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Thermodynamic parameters of adsorption of 1,10-phenanthroline and 2,2′-bipyridyl on hematite, kaolinite and montmorillonites

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Abstract

The thermodynamic equilibrium constant (K), free energy (ΔG), enthalpy (ΔH), entropy (ΔS), isosteric heat (q_{st}) of adsorption, and the constant (k_L) of the Langmuir adsorption equation using the adsorption isotherms (pH 6) of 1,10-phenanthroline (OP) and 2,2′-bipyridyl (BP) on hematite, sodium kaolinite (Na-K), sodium montmorillonite (Na-Mt) and hydroxy-aluminium montmorillonite (HAM) were obtained. The magnitude of enthalpy and isosteric heat established that adsorption on these minerals is a physical phenomenon.

The equilibrium reaction constant (K) was used to calculate the enthalpy (ΔH) and free energy (ΔG) for OP adsorption, parameters which could not be obtained by applying the constant (k_L) of the Langmuir equation of adsorption. The isosteric heat for hematite, Na-K, Na-Mt and HAM in kJ mol^{-1} was: 10.8–0.66, 13.4–28.6, 9.12–16.0 and 13.5–6.35, respectively.

The equilibrium reaction constant (K) was similarly used to obtain the enthalpy (ΔH) and free energy (ΔG) for BP adsorption on hematite, Na-K and Na-Mt, but this was not possible in the case of HAM. The k_L constant did not behave as K in the adsorption of BP; it was only possible to obtain ΔG with values close to the order of magnitude of those obtained with K, but not ΔH. Isosteric heat in kJ mol^{-1} was -28.2 to -17.1 for hematite, 0.388–7.43 for Na-K, 3.55–7.47 for Na-Mt, and -0.363 to 2.30 for HAM.

The adsorption of OP on hematite, Na-K, Na-Mt and HAM is an exothermic process, as is BP adsorption on Na-K and Na-Mt. BP adsorption on HAM, however, is endothermic at low surface cover and exothermic at a surface cover greater than 0.5 mol kg^{-1}.

The negative ΔS values obtained for both systems of adsorption are likely due to the displacement of solvent molecules on the surface by OP and BP solutes.

In the case of OP adsorption hematite presents a heterogeneous surface and the other minerals a homogeneous surface. In the case of BP, all the minerals present heterogeneous surfaces.

Keywords: Adsorption; Bipyridine; Enthalpy; Entropy; Free energy; Hematite; Hydroxy-aluminium montmorillonite; Isosteric heat; Kaolinite; Montmorillonite; Orthophenanthroline

1. Introduction

Knowledge of the main characteristics of minerals is extremely important for their separation in different mixtures for commercial applications. The adsorption capacity of certain minerals used to purify gases and fluids is also of interest. Their effectiveness depends in the selectivity or preferential adsorption of one species on the other, which generally depends on the energy of adsorption of different adsorbates on certain adsorbents.

Most adsorbents are characterized using traditional parameters such as adsorption isotherms from a single solution and/or binary liquid mixtures [1–3] pore size distribution, specific surface, density, etc., but the picture would not be complete without information on surface energy (enthalpy, free energy, isosteric heat, etc.) [4]. Determination of these energies can be accomplished through methods that involve adsorption of gases and liquids [5], adsorption of adsorbates mixtures [6–9], immersion calorimetry [4,6,9], and the use of adsorption isotherm of certain adsorbates at different temperatures. Success in obtaining adsorption isotherms depends on the affinity that the adsor-

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bates have for certain heterogeneous solid surfaces [10]. It also depends on the molecule size of the adsorbate [3,11–13], the pH of the system and whether the isotherm has a simple or binary system [3,14–16].

Surface pressure is a thermodynamic force that can be used to advantage to describe adsorption reactions, leading to the quantitative determination of fundamental properties of the adsorption reaction such as free energy and enthalpy [17].

The objective of this work is to show how the thermodynamic constant of the reaction, the enthalpy, the free energy, the isosteric heat and the constant of the Langmuir equation of adsorption can provide necessary basic information to characterize some adsorbents (oxides and clay minerals) as a function of the adsorption of 1,10-phenanthroline and of 2,2′-bipyridyl.

2. Theoretical background

To obtain thermodynamic parameters such as the equilibrium constant (K, cm) of reaction, free energy (ΔG, kJ mol^{-1}) and the enthalpy of adsorption (ΔH, kJ mol^{-1}), we should keep in mind that for an ideal monolayer located on the surface, the spreading or surface pressure (ϕ, dyne cm^{-1}) can be expressed as [18]:

$$\phi = \left(\frac{NkT}{A}\right) \ln\left[\frac{1}{(1-\theta)}\right], \tag{1}$$

where N is the total number of sites occupied by the adsorbate on the surface (molecule g^{-1}), k the Boltzmann constant (1.381×10^{-16} dyne cm molecule^{-1} K^{-1}), T the absolute temperature, A the total area occupied by a monolayer (cm^2 g^{-1}) and $\theta = n/N$ represents the relationship between the occupied sites (molecule cm^{-2}), adsorbed quantity at a certain equilibrium pressure p (dyne cm^{-2}), and the total available sites (N, molecule cm^{-2}). Using the Langmuir equation of adsorption we obtain:

$$n = \frac{k_\mathrm{L} N p}{1 + k_\mathrm{L} p}, \tag{2}$$

where k_L is a constant (cm^2 dyne^{-1}).

Knowing the spreading or surface pressure (ϕ), the thermodynamic equilibrium constant (K) can be obtained from [17]:

$$\phi = KCkT. \tag{3}$$

The constant (k_L) of the Langmuir equation of adsorption is related with the heat of adsorption [19]. Keeping in mind the reaction of adsorption, in equilibrium we can write:

$$k_\mathrm{d}\theta = p(1-\theta)k_\mathrm{a} \tag{4}$$

Desorption ⇐ | ⇒ adsorption

In Eq. (4), the constants $k_\mathrm{d} = k' \exp(\Delta E'/RT)$ and $k_\mathrm{a} = k \exp(\Delta E/RT)$, with k' and k constant, known as frequency or Arrhenius factors [19], where E' and E are energy desorption and adsorption, respectively, R is the universal constant of the gases (8.314 J mol^{-1} K^{-1}) and T is the temperature in Kelvin degrees. From Eq. (4) we have:

$$p = \frac{\theta k' \exp\left(-E'/RT\right)}{(1-\theta)k \exp\left(-E/RT\right)}. \tag{5}$$

Ordering and replacing gives:

$$p = \frac{\theta k_\mathrm{p}[(E-E')/RT]}{(1-\theta)}, \tag{6}$$

where k_p is a proportionality constant ($k_\mathrm{p} = k'/k$), and can be written as:

$$k_\mathrm{p} = \frac{k_\mathrm{d}}{k_\mathrm{a}} \exp\left(\frac{\Delta E}{RT}\right),$$

$k_\mathrm{L} = k_\mathrm{a}/k_\mathrm{d}$ is also a constant that depends on temperature but not on cover [19].

Supposing that the heat of adsorption $\Delta E = E - E' = -\Delta H^*$ is independent of the state of cover [18], we have:

$$k_\mathrm{L} = \frac{1}{k_\mathrm{p}} \exp\left(\frac{-\Delta H^*}{RT}\right). \tag{7}$$

Taking Napierian logarithms in Eq. (7) and ordering:

$$\left(\frac{\Delta H^*}{R}\right)\left(\frac{1}{T}\right) = -\ln k_\mathrm{L} - \ln k_\mathrm{p}, \tag{8}$$

and differentiating with respect to (1/T) we obtain:

$$\Delta H^* = -R\left\{\left[\frac{\partial(\ln k_\mathrm{L})}{\partial(1/T)}\right] + \left[\frac{\partial(\ln k_\mathrm{p})}{\partial(1/T)}\right]\right\}. \tag{9}$$

Eq. (9) can only be resolved if the constant of proportionality k_p (in dyne cm^{-2}) is constant with respect to temperature, but in fact it depends on this parameter [20]. If in practice it remains almost constant throughout an adsorption experiment as a function of temperature [21], the graphic representation of the first part of Eq. (9) is almost a straight line, so the behavior of the k_L constant of the Langmuir isotherm will be similar to that of a real equilibrium constant [22,23] and the same as Eq. (12). Other authors [24,25] also postulate the constant of the Langmuir equation of adsorption as a useful parameter for determining the enthalpy of adsorption.

The k_L constant of the Langmuir equation is also related to the thermodynamic equilibrium constant for [18]:

$$K^* = \phi_\mathrm{S} k_\mathrm{L}, \tag{10}$$

where $\phi_\mathrm{S} = NkT/A$ is the surface (or spreading) pressure of a mobile layer where all sites are occupied by molecules and is constant at constant temperature.

The free energy of adsorption (ΔG) [26], in the context of this study, refers to changes in free energy associated with the adsorption of an ion, molecule or other solute at a specific adsorption site on the surface:

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

and where the constant (k_L) of the Langmuir equation is used [27–29]:

$$\Delta G^* = -RT \ln k_\mathrm{L}. \tag{12}$$

The enthalpy of adsorption (ΔH), i.e. the quantity of heat ($\mathrm{kJ\,mol^{-1}}$) that a thermodynamic system can interchange with the environment under normal temperature and pressure conditions, can be obtained by using equation [30]:

$$\Delta H = -R\left[\frac{\partial(\ln K)}{\partial(1/T)}\right]. \tag{13}$$

and/or also [31]:

$$R \ln K = \frac{\Delta S - \Delta H}{T}, \tag{14}$$

where ΔS is the entropy of adsorption in $\mathrm{kJ\,mol^{-1}\,K^{-1}}$ and T is the absolute temperature (Kelvin degrees).

The thermodynamic parameter known as isosteric heat (q_{st}, $\mathrm{kJ\,mol^{-1}}$), which is the difference between heat content in the solute and adsorbate states, can be calculated on the basis of the Clausius–Clapeyron equation [32]:

$$q_{\mathrm{st}} = -R\left[\frac{\partial(\ln p)}{\partial(1/T)}\right]_v, \tag{15}$$

where p is the pressure ($\mathrm{dyne\,cm^{-2}}$), and v is the adsorbed quantity of gas (constant) gas in $\mathrm{cm^3\,g^{-1}}$. This equation is applicable for gas adsorption and in systems involving dissolution, for which certain assumptions must be made such as that the concentrations replace the activities when they are diluted and thus pressure p can be replaced by the equality $p = CkT$ [17], where C is the concentration ($\mathrm{molecule\,cm^{-3}}$) and k is the Boltzmann constant. Eq. (15) can thus be written as follows:

$$q_{\mathrm{st}} = -R\left[\frac{\partial(\ln CkT)}{\partial(1/T)}\right]_n, \tag{16}$$

where n is the adsorbed amount (constant) in $\mathrm{molecule\,cm^{-2}}$, $\mathrm{molecule\,g^{-1}}$, $\mathrm{mmol\,kg^{-1}}$, etc.

3. Materials and methods

3.1. Adsorbents

The following materials were used as adsorbents: (1) iron oxide ($\alpha\text{-Fe}_2\text{O}_3$) provided by May and Baker Co. (USA). X-ray analysis showed this to be a very well crystallized mineral known as hematite, with a specific surface (A) of $39.8\,\mathrm{m^2\,g^{-1}}$ obtained by adsorption of 1,10-phenanthroline (OP) [33]; (2) sodium kaolinite (Na-K) from Georgia (USA), provided by Davison Chemicals Co., Astra Glaze grade, pigmented and pre-dispersed. A sample of this clay was saturated with sodium by successive washing with NaCl 0.5 M, washed with water to eliminate the excess salt, centrifuged to obtain particles with a diameter <2 mm, dried at 60 °C, then pulverized until it passed through a 200 μm-mesh sieve. The cationic exchange capacity (CEC) as determined by the NaCl [34] method was $5.38\,\mathrm{cmol_c\,kg^{-1}}$ for the fraction <1 μm when saturated with sodium and $A = 31.5\,\mathrm{m^2\,g^{-1}}$ (for OP adsorption); (3) sodium montmorillonite (Na-Mt): a sample of a local montmorillonite, Cerro Bandera, Argentina [35] was saturated with sodium by successive washing with NaCl 1 M, then washed with water to eliminate the excess salt and to separate the fraction <2 μm for centrifugation. The clay was dried at 60 °C and then pulverized until it passed through a 200 μm-mesh sieve. This fraction has $85.6\,\mathrm{cmol_c\,kg^{-1}}$ of exchangeable sodium (Na was displaced by Ba and then the concentration of Na was determined with a flame spectrophotometer) and with $A = 781.8\,\mathrm{m^2\,g^{-1}}$ (for OP adsorption [33]); and (4) hydroxy-aluminium montmorillonite (HAM), prepared from the previous sample [36]. The hydroxy-aluminium clay has: $60.1\,\mathrm{mg\,Al\,g^{-1}}$ (equivalent to 11.35% $\mathrm{Al_2O_3}$), $50\,\mathrm{cmol_c\,kg^{-1}}$ of sodium (determined with Ba [37]), a basal spacing [$d(0\,0\,1)$] of 1.82 nm in the X-ray diagram and with $A = 451.8\,\mathrm{m^2\,g^{-1}}$ (for OP adsorption [33]).

3.2. Adsorbates

Adsorbates of analytic grade were provided by Merck (Germany): orthophenanthroline (OP); 1,10-phenanthroline ($\mathrm{C_{12}H_8N_2{\cdot}H_2O}$) with a water solubility of $14\,\mathrm{mmol\,L^{-1}}$ and dissociation reaction constants of $\mathrm{p}K_1 = -1.4$ and $\mathrm{p}K_2 = 4.85$ [33]; and bipyridine (BP): 2,2′-bipyridyl ($\mathrm{C_{10}H_8N_2}$) with a water solubility of $40\,\mathrm{mmol\,L^{-1}}$ and dissociation reaction constants of $\mathrm{p}K_1 = -0.20$ and $\mathrm{p}K_2 = 4.37$ [38].

3.3. Adsorption

The adsorption experiments were carried out by placing 1 g (dry weight at 110 °C) of hematite and kaolinite, and 0.1 g of Na-Mt and HAM in 40 mL centrifuge tubes with the addition of 25 mL of solution of different initial concentrations of the organic molecules (OP and/or BP), adjusting the pH for the addition of HCl and/or NaOH. The centrifuge tubes were covered, shaken for 30 min and then left to rest at constant temperature (0–42 °C, as appropriate) during 24 h. The pH values were measured at these temperatures. The samples were then centrifuged at 10,000 rpm in a thermostatic ultracentrifuge and the concentration of OP and/or BP in the supernatant liquids was determined using the methods described in the bibliography [33,38]. All the experiments were carried out in duplicate. The adsorbed amount of organic molecules at each temperature (n_T) was obtained from the difference between the initial (C_{i}) and final concentration (C): $n_T = [(C_{\mathrm{i}} - C)/w]_T$, where w is the amount of mineral in the suspension ($\mathrm{g\,L^{-1}}$) and the sub-index T refers to the temperature of each system.

3.4. Adsorption isotherm

The adsorption isotherms were analyzed by applying the Langmuir adsorption equation (see Eq. (2)), which is applicable to gas adsorption. For its correct application to solutions it is necessary to assume that the concentrations replace the activities when these are diluted, and the pressure p can be replaced by the equality $p = CkT$ [17], where C is the equilibrium concentration ($\mathrm{molecule\,cm^{-3}}$) and k is the Boltzmann constant. One of the lineal forms of the Langmuir equation (Hanes–Wolf [39]) is:

$$\frac{CkT}{n} = \frac{1}{k_{\mathrm{L}}N} + \frac{1}{N}CkT, \tag{17}$$

where n is the quantity adsorbed (in this case in molecules g^{-1}) at the equilibrium concentration CkT (dyne cm^{-2}), N is the maximum quantity adsorbed corresponding to the covering of a monolayer in molecules g^{-1} and k_L it is the Langmuir constant (cm^2 $dyne^{-1}$).

Another lineal form of the Langmuir equation (Lineweaver–Burk [39]) is:

$$\frac{1}{n} = \frac{1}{N} + \frac{1}{k_L N CkT}. \quad (18)$$

As pointed out by Schulthess and Dey [39], using Eqs. (17) and (18) with the experimental data gives rise to different results for the k_L and N constants. The most marked differences are observed in the value of the Langmuir constant (k_L) and in the adjustment of the data to the equation (r^2); by way of example we can mention that for OP adsorption on Na-Mt at 277 K we obtain $N = 132.1 \times 10^{19}$ molecule g^{-1}, $k_L = 1.16 \times 10^{-4}$ cm^2 $dyne^{-1}$ and $r^2 = 0.999$ with Eq. (17), and $N = 122.5 \times 10^{19}$ molecule g^{-1}, $k_L = 1.71 \times 10^{-4}$ cm^2 $dyne^{-1}$ and $r^2 = 0.974$ with Eq. (18). On the basis of the best fit with the experimental data, we used Eq. (17).

3.5. Statistical analysis

Analysis of variance (ANOVA [40]) was applied to the obtained data, taking the adsorbed quantities (n) as dependent variables and the equilibrium concentration (C) and temperature (T) as independent variables. Comparison between pairs of means was performed using the Student's t-test. Statistical significance was considered at a confidence level of 95% [41].

4. Results and discussion

4.1. Adsorption isotherm

Adsorption isotherms (pH 6) for OP and BP on hematite, Na-K, Na-Mt and HAM at three temperatures are shown in Figs. 1 and 2, representing significantly different averages for the three temperatures, with an interval confidence of 95%, except in the case of HAM where the data correspond to three groups whose averages are not significantly different. The form of the OP adsorption isotherm on hematite corresponds to the H class (high affinity), subgroup 2 in the classification of Giles et al. [42], whereas the isotherms of Na-K, Na-Mt and HAM are of the L class (Langmuir type), subgroup 2. The H curve is a special case of the L curve in which the solute has high affinity for the surface and the diluted solution is completely adsorbed, or at least there is no measurable quantity remaining in the solution. The adsorbed species are often large units such as ionic micelles (as in the case of OP molecules [33]) or polymer molecules [42], and in some cases the classic Langmuir adsorption equation is applicable.

Applying Eq. (17) we have obtained the corresponding parameters for the different materials at three temperatures (277, 301 and 313 K). From the equations, all with a very good correlation ($r^2 = 0.984$ at 0.999) with a 1% level of significance ($P > 0.01$), we obtained the maximum adsorption (N, molecule g^{-1}) and the constant (k_L, cm^2 $dyne^{-1}$) of the Langmuir equation of adsorption, as shown in Table 1. OP adsorption is dependent on temperature: on hematite adsorption increases with temperature, whereas on kaolinite and montmorillonite the opposite occurs and OP adsorption diminishes with increas-

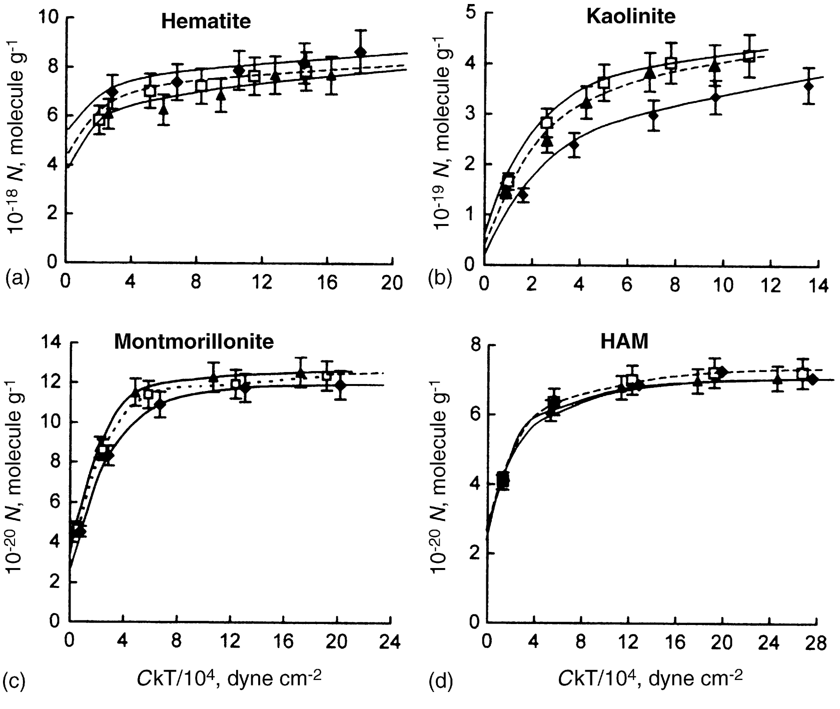

Fig. 1. Maximum adsorption of 1,10-phenanthroline (N, molecule g^{-1}) onto hematite (a), sodium kaolinite (b), sodium montmorillonite (c), and hydroxy-Al montmorillonite (d) as a function of the equilibrium concentration expressed as CkT (dyne cm^{-2}). The symbols represent the temperatures in K: (▲) 277, (□) 301 and (◆) 313. The data are averages of duplicates with of confidence level of 95%.

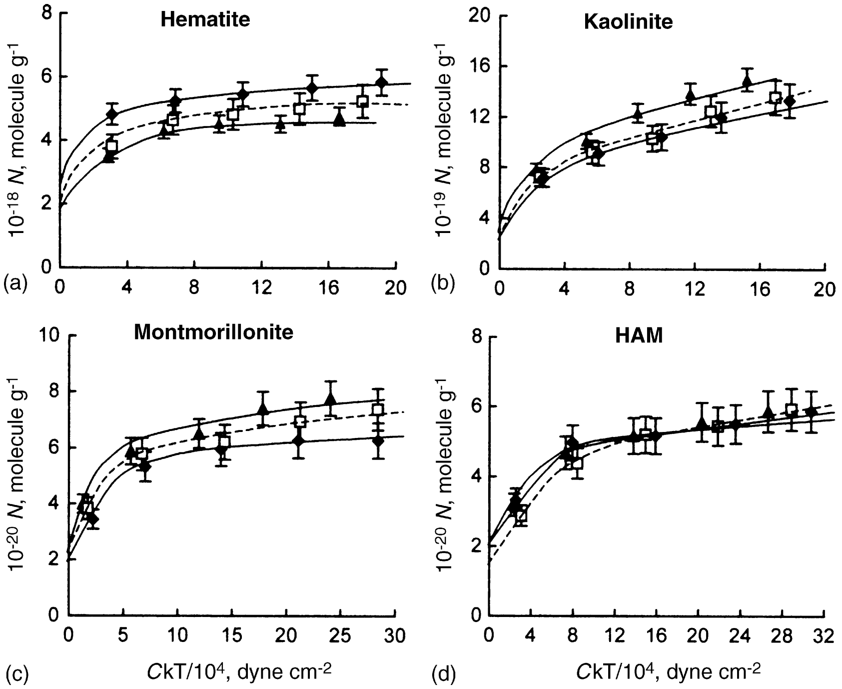

Fig. 2. Maximum adsorption of 2,2′-bipyridyl (*N*, molecule g^{-1}) onto hematite (a), sodium kaolinite (b), sodium montmorillonite (c), and hydroxy-Al montmorillonite (d) as a function of the equilibrium concentration expressed as *C*kT (dyne cm^{-2}). Symbols represent the temperatures in K: (▲) 273, (□) 297 and (◆) 315. The data are averages of duplicates with a significance interval of 95%.

ing temperature. These observations are based on the adsorbed maximum quantities (*N*), since the value of Langmuir constant obtained for each material diminishes as the temperature increases. This can happen due to the fact that the constant k_L is dependent on the temperature and not on the covering of the surface [19]. The adsorbed quantity (*N*) on the surface depends on the specific sites, more or less active, that depend in turn on the non-homogeneous nature of the surface. In the case of HAM adsorption seems to be indifferent to temperature. It should be mentioned that at pH 6 there are at least two OP species in solution, 6.61% of $[C_{12}H_9N_2]^+$ and 93.39% of $[C_{12}H_8N_2]$. This would suggest a process of cationic exchange in addition to physical adsorption, though this is not reflected in the energy magnitudes of the adsorption process. This could be explained by the formation of micelles with three molecules [33] which somehow impede exchange of the cation (except at a higher concentration of the OP cationic form) owing to a steric problem, saturating the charge of the montmorillonite surface.

The adsorption isotherm (pH 6) of BP on hematite has the form of the H class, subgroup 2 [42], whereas those of Na-K, Na-Mt and HAM correspond to the L class, subgroup 2. Applying Langmuir lineal Eq. (17) we obtain constants k_L and *N* for the different materials at the three temperatures (273, 298 and 315 K). The equations obtained have very good correlation ($r^2 = 0.962$–0.999) with a significance level of 1% ($P > 0.01$) except for hematite at 298 K, for which the correlation coefficient ($r^2 = 0.929$) has a significance level of 5% ($P > 0.05$). Hematite, kaolinite and montmorillonite show BP adsorption to be dependent on temperature, though whereas adsorption on hematite increases with temperature, with kaolinite and montmorillonite the opposite occurs: adsorption diminishes with increasing temperature (see Fig. 2). It should be noticed here that the data of the maximum quantity adsorbed (*N*) obtained from the Langmuir lineal equation show for hematite, kaolinite and montmorillonite that BP adsorption increases when the temperature decreases (see Table 2). This discrepancy between the analytic and experimental data can be due to the fact that the former do not show

Table 1
Maximum amount adsorbed (*N*, molecule g^{-1}), constant (k_L, cm^2 $dyne^{-1}$) of Langmuir equation of adsorption and thermodynamic equilibrium constant (*K*, cm), obtained for the adsorption of 1,10-phenanthroline on some minerals at three temperatures

Materials	277 K			301 K			313 K		
	$10^{-19}N$	10^4k_L	10^4K	$10^{-19}N$	10^4k_L	10^4K	$10^{-19}N$	10^4k_L	10^4K
Hematite	0.744	1.47	5.21	0.831	1.08	4.61	0.921	0.634	3.05
Na-kaolinite	4.80	0.570	2.54	5.25	0.403	2.04	4.40	0.299	1.65
Na-Mt	132.1	1.16	4.89	130.3	0.975	3.89	128.3	0.731	3.41
HAM	71.8	2.02	8.01	75.3	0.996	4.88	74.1	1.053	5.32

Table 2
Maximum amount adsorbed (N, molecule g^{-1}), constant (k_L, cm^2 dyne^{-1}) of Langmuir equation of adsorption and thermodynamic equilibrium constant (K, cm), obtained for the adsorption of 2,2′-bipyridyl on some minerals at three temperatures

Materials	273 K			297 K			315 K		
	$10^{-19}N$	10^5k_L	10^5K	$10^{-19}N$	10^5k_L	10^5K	$10^{-19}N$	10^5k_L	10^5K
Hematite	0.685	2.830	10.40	0.650	2.707	11.67	0.562	2.248	6.848
Na-kaolinite	1.83	2.556	4.353	1.38	5.282	1.803	1.60	2.691	1.210
Na-Mt	82.8	4.707	14.60	67.5	5.127	12.65	78.2	4.071	12.30
HAM	63.7	3.735	10.02	63.6	2.570	18.15	62.0	4.173	10.62

a correct the lineal fit to Langmuir equation. This is the reason why we have preferred to accept the experimental data shown in Fig. 2. The values of the maximum adsorption (N) and of Langmuir constant (k_L) show a clear sequence in hematite, and not so much in kaolinite and montmorillonite. This is possibly due to the fact that chemical adsorption is greater on hematite. The values of the maximum adsorption (N) and of the Langmuir constant (k_L) they show a clear sequence in hematite, and they are not it so much in kaolinite and montmorillonite. BP adsorption on HAM appears to be indifferent to the effect of the temperature. At pH 6 there are at least two species of BP in solution, 2.29% of $[C_{12}H_9N_2]^+$ and 97.71% of $[C_{12}H_8N_2]$, again implying a process of cationic exchange in addition to physical adsorption, but which is not reflected in the energy magnitudes of the adsorption process. It is highly likely that the amount of the cationic species is too small to be reflected in the energy value of adsorption, except as seen later on, when the constant of the Langmuir adsorption equation is used as an equilibrium constant in the determination of ΔG^* and ΔH^*.

4.2. The Langmuir constant (k_L)

When using the values of the k_L constant of the Langmuir equation in Eq. (12) we obtain the following ΔG^* for OP adsorption at 301 K: 22.86, 25.32, 23.11 and 23.06 kJ mol^{-1} for hematite, Na-K, Na-Mt and HAM, respectively. Statistical comparison of the data obtained using the equilibrium constant K and those obtained using the k_L constant shows significant differences in the averages. This implies that the constant of the Langmuir equation makes it possible in these systems to obtain ΔG with similar behavior to the equilibrium constant, but of different magnitudes (see Table 3).

The k_L values of the Langmuir equation were used in accordance with Eq. (9) to determine adsorption heat ΔH^*. For this the $\ln k_L$ regression equations were obtained as a function of $(1/T)$ (Fig. 3), giving good correlation indices ($r^2 = 0.866$ at 0.969) with a significance level of 95% ($P > 0.05$). The obtained values of ΔH^* in kJ mol^{-1} are: hematite, −15.49; Na-K, −12.43; Na-Mt, −8.53 and HAM, −14.41 (Table 2). Statistically, these ΔH^* values differ significantly (except for Na-Mt) in order of magnitude from those found for these materials using the equilibrium constant K. When using Eq. (10) to obtain the equilibrium constant (K^*) and with this to determine the enthalpy of adsorption, the results for hematite were −8.94; kaolinite, −10.94; montmorillonite, −6.65; HAM, −11.09 kJ mol^{-1}. These values for ΔH are different from those obtained when the equilibrium constant (K) is used as obtained by Eq. (13), from which it can be affirmed that although they are of the same order of magnitude (see Table 3), it is not appropriate to use the k_L constant.

Even though the lineal regression equation of K obtained by Eq. (3) with K^* determined by Eq. (10) is in most cases a straight line with good correlation indices, it corresponds to:

$$K^* = a + bK,$$

where the a constant is not equal to unity, with positive and negative values in the order of 9×10^{-5} and slope b, that should be 1, assumes values of 1.54, 1.67, 1.44 and 1.74 for hematite, kaolinite, montmorillonite and HAM, respectively. The correlation between equilibrium constants K^* and K for OP adsorption is relatively good (keeping in mind that there are three temperature values), with values of r^2 ranging from 0.848 to 0.999. In terms of OP adsorption on these minerals, the results express the real difference between K and k_L, as expressed in Eq. (10) [17], and indicate that k_L can only be used under very limited conditions to determine an approximate value of ΔH.

When using Eq. (12) to obtain free energy (ΔG^*) from the constant (k_L) of the Langmuir equation we obtain 25.97, 24.32, 24.39 and 26.10 kJ mol^{-1} for BP adsorption on hematite, Na-

Table 3
Free energy (ΔG, kJ mol^{-1}), enthalpy (ΔH, kJ mol^{-1}), entropy (ΔS, J mol^{-1} K^{-1}) and isosteric heat (q_{st}, kJ mol^{-1}) of adsorption of 1,10-phenanthroline and 2,2′-bipyridyl on some minerals obtained at different temperatures

Materials	1,10-Phenanthroline				2,2′-Bipyridyl			
	ΔG^a	ΔH	ΔS^a	q_{st}	ΔG^b	ΔH	ΔS^b	q_{st}
Hematite	19.22	−9.50	−95.43	10.8–0.66	22.36	−6.24	−96.30	−28.2–−17.1
Na-kaolinite	21.27	−8.25	−98.06	13.4–28.6	26.97	−22.05	−165.06	0.388–7.43
Na-Mt	19.65	−7.12	−89.04	9.12–16.0	22.16	−3.01	−84.75	3.55–7.47
HAM	19.08	−9.24	−94.09	13.5–6.35	21.27	2.32	−63.81	−0.363–2.30

[a] $T = 301$ K.
[b] $T = 297$ K.

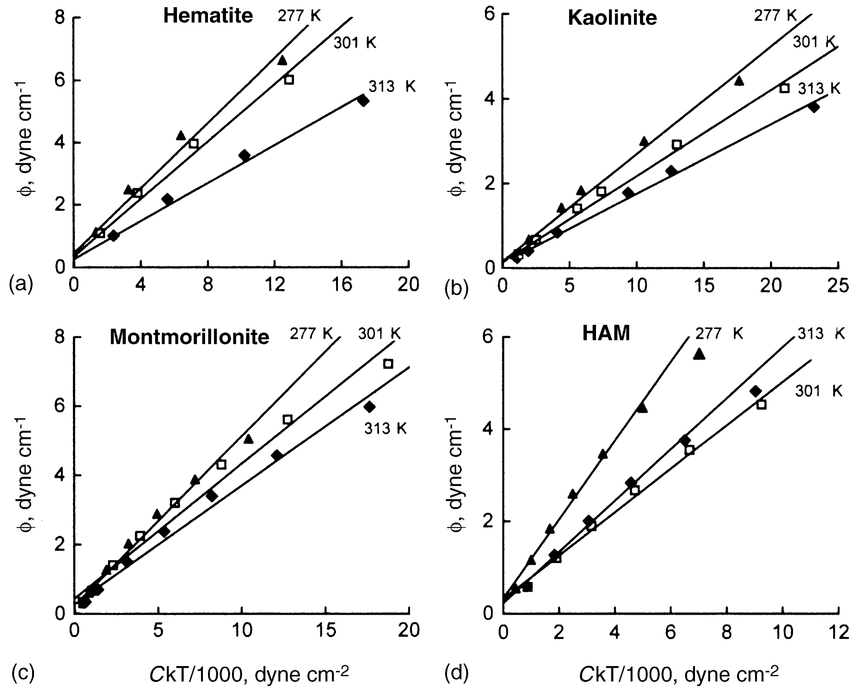

Fig. 3. Dependence of the thermodynamic equilibrium constant ($\ln K$) and of that of Langmuir ($\ln k_L$) of 1,10-phenanthroline adsorption with the reciprocal of the absolute temperature ($1/T$) in: (a) hematite, (b) sodium kaolinite, (c) sodium montmorillonite, and (d) hydroxy-Al montmorillonite. Symbols represent the temperatures in K: (▲) 277, (□) 301 and (◆) 313. The data are averages of duplicates with a significance interval of 95%.

K, Na-Mt and HAM, respectively (Table 2). The sign of these values is in agreement with that obtained using Eq. (11) and the magnitude approximately so. The statistical analysis showed significant differences between the weighted pairs of K and K^* averages.

When correlating $\ln k_L$ for BP adsorption on hematite as a function of ($1/T$) a very low correlation index was obtained ($r^2 = 0.801$) with a significance level lower than 95%, giving $\Delta H^* = -3.70\,\mathrm{kJ\,mol^{-1}}$. This completely different result to that obtained with K and the inability to obtain ΔH^* for the other materials permits us to affirm that in BP adsorption, the constant of the Langmuir adsorption equation does not behave like K, mainly owing to the fact that, as stated before, the proportionality constant k_p does not remain constant with temperature. It should also be mentioned that an increase in pH in the suspension takes place during BP adsorption owing to the detachment of OH groups from the surface of the adsorbent [43], indicating a chemisorption reaction like that reported by Coluccia et al. [44]. Since at pH 6 the ion concentration $[C_{10}H_9N_2]^+$ only reaches 2.29%, is can be assumed that the energy of the chemical unions has little effect on the magnitude of ΔH but a greater impact on the proportionality constant k_p of Eq. (5).

With Eq. (10) we obtain the value of the equilibrium constant (K^*) of BP adsorption on hematite, kaolinite, montmorillonite and HAM, allowing us to obtain the value of ΔH for hematite ($-4.48\,\mathrm{mJ\,mol^{-1}}$, $r^2 = 0.823$) and montmorillonite ($-1.04\,\mathrm{mJ\,mol^{-1}}$, $r^2 = 0.999$). The correlation in the other materials was not good. Nevertheless it should be noted that these enthalpy values are lower in absolute terms than those obtained with K (Table 3), though they are of the same order of magnitude.

The correlation between the equilibrium constant K^* of Eq. (10) and the equilibrium constant K of Eq. (3) for BP adsorption on hematite, kaolinite and HAM is relatively good (at only three temperature values), with values of r^2 ranging from 0.911 to 0.999, but not at all good for montmorillonite ($r^2 = 0.269$). Furthermore, the values of the slope (b) of the lineal regression equation do not equal one, reaching values of 0.78, 1.40, 0.53 and 5.88 for hematite, kaolinite, montmorillonite and HAM, respectively. The constant (a) also differs from unity, with positive and negative values in the order of 6×10^{-5}. In terms of BP adsorption on these minerals, and taken together with the non-obtention of the enthalpy values for kaolinite and HAM, these results express a difference between K and k_L, as indicated in Eq. (10) [17], and that as mentioned earlier, k_L can only be used to determine ΔH under very limited conditions.

4.3. Thermodynamic equilibrium constant of adsorption (K)

On the basis of the adsorbed maximum amounts of OP and BP, using Eq. (1) we calculated the surface or spreading pressures (ϕ) and expressed them graphically as a function of CkT (Figs. 3 and 4). The straight lines show a slight deviation from the origin that does not coincide with Eq. (3). Leaving these deviations aside as being negligible, then the value of the thermodynamic reaction constant (K) could be obtained from the slope of these straight lines for each adsorbate, adsorbent and at the three temperatures. The values are presented in Table 1. The values obtained for OP adsorption at 301 K are: 4.61×10^{-4}, 2.04×10^{-4}, 3.89×10^{-4} and 4.88×10^{-4} cm for

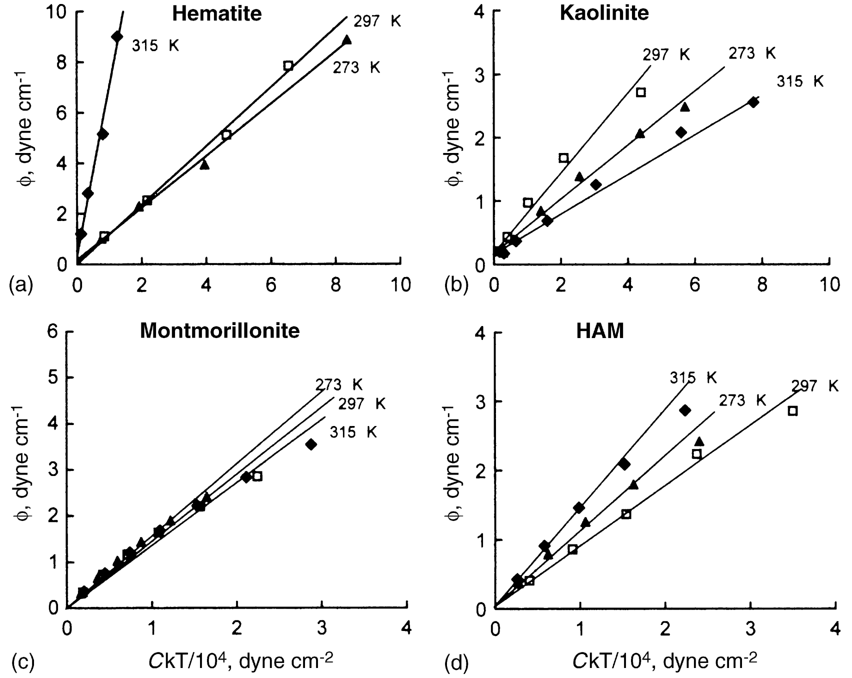

Fig. 4. Dependence of the thermodynamic equilibrium constant (ln K) of 2,2′-bipyridyl adsorption with the reciprocal of the absolute temperature (1/T) in: (a) hematite, (b) sodium kaolinite, (c) sodium montmorillonite, and (d) hydroxy-Al montmorillonite. Symbols represent the temperatures in K: (▲) 273, (□) 297 and (◆) 315.

hematite, Na-K, Na-Mt and HAM, respectively, all relatively low compared with those obtained for Al_2O_3 for phosphate adsorption, $K = 1.567 \times 10^{-2}$ cm [11], though this corresponds to an exchange reaction between the phosphate and a hydroxyl group on the oxide surface. This comparison serves to recall that the values of K obtained for hematite, Na-K, Na-Mt and HAM are of this order of magnitude because of the physical adsorption of the OP molecules.

The K values obtained for BP adsorption at 297 K are: 11.67×10^{-5}, 1.803×10^{-5}, 12.65×10^{-5} and 18.15×10^{-5} cm for hematite, Na-K, Na-Mt and HAM, respectively (Table 2).

4.4. Free energy of adsorption (ΔG)

The free energy (ΔG) calculated for OP adsorption from the equilibrium constants in accordance with Eq. (11) at 301 K are: 19.22, 21.26, 19.65 and 19.08 kJ mol^{-1} for hematite, Na-K, Na-Mt and HAM, respectively. All the ΔG values are positive and of the same order of magnitude for these materials (Table 3), which may imply that at not very high temperatures (277–313 K) adsorption of OP molecules is due to a physical process favoring adsorption rather than desorption.

The free energy (ΔG) calculated for BP adsorption from the equilibrium constants (K) at 297 K are: 22.36, 26.97, 22.16 and 21.27 kJ mol^{-1} for hematite, Na-K, Na-Mt and HAM, respectively (Table 3). They are all of the same order and are also of the same sign and magnitude as those reported in other studies using bipyridine (tetrazine) compounds [45,46], and they are a greater and of the opposite sign ($\Delta G = 13.85$–15.61 kJ mol^{-1} [47]) to those obtained by the methylene blue adsorption on kaolinite.

4.5. Enthalpy of adsorption (ΔH)

The ln K values obtained for OP and BP were expressed graphically as a function of the reciprocal of the absolute temperature in agreement with Eq. (13). Montmorillonite and kaolinite show good correlation, whereas the data for hematite and HAM are more dispersed possibly because of a lower affinity of OP for the surface of these minerals. From the slope of the straight lines and in accordance with Eqs. (13) and (14) we obtained the adsorption enthalpy ΔH for each material (Table 3): hematite, −9.50; Na-K, −8.25; Na-Mt, −7.12, and HAM, −9.24 kJ mol^{-1}. The values are negative, and the order of magnitude indicates that adsorption of OP on these minerals is favored at low temperatures (exothermic process) as seen in the adsorption isotherms (Fig. 1). The heat of physical adsorption (van der Waals adsorption) of gases is relatively low, in the order of 1–5 kcal mol^{-1} (~4–21 kJ mol^{-1}), whereas that of chemisorption is much higher, of a magnitude of 24–120 kcal mol^{-1} (~100–500 kJ mol^{-1}) comparable to that for a chemical union [20,42]. These concepts can be made valid for the adsorption of OP in watery solution, whereby it can be affirmed that this is due to a purely physical phenomenon.

The enthalpy (ΔH) of BP adsorption for each adsorbent can be determined from the slopes obtained when representing ϕ versus CkT graphically, in agreement with Eq. (3) (Table 3). Hematite, Na-K, Na-Mt and HAM show good correlation of the data, the enthalpy value for these minerals being: hematite, −6.24; Na-K, −22.05; Na-Mt, −3.01, and HAM, 2.32 kJ mol^{-1}. The magnitude of the values indicates a physical adsorption reaction and the sign indicates an exothermic process in hematite, Na-K, Na-Mt and endothermic–exothermic for HAM (see later on). The ΔH value in Na-kaolinite ($-22.05\,\mathrm{kJ\,mol^{-1}}$) is a relatively high value in comparison with that found for the other materials (hematite, Na-Mt and HAM), and can be explained by assuming that physical and chemical adsorption takes place on the kaolinite surface, this reaction occurring among the charges (protonation) of the N of the BP molecule that substitute some of the OH groups on the clay surface [38]. These values are the opposite sign but of the same magnitude ($\Delta H = 6.03$–$13.53\,\mathrm{kJ\,mol^{-1}}$ [47]) as those attached with the methylene blue adsorption on kaolinite.

4.6. Entropy of adsorption (ΔS)

Using Eq. (14) we obtained negative ΔS values in the order of -89.04 to $-98.47\,\mathrm{kJ\,mol^{-1}\,K^{-1}}$ for OP adsorption and -66.88 to $-164.48\,\mathrm{kJ\,mol^{-1}\,K^{-1}}$ for BP adsorption (see Table 3). In general, adsorption produces a certain order in the system, giving negative entropy. This is the case with the adsorption of many organic compounds [48] and is what we found for OP and BP adsorption on hematite, Na-K, Na-Mt and HAM. Positive ΔS values indicate a decrease in the order of the system during adsorption, and are considered to occur in processes with hydrophobic interactions [49,50] or as a result of the displacement of the solvent by adsorption of the adsorbate. The ΔS values obtained for the kaolinite are of the opposite sign but of the same magnitude ($\Delta S = 69.69$–$88.16\,\mathrm{kJ\,mol^{-1}\,K^{-1}}$ [47]) as those attached with the methylene blue adsorption on kaolinite. Negative entropy adsorption values suggest that the solids/OP/H_2O and solids/BP/H_2O adsorption systems are in a low state of disorder in the equilibrium, probably owing to the fact that the adsorption phenomenon is affected by liquid/solute interactions with hydrophilic surfaces.

It is interesting to note that the ΔS values for OP adsorption obtained using the k_L constant of the Langmuir equation instead of the thermodynamic equilibrium constant are negative, in the order of -105.90 to $-131.84\,\mathrm{kJ\,mol^{-1}\,K^{-1}}$, and the mean values are significantly different from the ΔS values obtained with K.

4.7. Isosteric heat (q_{st})

Representation of $\ln CkT$ in OP and BP adsorption as a function of the inverse of the absolute temperature obtains straight lines (with good correlation, except for the larger OP coverings on hematite and kaolinite, of 12 and $70\,\mathrm{mmol\,kg^{-1}}$, respectively) whose slope corresponds to the isosteric heat of adsorption for each adsorbed quantity as expressed in Eq. (16). The isosteric heat values for OP adsorption are all positive: hematite, 10.8 at 0.66; Na-K, 13.4 at 28.6, Na-Mt, 9.12–16.0 and HAM, 13.5 at $6.35\,\mathrm{kJ\,mol^{-1}}$ (Table 3), which is consistent with the negative values obtained for the enthalpy, indicating that OP adsorption on these minerals is an exothermic process [20]. The isosteric heat data as a function of the amount of OP adsorbed are shown in Fig. 5. Analysis of the variations in isosteric heat with the amount adsorbed brings out two phenomena worthy of mention. The first occurs in hematite (Fig. 5a), where isosteric heat diminishes from 12 to $0.66\,\mathrm{kJ\,mol^{-1}}$, within a range of adsorption of 0–$10\,\mathrm{mmol\,kg^{-1}}$. The variation in isosteric heat with the quantity adsorbed indicates that the surface is heterogeneous: the most active surface areas react first (higher isosteric heat values) followed by sites of lesser activity that eventually achieve a larger surface cover, giving rise to lower q_{st} values. The second phenomenon occurs in Na-K, Na-Mt and HAM, where it can be appreciated that within certain adsorption values, which of course depend on each material (Fig. 5b–d), isosteric heat remains almost without variation, which can be attributed to the inexistence of lateral interactions between the adsorbed molecules [24]. Furthermore, when they reach high

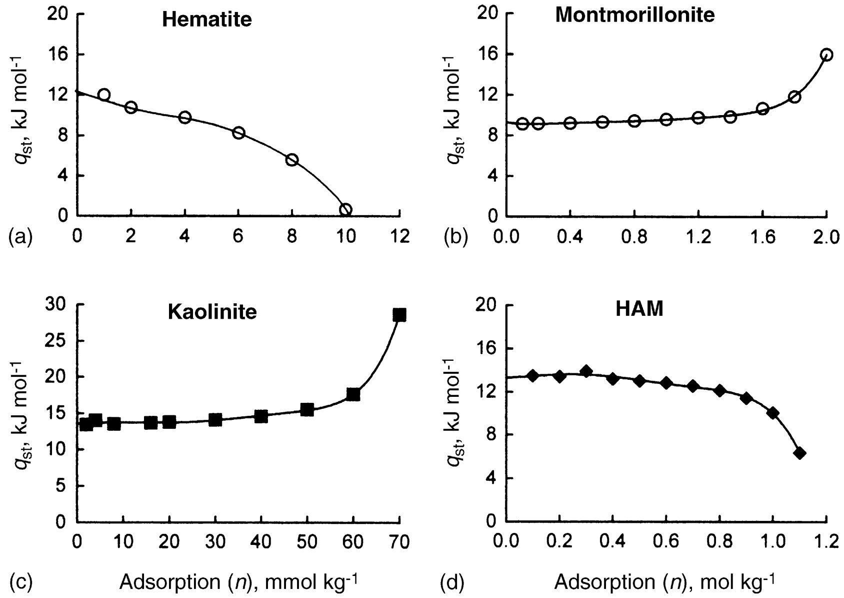

Fig. 5. Variation of the isosteric heat (q_{st}) of the 1,10-phenanthroline adsorption as a function of the adsorbed amount (x) for: (a) hematite, (b) sodium kaolinite, (c) sodium montmorillonite and (d) hydroxy-Al montmorillonite.

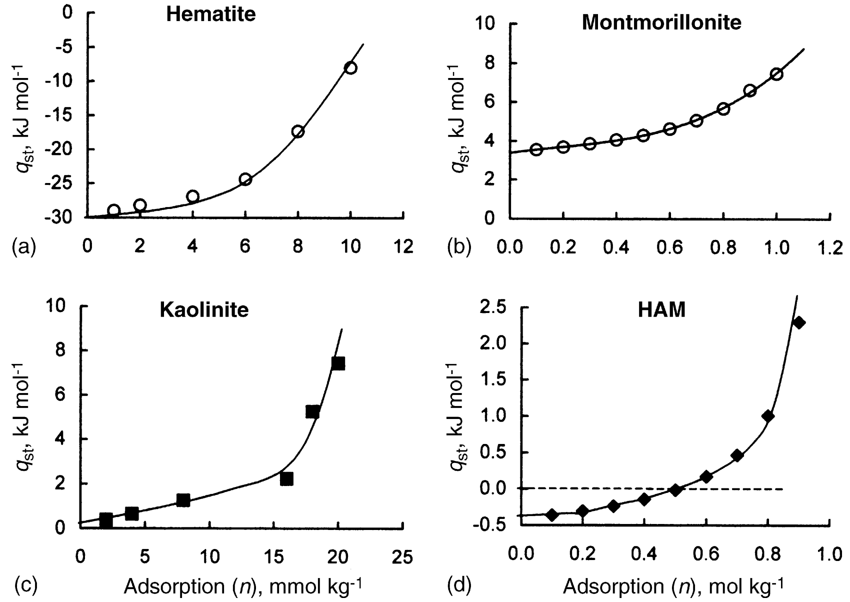

Fig. 6. Variation of q_{st} with the adsorbed amount (x) of 2,2′-bipyridyl for hematite (a), kaolinite (b), Na-montmorillonite (c) and hydroxy-Al montmorillonite (d).

surface cover values (Fig. 5b and c), in the case of both Na-K and Na-Mt the q_{st} values tend to diminish, showing a similar behavior in this phase of adsorption to that of hematite. The opposite occurs in HAM (Fig. 5d), where q_{st} values increase at high adsorbed amounts, indicating that adsorption is occurring in sites with greater energy but can only be achieved at higher OP equilibrium concentrations. This may be due to the existence of a composite $[\mathrm{Al_6(OH)_{16.5}}]^{1.5+}$ [36] between the clay laminae that impedes adsorption of the OP molecules: when the OP concentration in the solution increases, greater pressure is exerted on the interlaminar surface and this allows the OP molecules to reach the sites. In consequence, the surface of these materials appears heterogeneous to the adsorption of OP molecules.

The slopes (with good correlation for all data) of Fig. 6 for each amount of BP adsorbed permits calculation of the isosteric heat (Table 3) for hematite, −28.2 to −17.1; Na-Mt, 3.55–7.47; Na-K, 0.388–4.43 and HAM, −0.363 to 2.30 kJ mol^{-1} (see Fig. 6). The isosteric heat of BP adsorption on hematite, Na-K, Na-Mt and HAM increases with the quantity adsorbed. In hematite (Fig. 6a) the q_{st} sign shows that BP adsorption is an endothermic process and the variation in isosteric heat with the quantity adsorbed indicates that the surface is heterogeneous to the adsorption of BP molecules: the most active sites on the surface react first (high negative isosteric heat values, −28.2 kJ mol^{-1}) followed by sites of lesser activity that eventually achieve a larger surface cover giving rise to lower negative values (−17.1 kJ mol^{-1}) of q_{st}. What occurs on the surface of Na-Mt, Na-K and HAM during BP adsorption is a more complex process. The BP molecule is also adsorbed by a process of chemical reaction, replacing OH groups [37]. These OH groups become more accessible as the quantity of adsorbed BP increases, and thus at low levels of BP adsorption on the surface (at low q_{st} values) only the more accessible OH groups are replaced whereas for higher coverage, greater energy is required to replace the less accessible OH groups. At the highest levels of surface cover in Na-K and Na-Mt, equivalent q_{st} values are reached, around 8 kJ mol^{-1}. HAM is a very particular case (Fig. 6d) in which the external surface has montmorillonite characteristics but with an $[\mathrm{Al_6(HO)_{16.5}}]^{1.5+}$ cation between the clay laminae [36]. In the case of surface cover less than 0.5 mol kg^{-1} (Fig. 6d), adsorption occurs via a process of chemisorption (endothermic process) with a negative isosteric heat value of −0.363 kJ mol^{-1} for a BP adsorption of 0.1 mol kg^{-1}. Increasing the concentration of BP molecules in the solution favors physical adsorption (exothermic process) and increasing adsorption to values above 0.5 mol kg^{-1} gives positive q_{st} values of up to 2.30 kJ mol^{-1}. In general the heat given off during chemisorption diminishes as the surface is progressively covered, which may be due to inherent heterogeneity, induced heterogeneity or to a combination of both [51]. This process of physical and chemical adsorption is what makes the surface of this material appear to be heterogeneous with regard to the adsorption of BP molecules.

5. Conclusions

The q_{st} values, K, ΔG and ΔH, in sign and magnitude, obtained from OP adsorption isotherms at pH 6 on Na-kaolinite, Na-montmorillonite and hydroxy-Al montmorillonite, show that OP molecules are physically adsorbed on these materials. OP adsorption on hematite, Na-K, Na-Mt and HAM is an exothermic phenomenon; BP adsorption on hematite, Na-K and Na-Mt is an exothermic process; and in HAM it is endothermic at low surface cover and exothermic at surface cover above 0.5 mol kg^{-1}. In terms of OP adsorption, hematite has a heterogeneous surface whereas Na-K, Na-Mt and HAM present homogeneous surfaces. With BP adsorption, all the materials have a heterogeneous surface.

The constant (k_L) of the Langmuir equation of adsorption behaved almost like a true equilibrium constant (K) in the case of OP adsorption, permitting determination of the ΔH^* and ΔG^* values. In the case of BP adsorption, however, only free energy ΔG^* could be obtained, owing mainly to a chemisorption process associated to that of physical adsorption. This, together with the relationship of K^* as a function of K (where in all cases the slope values of the regression differed from unity), demonstrates that the constant of the Langmuir equation of adsorption is not always applicable and even in those cases where it can be used, some additional reference data is needed to obtain reliable results.

It can be inferred that the negative ΔS values obtained for the two adsorption systems is likely due to the displacement of solvent molecules on the surface by those of the OP and BP solutes.

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