are consistent with a polynomial function of second order in \(t\) Eq. (18). All other information provided by Fig. 6 virtually coincides with that contained in the previous one. As noted earlier, fitting the experimental results to the Bangham equation (19) allows one to determine \(m\) (Table 4), which provides and indication of the influence of diffusion on the adsorption process.

Based on the \(m\) values thus calculated, the kinetic model appears to be more coherent with that corresponding to the adsorption of non-electrolytes in solution by non-microporous solids [39]. According to the \(m\) values, a remarkable contribution of chemisorption occurs. Also, \(m\) decreases with increasing temperature, consistent

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**Fig. 5.** Plot of \(1/θ\) vs. \(1/t\).
4.2.2. Diffusion of adsorbate molecules through sorbent particles

In order to examine the potential influence of diffusion on the retention kinetics we fitted our experimental data to the equations of Banerjee et al. [40], Carman and Haul [41], and Aharoni and Suzin [30]. The results provided by all these equations were consistent; by way of example, Table 5 gives those provided by that of Banerjee et al.

As can be seen, the diffusion coefficient increased with increasing temperature, as the likely result of diffusion being activated by an increased
temperature and a potential decrease in the size of the diffusing adsorbate molecules through partial solvation. On the other hand, $D$ decreases as the sorbent microporosity increases. Only in BP-880 an unexpected behaviour occurs, which might be due to a low significancy of the micropores volume when compared with meso- and micropores.

4.2.2.1. Activation energies of the diffusion process. Provided it remains constant throughout the working temperature range, the activation energy, $E_a$, for the diffusion process can be calculated from

$$D = D_0 \cdot e^{-\frac{E_a}{RT}}$$  \hspace{1cm} (23)

A plot of $\ln D$ versus $1/T$ allowed us to calculate the $E_a$ and the frequency factor, $D_0$. Such parameters are included in Table 6. As can be seen, $E_a$ decreases as $S_{BET}$ increases. The frequency factor, $D_0$, may be considered as the limit value of $D$ obtained when the temperature increases to an infinite value. The values obtained for the frequency factor are similar, independently of the supposed model. In all cases, $D_0$ decreases as $S_{BET}$ increases. It should be noted that the $E_a$ values for the diffusion process are closer to those of the enthalpy of activation for the adsorption process ($\Delta H^*$), see Table 3) in adsorbents with more developed porous texture (i.e. BP-880 and BP-1300) than in sorbents with poorly developed texture (HAF-V3 and ISAF-V6). This, again, suggests that the kinetics of progesterone adsorption by the sorbents BP-880 and BP-1300 may be primarily determined by diffusion.

5. Nomenclature

$A$ adsorbate solute

$C$ solute concentration (mol $1^{-1}$)
\( C_e \) adsorbate concentration in solution at equilibrium time (mol \( \cdot \) l \(^{-1} \))

\( C_0 \) initial adsorbate concentration in solution (mol \( \cdot \) l \(^{-1} \))

\( D \) diffusion coefficient (cm\(^2\) s\(^{-1} \))

\( D_0 \) frequency factor (cm\(^2\) s\(^{-1} \))

\( E_a \) activation energy (kJ mol\(^{-1} \))

\( h \) Plank’s constant (J s\(^{-1} \))

\( k \) specific rate constant

\( k_b \) specific rate constant in Bangham equation

\( k_1 \) adsorption specific rate constant

\( k_2 \) desorption specific rate constant

\( N \) Avogadro’s number (mol\(^{-1} \))

\( n_1 \) parallel order of the overall retention process in the adsorbate concentration in solution

\( n_2 \) partial order of the overall retention process in the fraction of free sorbent active sites

\( n_3 \) partial order of the overall retention process in the fraction of occupied sorbent active sites

\( R \) molar gas constant (J mol K\(^{-1} \))

\( S \) solid sorbent

\( T \) temperature (K)

\( t \) time (s)

\( t_e \) equilibrium time (s)

\( t_i \) initial time (s)

\( t_p \) inflection point in the \( [1/(d\theta/dt)] \) curve (s)

\( \Delta G^* \) activation Gibbs free energy (kJ mol\(^{-1} \))

\( \Delta H^* \) activation enthalpy (kJ mol\(^{-1} \))

\( \Delta S^* \) activation entropy (kJ mol\(^{-1} \) K\(^{-1} \))

\( \theta \) fraction of sorbent active sites occupied by adsorbate molecules

\( \lambda \) wavelength (nm)

References


[23] M. Sitiou, Retencion de progesterona por negros de carbon y por un carbon acti


