Application of a Single Model to Study the Adsorption Equilibrium of Prednisolone on Six Carbonaceous Materials

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The knowledge of sorption processes of nonelectrolytes in solution by solid adsorbents implies the study of kinetics, equilibrium, and thermodynamic functions. However, quite frequently the equilibrium isotherms are studied by comparing them with those corresponding to the Giles et al. classification (1); these isotherms are also analyzed by fitting them to equations based on thermodynamic or kinetic criteria, and even to empirical equations. Nevertheless, information obtained is more coherent and satisfactory if the adsorption isotherms are fitted by using an equation describing the equilibrium isotherms according to the kinetic laws. These mentioned laws would determine each one of the unitary processes (one or more) which condition the global process. In this paper, an adsorption process of prednisolone in solution by six carbonaceous materials is explained according to a previously proposed single model, which allows to establish a kinetic law which fits satisfactorily most of C vs t isotherms (2). According to the above-mentioned kinetic law, equations describing sorption equilibrium processes have been deducted, and experimental data points have been fitted to these equations; such a fitting yields to different values of adsorption capacity and kinetic equilibrium constants for the different processes at several temperatures. However, in spite of their practical interest, these constants have no thermodynamic signification. Thus, the thermodynamic equilibrium constant (K) has been calculated by using a modified expression of the Gaines et al. equation (3). Global average values of the thermodynamic functions have also been calculated from the K values. Information related to variations of ΔH and ΔS with the surface coverage fraction was obtained by using the corresponding Clausius–Clapeyron equations.

Key Words: adsorption; equilibrium; isotherms; carbonaceous materials; prednisolone.

1. INTRODUCTION

As indicated in a previous paper (2), the study of adsorbent/sorbable systems from solution provides information about the number of active sites in the solid surface, as well as about the nature and magnitude of the interactions between these active sites and the sorbed molecules. In the above-mentioned paper, aspects related to the adsorption kinetics processes have been treated by using a single model. This model establishes that for a sorption process such as

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

the kinetic law is given by

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

where

\begin{align*}
C &= [A] = \text{Concentration of prednisolone (mol l}^{-1}\text{) in the supernatant at each time, } t.
\theta &= \frac{n_f}{n_e} = \text{Coverage surface fraction = prednisolone adsorbed (mol g}^{-1}\text{)/adsorption capacity of the adsorbent relating to prednisolone adsorbed in the monolayer (mol g}^{-1}\text{).}
k_\text{d} &= \text{Adsorption rate coefficient.}
k_\text{i} &= \text{Desorption rate coefficient.}
n_1, n_2, \text{ and } n_3 &= \text{Partial orders relating to } C, (1 - \theta) \text{ and } \theta, \text{ respectively.}
\end{align*}

The above equation has been used to study the sorption processes of prednisolone from ethanol solution on six carbonaceous materials. In this paper, results obtained by studying the equilibrium of such processes are given.

2. MATERIALS AND METHODS

The materials used as adsorbents for this series of experiments were four carbon black samples (ISAF-V6, BP-880, BP-1000, and BP-1300) from Cabot (Suresnes, France), and two activated carbon samples from Merck (CA-Merck) and ICASA (CA-ICASA) respectively. Analytically pure prednisolone (11β, 17α, 21-trihydroxy-1,4-pregnadien-3, 20-dione)—obtained from GUINAMA (Valencia, Spain)—was used as adsorbable in this study. The solvent used for preparing the different solutions of prednisolone was ethanol (96% analytical grade). Previously to carry out the experiments planned, the physical-chemistry surface characterization of the CA-ICASA sample was performed by using N2 adsorption at 77.4 K. The
remaining samples had also been previously characterized by other authors. All the carbonaceous samples, crushed to a particle size between 0.39 and 2.41 mm, were desiccated at 60°C to constant weight (mass variation in 24 h less than 0.01%) in a vacuum dessicator, in order to completely remove hydration water without modifying the composition of the surface active centers.

Experimental sorption equilibrium data were obtained as follows: varied amounts—exactly weighed—of each sorbent ranging from 0.01 to 2.00 g and 20 ml of 10−3 M prednisolone ethanol solution were placed in the adsorption cells (Pyrex glass 50-ml flasks). Then the flasks were placed in a thermostatted shaker bath (150 rpm) at 10, 20, 30, 40, and 50°C ± 0, 1°C for 15 days. A time of 15 days is long enough to ensure that equilibrium was reached between prednisolone adsorbed and prednisolone in solution (2). After shaking, the solutions were centrifuged and the concentration of prednisolone in the supernatant liquid was determined by UV spectrophotometry at 244 nm, the wavelength corresponding to its maximum absorbance. The difference in prednisolone concentrations between the initial and final equilibrium solutions was assumed to be due to adsorption and the amount of prednisolone retained per gram of adsorbent was calculated.

Blanks containing no prednisolone were used for each series of experiments and two replicates were analyzed at each prednisolone concentration for each carbonaceous sample.

3. THEORY

Sorption equilibrium isotherms, which are obtained from the sorption experiments, are usually plotted as either \( n^s \) vs \( C \), \( n^s \) vs \( (C/C_0) \), or \( n^s \) vs \( (C/C^* \) ), where

\[
\begin{align*}
n^s &= \text{moles of prednisolone adsorbed per gram of sorbent.} \\
C &= \text{equilibrium solution concentration of prednisolone.} \\
C_0 &= \text{initial solution concentration of prednisolone.} \\
C^* &= \text{prednisolone solubility in ethanol at each temperature.}
\end{align*}
\]

The isotherms plotted as \( n^s \) vs \( C \) and \( n^s \) vs \( (C/C_0) \) are equivalent both in relation to their shape and relating the way they are influenced by the temperature. Isotherms plotted as \( n^s \) vs \( (C/C^* \) present the same shape as those plotted as \( n^s \) vs \( (C/C_0) \) do; however, they may be influenced in an opposite way by the temperature, depending on the values of the adsorption and solution enthalpies of the corresponding adsorbable. From the equilibrium adsorption isotherms it is possible to obtain information about the adsorption capacity of the solid adsorbent, as well as about the nature and magnitude of the interactions taking place between the active sites at the solid surface and the adsorbable.

Such information is given by the values of \( n^s_0 \) (sorption capacity), \( K \) (thermodynamic equilibrium constant) and thermodynamic functions of the process, as well as by their variation with the coverage fraction, \( \theta \).

Frequently, in a previous analysis, experimental adsorption isotherms are compared by using the models proposed by Giles (1) in his classification. Occasionally, it can yield to an approximate value of \( n^s_0 \), and to give only a qualitative information about the relative affinity of the adsorbent by the adsorbable.

Normally, better results are obtained by fitting the experimental data points to any of the several equations proposed by different authors (4–17).

According to our own experience, fitting the experimental data points to the equilibrium equations derived from the appropriate kinetic law is more useful than fitting such data to any of the above-mentioned equations. In those processes studied in this paper, the kinetic law is given by Eq. [2], which yields to

\[
\theta = \frac{n_s}{n^s_0} = \frac{K_{ci} \cdot C^n}{1 + K_{ci} \cdot C^n} \tag{3}
\]

in which

\[
C = \text{equilibrium solution concentration of the adsorbable.} \\
n = \text{partial reaction order relating to } C \text{ (i.e., } n_1 \text{ in equation [2]).} \\
\theta = n_s/n^s_0 = \text{surface coverage fraction.} \\
n^s_0 = \text{retention capacity of the adsorbent.} \\
K_{ci} = \frac{k_i}{k_s} = \text{kinetic equilibrium constant.}
\]

Equation [3] easily leads to

\[
\frac{C^n}{n^s} = \frac{1}{K_{ci} \cdot n^s_0} + \frac{C^n}{n^s_0}. \tag{4}
\]

A straight line with slope equal to \( 1/n^s_0 \) and intercept equal to \( 1/(K_{ci} \cdot n^s_0) \) is obtained by plotting the experimental data of Eq. [4] as \( (C/C^n) \) vs \( C^n \). So, values of \( n^s_0 \) and \( K_{ci} \) can be calculated.

There is no doubt about the usefulness of \( K_{ci} \); however it has no thermodynamic significance. Going without the solvent, the thermodynamic equilibrium constant of process [1] is given by:

\[
K = \frac{a_{A(rot)}}{a_{A(dis)}} = \frac{X_A \cdot f_A}{m_A \cdot \gamma_A} \tag{5}
\]

where

\[
\begin{align*}
a_{A(rot)} &= \text{activity of solute } A \text{ in the sorbed phase.} \\
a_{A(dis)} &= \text{activity of solute } A \text{ in solution.} \\
X_A &= \theta = \text{equivalent fraction of solute } A \text{ in the adsorbed phase (i.e., coverage fraction).} \\
f_A &= \text{activity coefficient of solute } A \text{ in the adsorbed phase.} \\
m_A &= \text{molar concentration of the adsorbable in solution.} \\
\gamma_A &= \text{individual activity coefficient of the adsorbable in solution.} \\
K_s &= \text{selectivity coefficient (3).}
\end{align*}
\]

According to Henry’s and Raoult’s laws, for extremely diluted binary liquid solutions it can be supposed that \( \gamma_A = 1 \). Since in
all the experiments in this paper \(C \simeq 10^{-5}\text{M}\)

\[
K_s = \frac{\theta}{m_A} \quad [6]
\]

can be accepted.

For ionic exchange processes, the \(K\) value can be obtained from the \(K_s\) one, this latest being calculated at different values of \(X_A (0 \leq X_A \leq 1)\) by using a simplified Gaynes and Thomas’ equation (3):

\[
\ln K = (z_B - z_A) + \int_0^1 (\ln K_s) \cdot dX_A. \quad [7]
\]

In this case, solvent (B) and adsorbable (A) can be supposed to behave as “zero charge ions,” so \(z_B = z_A = 0\) and

\[
\ln K = \int_0^1 (\ln K_s) \cdot d\theta \quad [8]
\]

from which values of \(K\) can be calculated.

Since

\[
K = \exp \left( \frac{-\Delta G^\circ}{RT} \right) = \exp \left( \frac{\Delta S^\circ}{R} \right) \cdot \exp \left( \frac{-\Delta H^\circ}{RT} \right) \quad [9]
\]

from the plot of \(\ln K\) vs \(1/T\), values of \(\Delta H^\circ\) and \(\Delta S^\circ\) (average standard enthalpy and entropy, respectively) can also be obtained.

On the other hand, as the adsorption process takes place differential enthalpy (\(\Delta H\)) and entropy (\(\Delta S\)) vary as \(\theta\) increases and the adsorbable reaches less active sites at the sorbent surface. In order to obtain information about the variation of \(\Delta H\) vs \(\theta\) and \(\Delta S\) vs \(\theta\), modified Clausius–Claperyon equations have been used (18), (19)

\[
\Delta H = R \cdot \frac{T_1 \cdot T_2}{T_2 - T_1} \cdot \ln \left( \frac{C_1}{C_2} \cdot \frac{C_{S1}}{C_{S2}} \right) \theta \quad [10]
\]

and

\[
\Delta S = \frac{R}{T_2 - T_1} \cdot \left( T_1 \cdot \ln \frac{C_1}{C_{S1}} - T_2 \cdot \ln \frac{C_2}{C_{S2}} \right) \theta \quad [11]
\]

where \(C_1\) and \(C_2\) represent the adsorbable concentrations in solution at temperature \(T_1\) and \(T_2\), and \(C_{S1}\) and \(C_{S2}\) the adsorbable solubility in ethanol at those temperatures. Differential enthalpy and entropy values are calculated for fixed values of \(\theta\), in order to obtain further information about the energy distribution of the active sites at the solid surface.

### 4. RESULTS AND DISCUSSION

The experimental adsorption isotherms \(n^t\) vs \((\frac{C}{C^*})\) obtained by us in this paper do not appear clearly separated at different temperatures, so this kind of plotting does not give any information about the influence of temperature on the adsorption process. However, that information can be obtained from the adsorption isotherms \(n^t\) vs \((\frac{C}{C^*})\). The \(n^t\) vs \((\frac{C}{C^*})\) adsorption isotherms of prednisolone from ethanol solution on the six carbonaceous adsorbents at 10, 20, 30, 40, and 50°C are shown in Fig. 1. According to the slope of the initial portion of the curves, these isotherms may be classified as \(L\)-type, 1-subtype of the Giles classification (1), excepting those corresponding to the CA-ICASA sample which may be classified as \(S\)-type, 1-subtype.

According to Giles et al., \(L\)-1 type isotherms suggest that adsorbents have a medium affinity for the prednisolone molecules, the curves not tending to define a plateau. For CA-ICASA samples, \(S\)-1 type isotherms suggest that this sample has a very low affinity for prednisolone molecules.

Under our consideration, this affirmation is not necessarily true, since besides affinity, partial order of the process with respect to \(C\) may also affect the isotherm shape.

According to our own experience (2), the adsorption processes following the kinetic law [2] give rise to equilibrium isotherms that can be fitted to Eq. [3].

When \(n = 1\), Eq. [3] agrees with Langmuir equation, from which isotherms of \(S\), \(C\), \(L\), and \(H\) type can be respectively obtained for increasing values of \(K_{ci}\). Taking into account the limitations in using \(K_{ci}\) as a measure of the relative affinity of the active sites of the adsorbents by the prednisolone molecules, the increasing variation of \(K_{ci}\) agrees with that indicated by Giles et al., to establish the relationship between the affinity and the isotherm shape. However, when \(n > 1\), the corresponding isotherms are always \(S\)-type, even for very high values of \(K_{ci}\) (up to \(10^{-8}\)).

As it is well known, affinity is given by \(\Delta G^\circ\), which is closely related with the thermodynamic equilibrium constant (\(K\)).

According to the kinetic law corresponding to the different adsorption processes here studied (2) all the isotherms in Fig. 1 can be fitted to Eq. [3], \(n\) values being equal to one in all cases, excepting for the CA-ICASA/Prednisolone system for which \(n = 2\), since in this case the partial order of the process with respect to \(C\) is equal to two.

Experimental data points have been fitted to the transformed Eq. [4] and values of \(n_0\) and \(K_{ci}\) were calculated from the least square method applied to the straight lines obtained. Their values are summarized in Table 1 together with the corresponding correlation coefficients, which indicate a good correlation between the experimental data points and the regression straight line defined by Eq. [4].

The values of retention capacity obtained in this paper are much lower than those obtained by other authors using similar adsorbents and/or adsorbables. This fact might be explained taking into account the bigger size of the prednisolone molecule as well as its ability for binding, through the OH groups, to
FIG. 1. Adsorption isotherms of prednisolone in ethanol solution on different carbonaceous materials at (●) 283, (□) 293, (▲) 303, (○) 313, and (+) 323 K.
the solvent molecules (ethanol) giving rise to bigger adsorbable “species.”

For the carbon blacks samples in which micro- and mesoporosity is poorly developed, the value of \( n_0 \) increases as \( S_{\text{BET}} \) does. However, for the activated carbon samples (CA-Merck and CA-ICASA) micro- and mesoporosity seem to strongly influence the accessibility of the prednisolone molecules to the active sites of the solid surface. This could explain the lower adsorption capacity of the CA-Merck sample than the CA-ICASA one, since the CA-Merck sample has a much higher micro-porosity than that corresponding to the CA-ICASA sample. On the other hand, as can also be seen in Table 1, \( n_0 \) values vary with temperature in two different ways. For those adsorbents having lower surface area and porosity (ISAF-V6, BP-880, and BP-1000) \( n_0 \) varies slightly with the temperature, its values decreasing as temperature increases. The solids having bigger surface area and/or porosity (i.e., BP-1300 and activated carbons) just behave in the opposite way. To explain this different behavior, it is important to take into account the dual influence of temperature on both, prednisolone solubility in ethanol and solvation grade of prednisolone. Prednisolone solubility in ethanol increases as temperature increases. This fact may have a negative effect on the values, specially in the case of the carbon black samples, having a surface area and porosity poorly developed. On the other hand, as temperature increases, the solvation grade of prednisolone decreases, which originates a better diffusion of the prednisolone molecules through the adsorbent pores, so \( n_0 \) increases as temperature increases.

Obviously, the latest will be more important for those adsorbents which have more developed surface area and, specially, porous texture (i.e., the activated carbons).

The fit of the experimental data points to Eq. [4] also allows to calculate the values of \( K_{ci} \) which are shown in Table 1. As can be seen from Table 1, the \( K_{ci} \) values corresponding to the carbon blacks and CA-Merck samples \( K_{ci} \) are about \( 10^4 \), increasing as BET surface area increases. Actually, \( K_{ci} \) must depend in a higher extension on the chemical nature of the active sites of the adsorbents, than on the magnitude of specific surface area. Thus, excepting for the CA-ICASA sample, the \( K_{ci} \) values shown in Table 1 are similar to those found by Stitou (Stitou, personal communication) by studying the adsorption process of progesterone from ethanol solution on the same adsorbents. On the other hand, the \( K_{ci} \) values are about 10 times lower than those obtained by González Martín (20) relating to the adsorption process of p-nitrofenol from aqueous solution by the same series of adsorbents. This fact might be probably due to the differences in the molecule size, Lewis basicity and type solvent.

For those processes involving the CA-ICASA sample, \( K_{ci} \) values are about \( 10^8 \). However, this fact does not imply that this activated carbon has a much higher affinity by the prednisolone molecules since, as indicated above, \( K_{ci} \) has no thermodynamic signification.

In spite of the above mentioned, from the variation of \( K_{ci} \) with temperature might be deducted that the adsorption processes are endothermic for the ISAF-V6 and BP-880 samples and exothermic for all the remaining cases. However, this can only be stated after studying the variation of the thermodynamic equilibrium constant (K) with the temperature.

From Eq. [8] values of \( K \) have been calculated and they are summarized in Table 2. As can be seen from Table 2, values of \( K \) are about \( 10^3 \), these values showing no correlation with the \( S_{\text{BET}} \) and \( n_0 \) parameters of the adsorbents. This fact confirms the above stated about the existing relationship between the affinity of the adsorbent by prednisolone and the chemical nature of the active sites at the solid surface.

| Sample [\( S_{\text{BET}} \) (m²/g)] | \( T \) (K) | \( n_0 \times 10^{16} \) (mol/g) | \( K_{ci} \times 10^{-3} \) | \( R^2 \) | | Sample [\( S_{\text{BET}} \) (m²/g)] | \( T \) | \( n_0 \times 10^{16} \) (mol/g) | \( K_{ci} \times 10^{-3} \) | \( R^2 \) |
|-----------------|---|-----------------|-----------------|---|-----------------|---|-----------------|-----------------|---|
| ISAF-V6 [101]   | 283 | 3.4 | 8.6 | 0.9961 | BP-1300 [548] | 283 | 22.3 | 22.5 | 0.9904 |
| 293 | 3.4 | 8.8 | 0.9971 | 293 | 24.0 | 20.3 | 0.9896 |
| 303 | 3.4 | 9.6 | 0.9800 | 303 | 25.6 | 14.9 | 0.9727 |
| 313 | 3.2 | 11.1 | 0.9872 | 313 | 29.6 | 12.1 | 0.9868 |
| 323 | 3.2 | 13.2 | 0.9948 | 323 | 33.3 | 9.4 | 0.9827 |
| BP-880 [232]    | 283 | 6.4 | 18.0 | 0.9925 | CA-MERCK [1078] | 283 | 13.4 | 54.7 | 0.9935 |
| 293 | 6.0 | 20.3 | 0.9870 | 293 | 16.2 | 43.4 | 0.9960 |
| 303 | 5.5 | 21.0 | 0.9933 | 303 | 19.0 | 32.1 | 0.9932 |
| 313 | 5.2 | 33.2 | 0.9951 | 313 | 22.7 | 17.8 | 0.9917 |
| 323 | 4.9 | 39.0 | 0.9947 | 323 | 30.4 | 16.6 | 0.9861 |
| BP-1000 [343]   | 283 | 8.0 | 15.1 | 0.9925 | CA-ICASA [586] | 283 | 43.4 | 761407 | 0.9935 |
| 293 | 7.9 | 15.0 | 0.9913 | 293 | 45.2 | 500124 | 0.9892 |
| 303 | 7.9 | 14.7 | 0.9971 | 303 | 47.0 | 356965 | 0.9896 |
| 313 | 7.9 | 11.1 | 0.9872 | 313 | 49.2 | 269995 | 0.9896 |
| 323 | 7.9 | 14.4 | 0.9864 | 323 | 47.0 | 356965 | 0.9896 |

TABLE 1
Retention Capacity of Prednisolone by the Different Carbonaceous Adsorbents and Kinetic Equilibrium Constant
TABLE 2
Thermodynamic Equilibrium Constant (K) of the Adsorption Process of Prednisolone on Six Carbonaceous Adsorbents

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (K)</th>
<th>K</th>
<th>(\Delta H^\circ) (kJ/mol)</th>
<th>(\Delta S^\circ) (J/K·mol)</th>
<th>(R^2)</th>
<th>Sample</th>
<th>T (K)</th>
<th>K</th>
<th>(\Delta H^\circ) (kJ/mol)</th>
<th>(\Delta S^\circ) (J/K·mol)</th>
<th>(R^2)</th>
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Values of \(\Delta H^\circ\) were calculated from K by using Eq. [9] and they are also shown in Table 2. As can be seen from Table 2, the \(\Delta H^\circ\) data confirm the above indicated about the thermodynamic characteristics of the adsorption processes here studied. Values of \(\Delta S^\circ\) are also included in Table 2. Obviously, the adsorption of prednisolone will only take place if \(\Delta G^\circ\) < 0.

Thus, for the ISAF-V6/prednisolone and BP-880/prednisolone systems, for which \(\Delta H^\circ\) > 0, the positive entropy variation, \(\Delta S^\circ\) > 0, is the factor allowing the process to take place. This fact suggests that the prednisolone molecules, strongly solvated in solution, lose a considerable number of the solvent molecules during the adsorption process. This also happens in ion change processes.

The same entropic effect occurs in all of the remaining systems, excepting for the CA-Merck/prednisolone, which is weakly exoentropic. This fact can be due to either the higher bond energy active site and prednisolone or to the smaller desolvation of prednisolone. The former seems to have the biggest influence.

For the reasons indicated in Section 3 (Theory), differential enthalpy (\(\Delta H\)) and entropy (\(\Delta S\)) values for 0 \(\leq\) \(\theta\) \(\leq\) 1 have been also calculated from the adsorption isotherms obtained at \(T_1 = 10^\circ C\) and \(T_2 = 40^\circ C\) for all of the adsorption processes here studied. Such values of \(\Delta H\) and \(\Delta S\) have been plotted versus \(\theta\), the results are shown in Fig. 2.

The energy distribution of the active sites at the solid surface is expected to fit the Maxwell–Boltzmann law (21). Thus, \(\Delta H\) should be less than zero in the whole interval (0 \(\leq\) \(\theta\) \(\leq\) 1) increasing from \(\Delta H\) equal to \(-\infty\), for \(\theta = 0\), up to \(\Delta H\) \(\simeq\) 0, for \(\theta = 1\).

From the results obtained in this paper, this behavior is only observed for the BP-1000 sample, which could be due to an extremely low affinity of this adsorbent by the solvent in relation with the affinity of this adsorbent by the prednisolone molecules.

**FIG. 2.** Variation of differential adsorption (left) enthalpy and (right) entropy with coverage fraction (\(\theta\)) calculated from adsorption isotherms of prednisolone in ethanol solution at \(T_1 = 283\) K and \(T_2 = 313\) K by different carbonaceous materials: (●) ISAF-V6, (□) BP-880, (▲) BP-1000, (○) BP-1300, (●) CA-MERCK, and (+) CA-ICASA.
For values of coverage fraction below 0.15, the ISAF-V6 sample presents the same above indicated behavior. However, for higher values of \( \theta \), \( \Delta H \) decreases probably due to lateral interactions between the adsorbed molecules. This fact implies a stronger retention than that expected according to the Maxwell–Boltzmann law.

The decreasing portions of the curve \( \Delta H \) vs \( \theta \) for the samples BP-880 (\( \theta < 0.10 \)), BP-1300 (0 \( \leq \theta \leq 1 \)), and CA-Merck (\( \theta < 0.15 \)), might be related to a higher affinity of these adsorbents by the ethanol molecules at very low concentration of prednisolone.

The relative minima appearing in curves \( \Delta H \) vs \( \theta \) corresponding to BP-1300 (\( \theta \approx 0.25 \)) and CA-Merck (\( \theta \approx 0.15 \)) might be due to lateral interactions between the yet retained prednisolone molecules. The relative maximum observed for the CA-Merck sample (\( \theta \approx 0.30 \)) could probably be due to Van der Waals-type interactions between the adsorbed ethanol molecules.

All of the above indicates that the carbonaceous materials used as adsorbents in this paper present a varied physical-chemist behavior, not only in relation to the accessible solid surface to the prednisolone molecules, but also in relation to the affinity of the adsorbents by prednisolone. This might be due to the composition and concentration of the surface activated sites at the solid. The above mentioned differences are specially significant between the activated carbon samples. For the CA-ICASA samples, \( \Delta H \) is negative in the whole interval 0 \( \leq \theta \leq 1 \), decreasing as \( \theta \) increases.

On the other hand, \( \Delta S \) is positive along the interval 0 \( \leq \theta \leq 1 \), which suggests that retention of prednisolone molecules present in solution takes place together with a partial desolvation of those molecules as well as of the active sites at the solid surface. In addition, the \( \Delta S \) vs \( \theta \) curves present, as usual, the opposite behavior to that corresponding to \( \Delta H \) vs \( \theta \) curves in relation to their shape as well as about the variation of \( \Delta S \) with \( \theta \).

From the results obtained in this paper, and considering those obtained by us in a previous paper (2), it is possible to deduce that the study of the adsorption processes of nonelectrolytes from solution can be carried out by using a single model which involves both, kinetic and equilibrium aspects. This model shows that the mathematical law conditioning the equilibrium agrees with the kinetic law. It is also possible to obtain information relating to the number of active sites at the solid surface which are accessible to the adsorbable molecules, as well as about the nature and extension of the interactions between those active sites and the adsorbable molecules.

5. SUMMARY

The adsorption process of prednisolone (11\( \beta \), 17\( \alpha \), 21-trihidroxi-1,4-pregnadien-3, 20-dione) on six carbonaceous adsorbents from ethanol solution under conditions of varied temperatures (283 to 323 K) has been studied.

The experimental results have been successfully correlated with equilibrium equations obtained from kinetic laws which were deducted from a single model. This model supposes that the global process involves a single process with a partial order equal to one with respect to (1 – \( \theta \)) and \( C \) (excepting for the case of CA-ICASA sample, for which partial order with respect to \( C \) is equal to two). Values of the sorption capacity (\( m^o_0 \)) and kinetic equilibrium constant (\( K^\beta \)) have been obtained. From the experimental results, average thermodynamic equilibrium constants (\( K \)) and thermodynamic functions (\( \Delta H^\circ \) and \( \Delta S^\circ \)) of the adsorption processes have also been calculated. Values of \( K \), \( \Delta H^\circ \), and \( \Delta S^\circ \) suggest fundamentally that such processes take place in endothermic conditions for those adsorbents having the lower specific surface area (ISAF V-6 and BP-880) and in exothermic conditions for all the remaining adsorbents. The adsorption processes take place in endoentropic conditions. The variation of adsorption differential enthalpies and entropies (\( \Delta H \) and \( \Delta S \)) with the coverage fraction (\( \theta \)) has also been studied by using the Clausius–Clapeyron equations.

REFERENCES