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Application of the Thermodynamic Model to the Couple Water vapor-Raw Clay

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Abstract

This work is based on data from adsorption isotherms and isosteric enthalpies of El Hamma raw clay at different temperatures (30, 40, 50 and 60°C). These previously obtained data were used here to show the variation of the thermodynamic properties of water adsorbed on the surface of the clay: Gibbs energy, enthalpy and entropy. Then we present a model of solid solution based on a polynomial expression of degree 7. This model was applied to calculate the excess quantities: excess Gibbs energy of mixing, entropy term and Gibbs energy of mixing. The variations of free energy, enthalpy and entropy of adsorbed water show fluctuations that characterize three areas. For low water contents the entropy of the adsorbed water is greater than that of liquid water. As the amount of adsorbed water increases the entropy gradually approaches the normal value. Close to saturation, the model shows that the term of excess energy of mixing is always positive, although the water remains bound to the solid. Since the term of enthalpy of mixing is negative this means that the solution is stable.

Keywords: Adsorption; Hydration; Thermodynamic properties; Solid solution

Introduction

The study of water transfers in soil has interested scientists and engineers in different fields. Indeed, the amount and condition of the water in the soil can significantly affect its agronomic, hydraulic and geological. If knowledge of the two extreme states of the soil, saturated or dry, seems well under way, an unsaturated state, particularly at low water contents, merits further investigation.

Application techniques of adsorption are found in many industrial processes. Systems using solid adsorbents such as activated carbons, activated aluminas and clays play an important role in the process of separation, purification, drying, dehumidification, air handling and water treatment. In the case of the solid adsorption, the mode of association between the molecules of water vapor and the adsorbent is purely physical. The adsorption does not change the volume of the solid, it means a variation of the adsorbed mass and physical and thermodynamic properties of couple's adsorbent/adsorbate.

El Hamma raw clay was chosen as the adsorbent material in this study. The object of this work was to investigate the equilibrium and thermodynamic parameters of the adsorption of water vapor on raw clay surface and determine the adsorption.

A thermodynamic model can be implemented using known thermodynamic properties of pure poles and writing that all the adsorbent properties are expressed by varying the activities of these poles. This work focuses on the thermodynamic modeling of defining a model with parameters that have a physical meaning that it is possible to determine from experimental data. For solid solutions the model used is that based on polynomial expression. This model takes into account the short range order in the solution via the interaction between first and second neighbors.

We propose in this study a model in terms of ideal solid solution between the surface layer of El Hamma raw clay and different amounts of water adsorbed.

Characterization of Natural Clay

The adsorbent used in this study is a raw clay material from Jebel Haidoudi. Its physical and chemical characteristics were studied by Srasra [1] and confirmed by Ben Zina [2].

The results of physicochemical analysis are listed in table 1. The chemical composition of El Hamma raw clay is obtained by using various techniques, as classical analysis, atomic emission spectroscopy (ICP) and X-ray diffraction, and categorized in table 2. Its specific area was found about 60 m²/g using BET method.

The results of this analysis and the swelling index have shown that this raw clay is an illite-smectite system with the presence of iron, calcium and very little of kaolinite.

Formula	$[Al_{1,94}Fe_{0,7}Mg_{0,5}][Si_{7,5}Al_{0,5}]O_{20}(OH)_4Ca_{1,56}Na_{0,32}K_{0,154}$
Molecular weight	791,711 g
Density	2,75 g/cm³
BET specific area (Nitrogen)	60 m²/g
Methylene Blue specific area	520 m²/g
Total pore volume	143,9.10⁻⁰³ cm³/g
Average particle diameter	140 µm
Elemental mass of grain	40.10⁻⁶ g

Table 1: Textural characterization of raw clay.

i	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	L.I*
%	50,8	18,8	8,5	2,3	1,5	1,4	2,2	1,9	14,0

*L.I: loss on ignition.

Table 2: Chemical composition of raw clay.

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The swelling index values (between 35 to 75%) were determined by addition of 2 g of raw clay to 100 ml of distilled water. After 24 hours the volume of sediment was read. The results obtained were relative values in order to compare the behavior of different samples.

On The basis of 20 structural oxygen plus two OH, the structural formula of El Hamma raw clay was calculated

using Ross and Hendricks technique [3,4]: $[Al_{1,94}Fe_{0,7}Mg_{0,5}][Si_{7,5}Al_{0,5}]O_{20}(OH)_4Ca_{1,56}Na_{0,32}K_{0,154}$. The cation exchange capacity [1] of calculated material was found between 29 to 71 meq/100 g.

Materials and Methods

The simplest way to characterize the adsorption at a surface is to calculate the number of adsorbed molecules as a function of applied pressure. The adsorption isotherms displays information of how much material will adsorb for a given set of state variables (pressure P and temperature T when using gases as adsorptive, concentration c and temperature T when dealing with adsorption from solutions). The amount of adsorbed material can be given as surface coverage, or by the volume taken up by the sum of particles adsorbed in the first monolayer.

The experimental determination of the adsorption isotherm can be done by several methods: volumetric, gravimetric and chromatography. In our case the volumetric method is difficult to use, and the chromatographic method, as we have seen [5,6] allows only the part of the adsorption isotherm located at low relative pressures p/p^0. To accomplish this work, we opted for a dynamic gravimetric method, which is relatively slow but allows for complete isotherms.

Gravimetric adsorption is a method to evaluate directly the mass of adsorbate by making successive weighing. This technique is based on measuring changes in mass of the porous sample when it is contacted with the adorable gas. The first systems based on this principle have been developed by McBain and Bakr [7] and were equipped with silica springs at the end of which is placed a crucible containing the porous adsorbent.

Nowadays, the weighing are performed either on principles based on oscillators or from displacement measurement using electromagnet. Among the principles based on oscillators, we can cite the microbalance quartz crystal. It involves placing the adsorbent, usually in liquid form, onto a quartz crystal.

With the magnetic suspension balance [8-10] gravimetric measurements in a wide temperature and pressure range and under aggressive media can be done. Such a magnetic suspension balance consist of a balance for recording the measurement values, a suspension coupling which carries the weight of the sample, a sensor for the position measurement of the levitation part and a control unit to control the suspension coupling.

In this work, we have chosen a gravimetric system and we used an analytical balance (type Sartorius: 1409, sensitivity 10^{-4}). Our installation is composed of an air compressor, 5 thermostatic baths, a vacuum pump and a main tube through which derive four smaller diameter tubes each emerging into an adsorption chamber where the temperature is fixed as desired. This experimental device can lead four parallel adsorption experiments at four different temperatures (30, 40, 50 and 60 °C).

The main tube is covered with electric heating resistors and then wrapped with insulation in order to avoid heat loss and therefore the risk of condensation. The power of the heating resistors and the

temperature of the water thermostatic baths are adjusted so that the temperature of the gas inside each adsorption chamber has the value set in advance (with precision of one degree).

Samples that have previously spent more than 48 hours in an oven at T=60°C are first cooled under vacuum for 24 hours and then weighed and finally introduced very quickly within the confines of adsorption. The two bubblers are used to generate the air saturated with water vapor at the temperature of the thermostatic bath. Empty columns are designed to hold any water droplets entrained by the air flow. Finally, the column filled with silica gel is used to remove air derived from the compressor from his residual moisture.

The amount of adsorbed water vapor is measured from the change in weight of the samples by means of an analytical balance. The balance is considered established when the change in mass of the solid is less than 1%.

Thermodynamic Properties of Adsorbed Water

To understand the adsorption properties of adsorbed water along the adsorptions isotherms into raw clay surface, we have to study the energy of the clay-water interface. So, we have used the thermodynamic approach which is considered the most widely used approach.

Thermodynamic data relating to adsorbed water reflect the evolutions of water-clay system during adsorption process. Thermodynamic properties are estimated using the experimental results obtained from adsorption isotherms and isosteric enthalpy, over a range of temperature.

The thermodynamic values which reflect the changes of the water system from the adsorbed state to the free liquid state are:

Gibbs differential of adsorption

Free energy is the total energy required to transfer water molecules from vapor state to a solid surface or vice-versa. The value of the Gibbs differential adsorption is obtained from the adsorption isotherm (Figure 1).

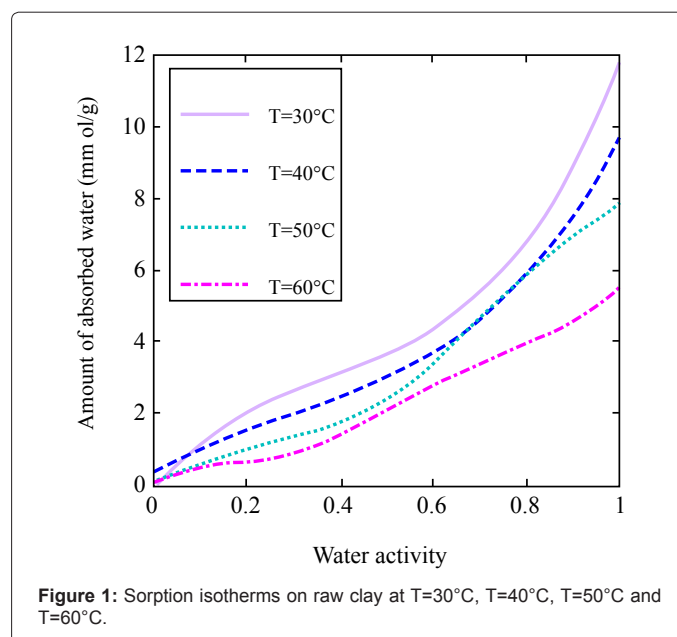At each value of the water activity corresponds a value to the Gibbs

Figure 1: Sorption isotherms on raw clay at T=30°C, T=40°C, T=50°C and T=60°C.

energy of adsorption calculated for one mole of water corresponding to the energy of the adsorption reaction of dN moles of water to the surface clay in which are already adsorbed N moles of water.

The Gibbs energy (kJ/mmol) can be calculated as follows:

$$dG_R = dN \times RT \times \ln(\frac{p}{p_0}) \qquad (1)$$

$$\Delta G_{R,N} = RT \times \ln(\frac{p}{p_0}) \qquad (2)$$

Differential enthalpy of adsorption

The differential enthalpy of adsorption reaction is calculated from the curve of variation of the isosteric heat as a function of N recovery rate of raw clay. For a given value p/p^0, N moles of water are adsorbed on the raw clay. A small change in enthalpy of the hydration reaction, when measured dN moles of water added to the clay surface already covered by N moles of water is obtained as follows:

$$d\Delta H_{R,N} = -\Delta H_{is}(N + dN) + \Delta H_{is}(N) \qquad (3)$$

For one mole of adsorbed water, we have:

$$\Delta H_{R,N} = -\frac{d(\Delta H_{is})}{dN} \qquad (4)$$

Differential entropy of adsorption

Differential entropy of adsorption is determined by Tardy et al. [11] from the following equation:

$$\Delta S_{R,N} = \frac{1}{T}(\Delta H_{R,N} - \Delta G_{R,N}) \qquad (5)$$

According to tardy et al. [11] the average free energy of all the water adsorbed to the stage p/p^0, is calculated as follows:

$$\Delta G^*_{R,N} = \frac{1}{N}\int_0^N RT \times \ln\left(\frac{p}{p^0}\right)dN \qquad (6)$$

Gibbs adsorption average

To avoid errors in the evaluation of the mean energy of adsorption, Trolard et al. made from the integration of the first known experimental point by asking:

$$N' = N - N_1 \qquad (7)$$

Where, N_1 represent the first amount of adsorbed water. Equation (7) becomes:

$$\Delta G^*_{R,N} = \frac{1}{N'}\int_{N_1}^N RT \times \ln\left(\frac{p}{p^0}\right)dN \qquad (8)$$

Average enthalpy adsorption

The average enthalpy of adsorption is defined, while putting into consideration the assumption made in the preceding paragraph by the following expression:

$$\Delta H^*_{R,N} = \frac{1}{N'}\int_{N_1}^N \Delta H_{R,N} dN \qquad (9)$$

Average entropy of adsorption

The average entropy of adsorption of one mole of water is the difference between the average free energy and enthalpy average, writes:

$$\Delta S^*_{R,N} = \frac{1}{T}(\Delta H^*_{R,N} - \Delta G^*_{R,N}) \qquad (10)$$

Modeling and calculation of mixing energy

Solid solution model

Saxena et al. has introduced the concept of a solid solution, and the associated mathematical models to try to predict the behavior of these phases depending on environmental conditions. We can also see those of Ganguly and Saxena [12], Glynn and Reardon [13], Geiger [14].

Several models have been developed [15]. Most of these empirical models include for example: Quasi-chemical notions of order, solid solution ionic and molecular and models based on a polynomial expression of the excess enthalpy of mixing. The model on which our study is based is described below.

Models based on a polynomial expression of the excess enthalpy of mixing

The expression of the energy of mixing between i poles in a solid solution is decomposed into two terms: entropy function (TE) and excess enthalpy of mixing. The first of these terms results from the ability of the constituents of the solid solution to mix freely in this phase. It reduces, in fact, an entropic term type:

$$TE = RT\sum_i X_i \ln X_i \qquad (11)$$

X_i represent the mole fraction of a macroscopic component i.

The difference between the Gibbs energy of a real solution and that of an ideal solution is known as the excess Gibbs energy of mixing of the solution. Thus, we have:

$$\Delta G^{ex}_M = RT\sum_i X_i \ln \gamma_i = RT(X_1 \ln \gamma_1 + X_2 \ln \gamma_2) \qquad (12)$$

γi which represents the activity coefficient of the pure dipoles in the solid solution.

$$\Delta G_M = TE + \Delta G^{ex}_M \qquad (13)$$

Depending on the model of solid solution can be expressed in different ways. One of these classical forms is to approximate the excess Gibbs energy of mixing by a polynomial function. For a binary solid solution between a pure dipole 1 and 2, Guggenheim suggested that the excess energy of mixing can be represented by the following polynomial expression [15]:

$$\Delta G^{ex}_M = X_1 X_2 \left[A_0 + A_1(X_1 - X_2) + A_2(X_1 - X_2)^2 + ... \right] \qquad (14)$$

$$\Delta G^{ex}_M = X_1 X_2 \sum_{j=0}^J A_J(X_1 - X_2)^j \qquad (15)$$

The coefficients A_j (i = 0, 1, 2) are constants at fixed P and T. The simplest models of this class are obtained when all coefficients are zero except A_0 which represents the interaction energy between species 1 and 2.

If the coefficients A_1, A_2, ... are different from 0, this amounts to consider that the 1-2 interaction depends on the chemical nature of the first neighbors if $A_1 \neq 0$ and the nature of the first and second neighbors if $A_1 \neq 0$ and $A_2 \neq 0$. In this case, equation (15) shows that the shape of the Gibbs energy of mixing function is asymmetric with respect to the composition of the solution, so this type of model is solid solution called asymmetric.

Powell and Ganguly [16,15] showed that in the case of a regular solution, we have:

$$RT \ln \gamma_1 = A_0 X_2^2 = A_0(1 - X_1)^2 \qquad (16)$$

and: $$RT \ln \gamma_2 = A_0 X_1^2 \qquad (17)$$

By combining equation (16) and (17), we obtained:

$$RT(X_1 \ln \gamma_1 + X_2 \ln \gamma_2) = A_0 X_1 X_2 \qquad (18)$$

Thus, the major difficulty in the definition of a thermodynamic model describing the behavior of a solution is how to express properties excess.

Mixing energy: Implicated at the adsorption isotherm

Averaging the data of adsorption isotherms, Trolard et al. propose to compute a function that best describes these isotherms, the shape of the expression (19) and a polynomial of degree 7 has proved adequate for the description of ln (p/p^0) according to X_{H_2O}.

$$\ln\left(\frac{p}{p^0}\right) = \ln X_{H_2O} + \frac{1}{RT}\left[\left(1-X_{H_2O}\right)^2 \sum_{j=0}^{j=7} A_j \left(2X_{H_2O}-1\right)^j\right] + \frac{1}{RT}\left[2X_{H_2O}\left(1-X_{H_2O}\right)^2 \sum_{j=0}^{j=7} jA_j \left(2X_{H_2O}-1\right)^{j-1}\right] \quad (19)$$

The first-degree polynomial model representing this function is given by the following equation:

$$Y_{the} = A_0 + A_1 X_1 + A_2 X_2 + A_3 X_3 + A_4 X_4 + A_5 X_5 + A_6 X_6 + A_7 X_7 \quad (20)$$

Experimental expression is giving by:

$$Y_{exp} = \frac{RT}{(1-X_{H_2O})^2}\left[\ln\left[\frac{p}{p^0}\right] - \ln X_{H_2O}\right] \qquad (21)$$

With: $X_j = (2X_{H_2O}-1)^{j-1}\left[2(j+1)X_{H_2O}-1\right]$ (22)

Where X_{H_2O} represents the mole fraction of oxygen bound to the water relative to the total number of oxygen atoms involved in the adsorption reaction of N moles of water, is:

$$X_{H_2O} = \frac{N_O(H_2O)}{N_O(H_2O) + N_O(rawclay)} \qquad (23)$$

The number of oxygen atoms of water is given by:

$$N_O(H_2O) = N.Av \qquad (24)$$

The number of oxygen atoms on the surface of raw clay $N_O(rawclay)$, is a fixed number:

$$N_O(rawclay) = 2,5848.10^{22} \qquad (25)$$

Results and Discussion

The determination of the thermodynamic properties of the adsorbed water at the surface of raw clay is carried out using the experimental data of adsorption isotherms obtained at different temperatures. The numerical values of these functions at temperature T=30°C, are compiled in table 3.

Adsorption isotherms

Figure 1 illustrates adsorption isotherms of adsorbed water vapor in the El Hamma raw clay surface at different temperature (30, 40, 50 and 60°C). These results are obtained by Kalfat et al. [17] using gravimetric method. The amount of adsorbed water vapor is measured from the change of mass of the samples using an analytical balance. Equilibrium is considered established when the change in mass of the solid is less than 1%.

The general shape of these isotherms corresponds to type II of Brunauer and classification. Whereas, when the temperature increases the shape of the isotherm approaches type III rather than type II. This phenomenon can be explained by the swelling of the clay under the influence of moisture.

By comparing the adsorption isotherms at different temperatures over the range of water activity from 0 to 1, it was noted that the experimental curves obtained show that the ability of raw clay to adsorb water is greater when the temperature decreases, which confirms the exothermic character of adsorption process. For a water activity p/p^0=0.95, the amount of adsorbed water at 30°C is about 10 mmol/g of clay, whereas for a higher temperature T=60°C is about 5 mmol/g of clay.
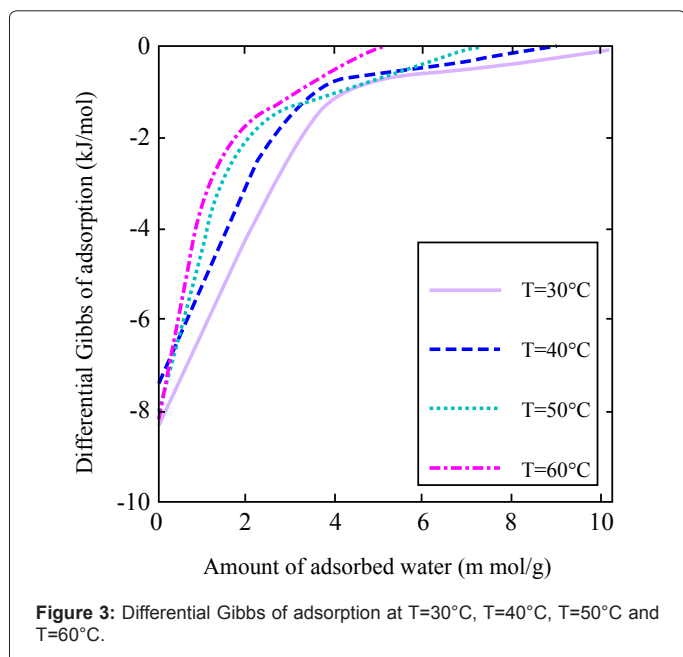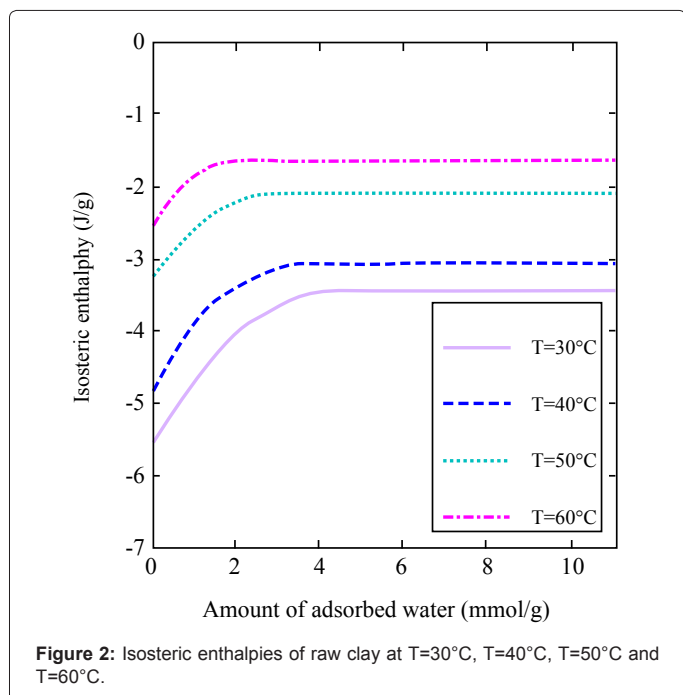
Isosteric enthalpies

The molar enthalpy of adsorption isosteric enthalpy is often called a fundamental factor for the calculation of energy balances, noting that it is related to the adsorption isotherms by the Clapeyron equation:

$$\Delta H_{is} = RT\left[\frac{\partial \ln p}{\partial T}\right]_N \qquad (26$$

Usually the isotherms are from a plot the content of adsorbed water related to the activity and repotted as ln (p) related to (-1/T) for various values of the converge.

Figure 2 show that the isosteric enthalpy of adsorption, in absolute terms, has been decrease with increasing water content. We also note that the isosteric enthalpy is greatest for very low values of N, and it decreases rapidly and tends to zero as far as N grows. This implies that the formation of the first monolayer of water vapor is more energetic than the upper layers and the water was adsorbed in the most accessible places on the outer surface of the solid. As the water content increased swelling of the adsorbent and thus, new high-energy sites are open for

p/p⁰	N	n	e	N'	ΔGR,N	ΔH_is	ΔHR,N	ΔSR,N	ΔG*_R,N	ΔH*_R,N	ΔS*_R,N
0.06	0.52	0.28	0.85	0.0	-7.091	-5.1680	-791.300	-2586.87	-	-	-
0.16	1.96	1.07	3.21	1.4	-4.619	-4.0285	-739.149	-2422.99	-5.855	-765.22	-2504.93
0.20	2.09	1.14	3.43	1.6	-4.056	-4.0075	-316.520	-1030.72	-5.729	-745.57	-2440.50
0.25	2.36	1.29	3.87	1.8	-3.494	-3.9019	-432.287	-1414.46	-5.442	-691.10	-2261.79
0.29	2.48	1.36	4.07	2.0	-3.120	-3.8389	-324.215	-1059.46	-5.312	-671.95	-2199.04
0.33	2.88	1.57	4.72	2.4	-2.794	-3.7333	-238.883	-778.79	-4.913	-605.78	-1982.08
0.40	3.01	1.64	4.93	2.5	-2.309	-3.7123	-283.846	-928.70	-4.789	-587.80	-1923.17
0.46	3.40	1.86	5.57	2.9	-1.957	-3.5857	-324.215	-1063.03	-4.430	-549.37	-1797.60
0.56	3.53	1.93	5.79	3.0	-1.461	-3.5437	-116.062	-378.03	-4.312	-535.15	-1751.08
0.61	4.31	2.36	7.07	3.8	-1.246	-3.4801	-25.658	-80.53	-3.703	-439.60	-1437.89
0.70	6.01	3.28	9.85	5.5	-0.899	-3.4801	0.000	2.97	-2.889	-307.45	-1004.65
0.79	7.06	3.86	11.57	6.5	-0.594	-3.4801	0.000	1.96	-2.545	-258.09	-842.96
0.84	7.58	4.14	12.43	7.1	-0.439	-3.4801	0.000	1.45	-2.395	-239.08	-780.74
0.89	8.11	4.43	13.30	7.6	-0.294	-3.4801	0.000	0.97	-2.254	-222.38	-726.14
0.94	10.30	5.63	16.89	9.8	-0.156	-3.4801	0.000	0.51	-1.799	-172.59	-563.37

Table 3: Thermodynamic properties of adsorbed water on the surface of raw clay at T =30°C.

Figure 2: Isosteric enthalpies of raw clay at T=30°C, T=40°C, T=50°C and T=60°C.

Figure 3: Differential Gibbs of adsorption at T=30°C, T=40°C, T=50°C and T=60°C.

water: this causes an increase in the isosteric enthalpy of adsorption with decreasing water content.

Differential Gibbs of adsorption

The differential Gibbs of adsorption of adsorbed water on raw clay surface calculated from Eq (3) is presented in Figure 3. We can observe that the free energy decreases as the water content increases. Above 8.5 mmol/g of raw clay the Gibbs differential adsorption in the different temperature is similar, and approaches zero. This indicates that as water content increases, the adsorbed water has properties similar to those of bulk water and the influence of the clay surface does not extend beyond a few molecular layers of adsorbed water. The

negative values of Gibbs differential adsorption confirm the feasibility of the adsorption process.
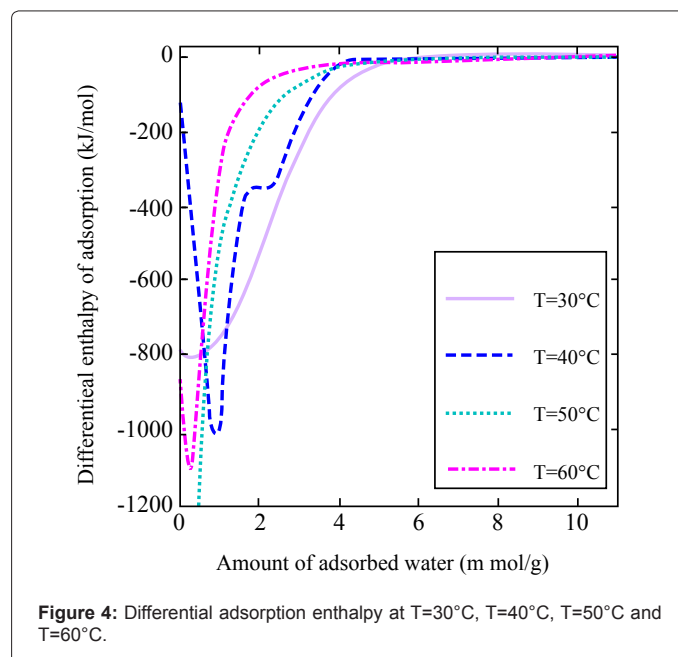
Differential adsorption enthalpy

The differential enthalpy of adsorbed water on raw clay obtained from water adsorption isotherms at different temperatures is shown in figure 4. The variation of differential enthalpy with water content showed that when the amount of water increase the differential enthalpy decrease and the trend seemed to become asymptotic as a water content of 2 mmol/g was approached. The differential enthalpy is negative; this implies that water molecules lose energy upon being transferred from bulk water into the adsorbed state and indicate the exothermic nature of the adsorption process. This also confirms the possibility of physical adsorption as with increase in temperature of system. Above 5mmol/g of raw clay the evolution of the function is very rapid and gets very close to zero.
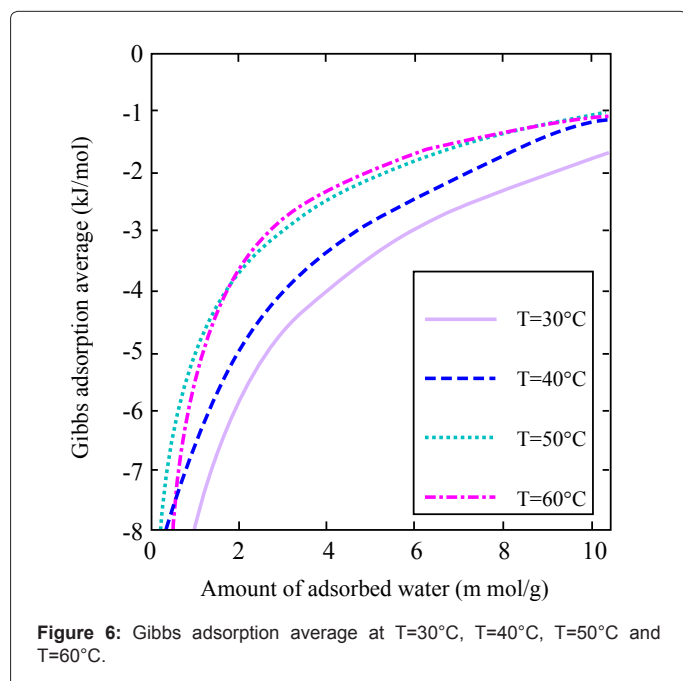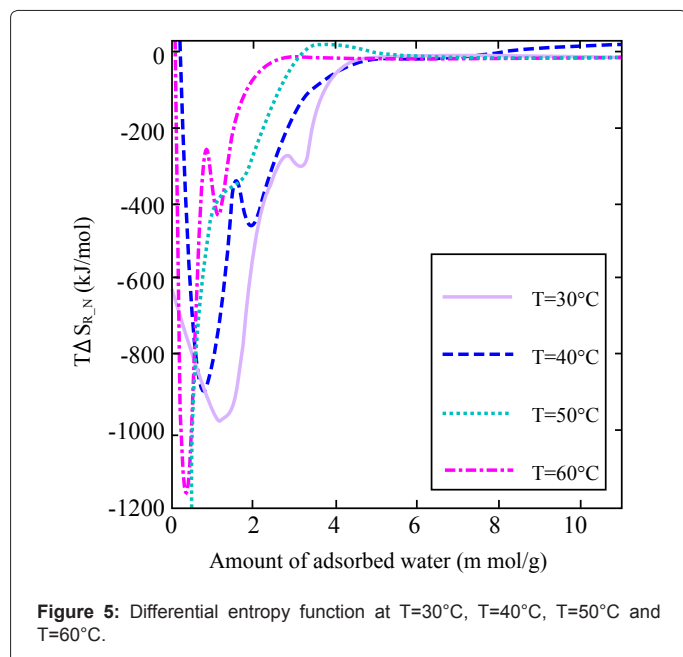
Differential entropy function

The variation of differential entropy function is given in figure 5. This differential entropy decreases continuously as the amount of adsorbed water increases and thereafter, remained constant. Figure 5 showed that the entropy decreases with increasing temperature and which is very close to zero for a water content greater than 5 mmol/g of raw clay. The negative values of differential entropy of adsorption correspond to decrease of freedom of the adsorbed water.

Gibbs adsorption average

Figure 6 shows the variation of Gibbs adsorption average as related to the adsorbed water content at different temperatures. The increase in the amount of water adsorbed on the surface of the clay leads to a decrease in the average free energy of adsorption. While the increase in temperature causes an increase in the enthalpy. For a temperature T=30°C and a water content of 2.8 mmol/g of clay Gibbs adsorption average is about -5 kJ/mol, while for a higher temperature T=60°C and for the same water content the Gibbs adsorption average is about -3 kJ/mol. From the figure 4 we noticed that there is a very rapid evolution of the function that gets very close to zero for water content greater

Figure 4: Differential adsorption enthalpy at T=30°C, T=40°C, T=50°C and T=60°C.

Figure 5: Differential entropy function at T=30°C, T=40°C, T=50°C and T=60°C.

Figure 6: Gibbs adsorption average at T=30°C, T=40°C, T=50°C and T=60°C.

than 2 mmol/g of clay. The negative values of average Gibbs adsorption average indicate that the hydrated raw clay is stable.

Average adsorption enthalpy

The results of this integration, illustrated on the figure 7, show that the average adsorption enthalpy has a shape similar to that of the differential enthalpy of adsorption. Indeed, the increase in the amount of water adsorbed on the surface of the studied adsorbent causes a decrease of the enthalpy and that any increase in temperature causes a decrease of the function. We have also noted a very rapid evolution of the function that gets very close to zero for water content greater than 6 mmol/g of clay.
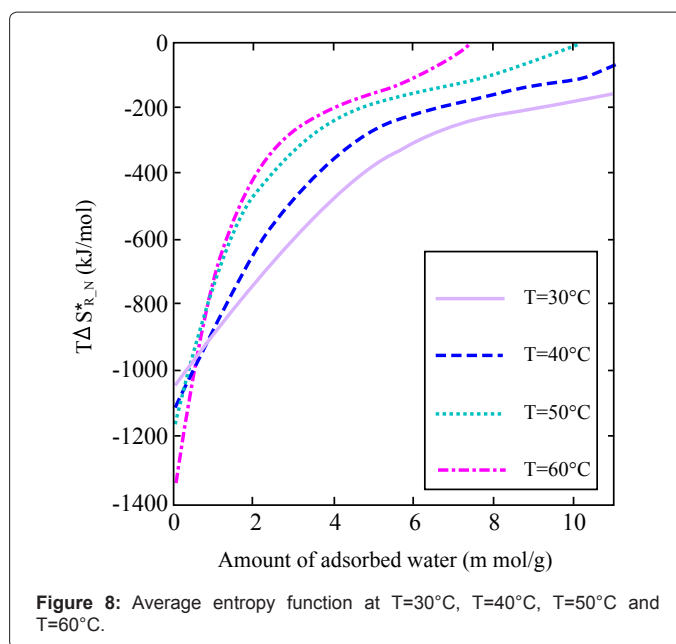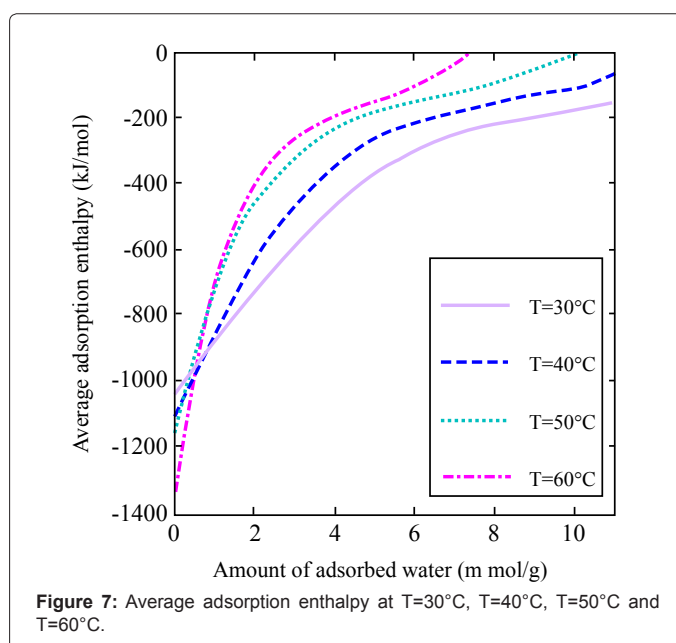
Average entropy function

Figure 8 present the changes of average entropy function. If we consider integrating the change of entropy of adsorbed water, it is clear that the average entropy decreases continuously when the amount of adsorbed water increases. It is also clear that the strong interaction with adsorbed water molecules at a high level of water content resulting in lower entropy.

Coefficients of the polynomial

The coefficients of the regression equation of first order of raw clay at different temperatures are summarized in table 4.

Thermodynamic functions modeled by using the polynomial equation

The determination of thermodynamic functions of water adsorbed

Figure 7: Average adsorption enthalpy at T=30°C, T=40°C, T=50°C and T=60°C.

Figure 8: Average entropy function at T=30°C, T=40°C, T=50°C and T=60°C.

	T=30°C	T=40°C	T=50°C	T=60°C
A_0	-324738.4	-606940.27	685955.22	-969697.62
A_1	-1929226.5	-3159694.2	2861343.1	-4007621.1
A_2	-3921027.8	-4853810.7	2726160.3	-5272665.8
A_3	-2569524.4	565890.18	-4196964.5	-2406942.1
A_4	1127999	7537255.9	-9973877.8	-3117353.5
A_5	1236270.4	4622348.9	-6039924.7	-7950928.6
A_6	-916203.12	-1589693.4	-160087.31	-6996808.8
A_7	-777951.17	-1550488	647780.06	-1996296.7

Table 4: Coefficient of the polynomial equation.

p/p^0	N	$XH2O$	ΔG_M^{ex}	T.E	ΔG_M
0.06	0.52	0.012	60	-163.5	-103.5
0.16	1.96	0.0437	165.3	-452.3	-287
0.2	2.09	0.0464	175.3	-473.6	-298.2
0.25	2.36	0.0521	197.1	-516	-318.9
0.29	2.48	0.0546	207.2	-534.1	-326.9
0.33	2.88	0.0629	242.4	-591.9	-349.5
0.4	3.01	0.0655	254.2	-609.8	-355.6
0.46	3.4	0.0734	290.8	-661.3	-370.5
0.56	3.53	0.076	303.2	-677.7	-374.5
0.61	4.31	0.0913	378.1	-769.9	-391.8
0.7	6.01	0.1228	529.8	-939	-409.2
0.79	7.06	0.1413	611.8	-1026.5	-414.6
0.84	7.58	0.1501	649.9	-1065.9	-416
0.89	8.11	0.1589	687.4	-1103.7	-416.3
0.94	10.3	0.1936	829.7	-1238.4	-408.6

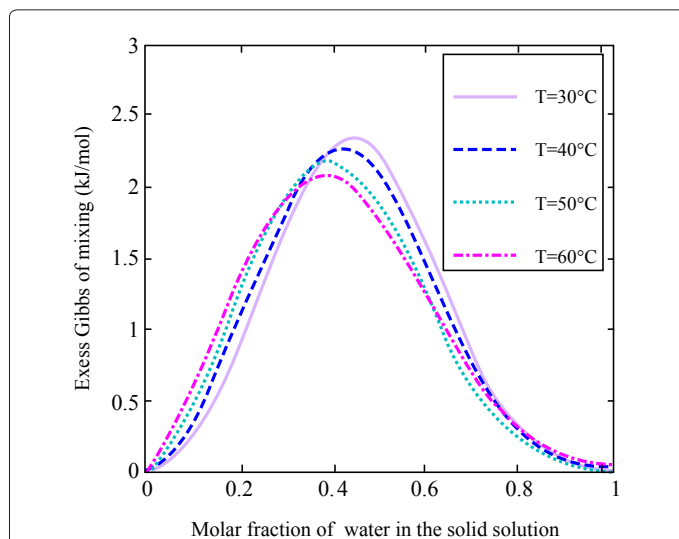**Table 5:** Thermodynamic functions modeled by using the polynomial.

Figure 9: Excess Gibbs of mixing at T=30°C, T=40°C, T=50°C and T=60°C.

on the surface of raw clay is performed using the experimental data of adsorption isotherms obtained at different temperatures. The numerical values of these functions at a temperature T=30°C, are grouped in table 5.

Excess Gibbs energy of mixing: Figure 9 show the variation of the excess Gibbs energy of mixing at a range of temperature going from 30°C to 60°C for the raw clay of El Hamma depending on the composition of adsorbed water. Positive values of the excess Gibbs energy of mixing as shown by the figure 9 indicate a strong interaction between adsorbate/adsorbent and a high stability of the solid solution.

The excess Gibbs energy of mixing is symmetrical and has a maximum for a composition of adsorbed water by 40%, approximately. For a temperature of 50°C, we obtain an excess Gibbs energy of mixing of about 2 kJ/mol at x = 0.4. The figure 9 also shows that changes in the excess free energy of mixing are very close to that of a simple solution.

Entropy Function: Figure 10 show the changes in entropy Function of adsorbed water on El Hamma raw clay surface related to molar fraction of water in the solid solution. The values of the entropy of mixing calculated by means of the relation (12) are all negative as shown in table 5. The entropy of mixing decreases while increasing the temperature, this decrease is due to connections of water molecules to the adsorbent and their rearrangement leads to the appearance of order in their mutual arrangement. Entropy of mixing, as in the case of the excess Gibbs energy of mixing, has a minimum value for a given composition. For a temperature T=50°C, the mixing entropy minimum is -2.3 kJ/mol for El Hamma raw clay.

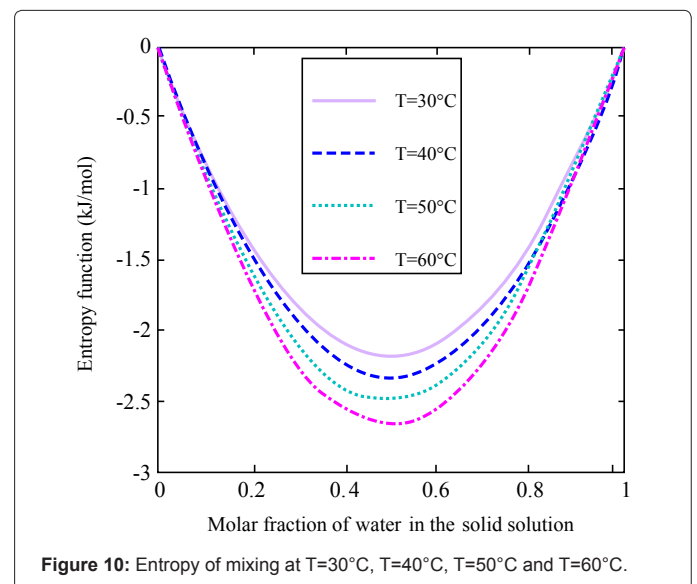**Gibbs energy of mixing:** The results obtained from modeling

Figure 10: Entropy of mixing at T=30°C, T=40°C, T=50°C and T=60°C.
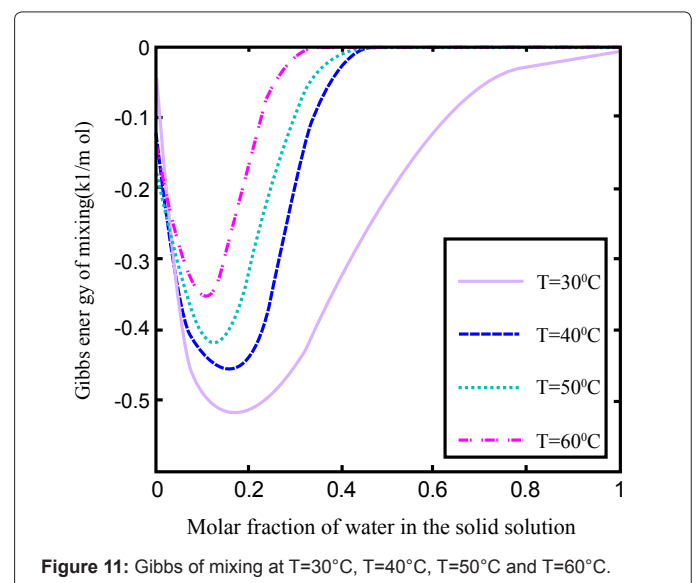

Figure 11: Gibbs of mixing at T=30°C, T=40°C, T=50°C and T=60°C.

equation (14) for El Hamma raw clay are shown in figure 11. We note from the result of modeling of the studied solid solution that he has a negative value of Gibbs energy of mixing which proves the system stability. The free energy of mixing for a given composition of water, increases with temperature indicating a decrease in the stability and the molecules are pressed against each other.

Conclusion

In this study, we conducted a comprehensive analysis of the adsorption isotherms of water vapor adsorbed on the surface of El Hamma raw clay in a range of temperature from 30°C to 60°C. The adsorption isotherm of water vapor on clay corresponds to type II of BDDT classification.

The isosteric enthalpy is maximum for very small values of N (adsorbed water content), which implies that the formation of the first layer of water vapor is more energetic than the upper layers and the water was adsorbed in the most accessible places on the external surface of the solid.

Also, this work is devoted to the calculation of thermodynamic properties of water adsorbed on the surface of the studied adsorbent, namely, the differential and average Gibbs energy, enthalpy and entropy. For low pressures, the differential and average enthalpies are greater than 1000 kJ/mol. To high pressures, the differential and average enthalpies are decreasing functions and tend to the enthalpy of liquid water. The entropy of adsorbed water is lower than that of liquid water which is the fact that the adsorbed molecules are ordered. When the amount of adsorbed water on the solid solution increases the thermodynamics functions are close to those of liquid water, on one hand, on the other hand, we see that the entropy of adsorbed water tends rapidly to that of liquid water, which corresponds to the fact that water molecules are ordered in a state.

The last part was devoted to the thermodynamic modeling of solid solutions. The expression of Saxena allowed us to estimate the excess energy of mixing and enthalpy of mixing of the solid solution under consideration. The modeling results show that the free energy of mixing for a given composition of water increases with temperature indicating a decrease in stability, a strong interaction between water vapor and the adsorbent, the rearrangement of water molecules leads to the appearance of order in their arrangement and the increase in temperature leads to a decrease in the stability of solid solutions.

References

1. Srasra E, Kebir AN, Ayedi F, Bergaya F, Van DH (1988) Mineralogical identification of a bentonite clay deposit located near gabes (Tunisie). Journal de la société chimique de tunisie 2: 37-45.

2. Ben Zina M (1987) Mineralogical characterization, physicochemical properties and application of the clay deposit Haidoudi, PhD Thesis, Faculty of Science of Tunis.

3. Bagané M, Guiza S (2000) Elimination des colorants des effluents de l'industrie textile par adsorption. Ann Chim fr 3: 615-625.

4. Weaver CE (1989) Clays, Muds and Shales Developments in sedimentology. Elsevier.

5. Gannouni A, Bagané M, Bellagi A (1994) Sulfur dioxide adsorption isotherms on activated clay. Annale de chimie 19: 27-37.

6. Bagané M, Gannouni A (1995) Study of water vapor adsorption at high temperatures on activated alumina. Annale de chimie 20: 72-80.

7. Mc Bain JW, Bakr AM (1926) A new sorption balance. J Am Chem Soc 48: 690-695.

8. Dreisbach F, Staudt R, Keller JU (1999) High pressure adsorption data of methane, nitrogen, carbon dioxide and their binary and ternary mixtures on activated carbon. Adsorption 5: 215-22.

9. Dreisbach F, Lösch HW (2000) Magnetic suspension balance for simultaneous measurement of a sample and the density of the measuring fluid. Journal of Thermal Analysis and Calorimetry 62: 515-521.

10. Dreisbach F, Lösch HW, Harting P (2002) Highest Pressure Adsorption Equilibria Data: Measurement with Magnetic Suspension Balance and Analysis with a New Adsorbent/Adsorbate-Volume. Adsorption 8: 95-109.

11. Tardy Y, Fritz B (1980) An ideal solid solution model for calculating solubility of clay minerals. Clay minerals 16: 361-373.

12. Ganguly J, Saxena SK (1987) Mixtures and mineral reactions. Springer-Verlag 291.

13. Glynn PD, Reardon EJ (1990) Solid-solution aqueous-solution equilibria: thermodynamic theory and representation. American Journal of Science 290: 164-201.

14. Geiger CA (2002) Solid solution in Silicate and Oxide systems. Mineralogy Magazine 66: 1107-1108.

15. Ganguly J (2001) Thermodynamic modeling of solid solution, EMU Notes in Mineralogy 3: 37-69.

16. Powell R (1987) Darken's quadratic formulism and the thermodynamics of minerals. American Mineralogist 72: 1-11.

17. Kalfat (1995) Adsorption isotherms of water vapor on natural clay, Final Project study. Ecole National d'Ingénieur de Gabès.