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Calculation Values of potential Stickiness (S*) and Apparent Activation Energy (AAE) from Adsorption of Some Aromatic Carboxylic Acids on the Surface of a New Adsorbent Substance

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Abstract:
This study includes calculation of the potential stickiness (S^*) and apparent activation energy (AAE) by the adsorption process of some aromatic carboxylic acids using sand (clay) as a new adsorbent material. This clay was collected from dust storms coming to the city of Mosul. The obtained results showed that physical adsorption which is achieved by applying the modified Arrhenius equation through the values of (S *) and (AAE) which have low values and bear a negative charge is preferable. Adsorption process occurs in two-step mechanism. The effect of the concentration of the acidic solution, temperature and the substituted groups SO_3, NO_2, OH, NH_2 on the aromatic ring) was studied to clarify the nature of the association between organic carboxylic acid anions and inorganic metal oxides to form a complex surface model. The study concluded that the values of (S *) for all acids were less than one and they were more than the value of zero. Also, the values of (AAE) gave an indication that the adsorption process is exothermic and spontaneous. The presence of water molecules and (H^+) ions in solution is very important to change the nature of the clay surface.

Keyword: Potential stickiness, apparent activation energy, aromatic carboxylic acids, new adsorbent material.

حساب قيم احتمالية الالتصاق (S*) وطاقة التنشيط الظاهرية (AAE) من امتزاز بعض الحوامض الكربوكسيلية الاروماتية على سطح مادة مازه جديدة

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قسم الكيمياء, كلية التربية للعلوم الصرفة, جامعة الموصل, الموصل, العراق

الخلاصة

يتضمن البحث حساب جهد احتمالية الالتصاق (S*) وطاقة التنشيط الظاهرية(AAE) بعملية الامتزاز لبعض الحوامض العضوية الكربوكسيلية الاروماتية باستعمال رمل (طين) تم تجميعيه من العواصف الترابية القادمة الى مدينة الموصل كمادة مازه جديدة . النتائج التي تم الحصول عليها أظهرت حصول امتزاز فيزيائي وهو المفضل وذلك بتطبيق معادلة ارهينوس المطورة من خلال قيم كل من (S*) و (AAE) والتي تمتلك قيمة قليلة وتحمل شحنة سالبة، تحدث عملية الامتزاز بميكانيكية تتألف من خطوتين ، وتم دراسة تأثير التركيز ودرجة الحرارة فضلا عن تأثير المجاميع المعوضة على الحلقة الاورماتية على طبيعة الارتباط بين انيونات الحامض

الكربوكسيلي العضوي والاكاسيد الفلزية اللاعضوية لتكوين نموذج معقد السطح وتوصلت هذه الدراسة الى ان قيم (S^*) لكل الحوامض هي اقل من الواحد واكثر من قيمة الصفر كما ان قيم (AAE) أعطت مؤشرا على ان عملية امتزاز باعثة للحرارة وتلقائية ان وجود جزيئات الماء وايونات (H^+) مهم جدا لتغير طبيعة سطح الرمل .

الكلمات المفتاحية: احتمالية الالتصاق، طاقة التنشيط الظاهرية، حوامض كربوكسيلية اروماتية، مادة مازه جديدة

Introduction:

Adsorption is an effective and important method to remove pollution. It is simple and low-cost [1][2]. The substituted benzoic acids (5SSA, ONBA, OABA) are used in chemical industry, these acids are considered harmful substances for humans [3] [4] [5]. As an adsorbent material, Clay, consists of poly metal oxides from a rocky source [6] and different inorganic materials [7]. Metal oxides on the clay surface contain negative polar charges [8] as active sites that attract positive ions by absorbing them through physical forces. This type of attraction is called physical adsorption, while the chemical absorption occurs when the surface contains unsaturated electrons. Knowledge of adsorption mechanism is important for designing physical type of adsorption systems, through which absorbent material can be recovered and the process accomplished in an easy and inexpensive way. The (AAE) values represent the desired degree of the optimum temperature to achieve the complete adsorption process. Whether it occurs spontaneously or not and whether the adsorption process is endothermic or exothermic, the positive or negative values of (AAE) give a good description of the thermodynamic condition for the adsorption process.

Materials and Methods :

1- The chemicals were used without further purification and they were supplied by Fluka and BDH companies.

2- The new clay was used as an adsorbent material. This clay was collected (using clean and dry plastic containers) from dust storms that hit the city of Mosul. The clay has been sifted (filtered out) using a sieve (75) micrometer and the surface area was (3434) cm^2/gm. It was measured using the "plaine device" at the Technological Institute in Mosul. The clay components (listed in Table 1) were measured using X-rays Appearance-Type (pan analytical 7602 EA, Almelo) at Badush Cement Factory.

Table 1. The components of clay

pH	8.5
CaO	37.36%
SiO_2	19.71%
AL_2O_3	5.91%
MgO	3.47%
Fe_2O_3	1.89%
SO_3	0.48%

3- Preparation of solutions:

a- Solutions of three acids (5SSA, ONBA, OABA) at different concentrations using a mixture solvent (5% absolute ethanol and 95% distilled water) have been prepared.

b- Standard solution of (0.1), (0.01) M sodium hydroxide by titration with (potassium hydrogen phthalate) using (phenolphthalein) as indicator has been prepared.

4- Study the adsorption process using batch method.
5- A programmed water bath equipped with a vibrator at speed of 100 cycle/ min was used.
6- An equal amount of adsorbent in the adsorption process for all concentrations was used.
7-The optimum conditions for adsorption were as follows:
A-The weight of clay used =0.06 gm.
B-Concentration of acids =5x10^{-3} molar
C-The favorite pH = natural pH for each acid
D-Contact time for each acid with percentage of adsorption is shown in table 2.

Table (2). Contact time and percentage of adsorption for acids on clay surface at 25 C°

Acid	Contact time (min)	% Adsorption
5SSA	40	76
ONBA	30	92
OABA	40	74

E- The adsorption process was studied at temperature ranging from (20-60) C° to obtain values of (S^*).
F- The concentration of acid remaining in solution after the adsorption was calculated using spectrophotometric method.
G- The amount of ions covered on the surface of the sorbent material was calculated at each concentration using different temperatures (20-60) ° C.
H- The modified Arrhenius equation [9] that was applied, can be written as follows:

$S^* = (1 - \theta)\, e^{-\frac{Ea}{RT}}$ (modified Arrhenius equation)
$\text{Ln}\,(1 - \theta) = \ln S^* - \frac{Ea}{RT}$

When draw Ln (1-θ) at (x) axis and $\frac{1}{T}$ at (y) axis gives intercept (Ln S*) while slope equal $\frac{-Ea}{R}$ which gives (AAE).
8- The instruments:
a- Vibratory water path type (julabo sw23).
b- Electric oven type (memmert).
c- Double-beam spectrophotometer (schimaduz) model UV-1800.
d- The surface area of the clay was measured using (a plain) device and the amount of surface area was (3434) cm^2 / gm .

Results and Discussion:

The modified Arrhenius equation (MAE) [9] depends on the amount of ions covering the surface at any concentration by using different temperatures. When experimental adsorption results are applied to (MAE), we obtain a value of (S *) through which the type of chemical or physical adsorption prevails. In addition, the value of (AAE) provides a qualitative description of the thermodynamic state of the adsorption process.

The value of (S *), which represents the potential stickiness to the surface, is the preferred (adsorbed / adsorbent) system function of the range (o <s * <1) for the absorption process. This value depends on temperature and concentration. The values of (S *) can be calculated from the modified Arrhenius equation via the experimental results used.
If S* >1, it means that the adsorbent substance is non-sticking on the adsorbed substance.
If S* =1, it means that the liner relationship of stickiness between the adsorbed and adsorbent is predominated for a mixture of physical and chemical adsorption.
S*=0 stickiness has occurred on adsorbed material and chemical absorption is predominant.
If 0 < S , this represents the preferred stickiness of the adsorbent material on the clay, and the physical absorption is predominant.

In this study, the positive and negative values of (AAE) do not represent the areal activation energy, but rather give a description of the thermodynamic state of the adsorption process, since the acid ions prefer adsorption at low temperatures and the adsorption process is exothermic by nature .The low negative values of (AAE) give the conclusion that the adsorption process is a controlled diffusion process. The best value for (S^*) is shown when it is less than one. This indicates that the physical adsorption of ions occurs on the surface. In this case the adsorbent substance can be retrieved and used again, and this is economically important.

Tables (3 – 5) Values of (S*) and (AAE) for (5SSA),(ONBA), (OABA) at different concentrations on the clay surface
Table3 (5SSA)

Table 3 (5SSA)

Conc(M)	S*	AAE KJ/mole	R^2
0.005	142×10^{-7}	-21.100	0.9698
0.007	0.1474	-2.646	0.9739
0.009	0.1560	-1.472	0.9529
0.011	0.3109	-1.168	0.9824
0.013	0.9078	-1.085	0.9979

Table 4(ONBA)

Conc(M)	S*	AAE(Kj/mole)	R_2
0.005	611×10^{-9}	-29.488	0.97
0.007	0.0480	-4.568	0.93
0.009	0.1590	-2.547	0.98
0.011	0.3078	-1.397	0.99
0.013	0.4043	-0.961	0.99

Table 5(OABA)

Conc(M)	S*	AAE(Kj/mole)	R^2
0.005	0.0125	-7.423	0.99
0.007	0.1460	-2.749	0.99
0.009	0.2878	-1.654	0.99
0.011	0.3905	-1.192	0.99
0.013	0.4885	-0.835	0.99

The results in tables (3-5) which refer to acids (5SSA,ONBA,BABA) at different concentrations. The used temperatures were ranged from (20-60)°C at each concentration. Depending on the obtained results, the following conclusions can be reached:

1. The predominance of the physical adsorption in the adsorption process and this is preferred for the ease of recovery of the absorbent material [9][10].

2. The increase in the concentration of the acid solution increases the values of (S*). This means that the conversion of the physical adsorption into a mixture of physical and chemical adsorption is at the highest concentration when the value of (S*) is one. Diluting the acidic concentration makes the value of (S*) very low because the ions have free movement within the solution (they easy move to the surface of the absorbent material (clay) as well as, the availability of the active sites on it which means that there is no competition between ions to adsorption on the surface. Thus the chemical adsorption becomes predominant.

3- (AAE) values are negative and low, and they decrease as the concentration of the acid solution is increased by converting it from the highest negative values to the negative values that are close to the zero values. These results indicate that the adsorption process in the case of the acidic dilute solution (0.005) M prefers low temperature and ultimately it will be exothermic. This is because the ionic, molecular reaction and interferences are decreased in the case of the dilute acidic solution, then the adsorption process occurs spontaneously. Whereas in a concentrated acid solution (0.013) M , these interferences are increased, which leads to a decrease in the negative values of (AAE). This indicates the need for the adsorption system to have a low energy to complete the adsorption process, so that it turns from high spontaneously to low one. In addition, it converts from an exothermic to an endothermic process [9][10][11][12].

4- In order to study the effect of the substituent group (for the acids 5SSA, ONBA, OABA) on the values of (S *) and (AAE) at the optimal concentration, the nitro group (NO_2 electron withdrawing group) in the (ONBA) causes a distribution of the negative charge, which leads to increase both the acid anion stability and the ionization process [13]. Also it causes a significant decrease in the value of (S *) in the acid dilute solution (0.005) M and it has a spontaneous rise in adsorption on the surface through a high negative value of (AAE). While at a high concentration (0.013) M the value of (S *) is the preferred value for adsorption process. The amino group (NH_2) in (OABA) localize the negative charge that decreases the stability of the acid anion and the ionization causing an increase in value of

(S^*) at dilute and concentrated acid solution to give a mixture of physical and chemical adsorption. The (AAE) value for (OABA) showed that the adsorption process of (OABA) is less spontaneous than (ONBA). At a high concentration, both acids (OABA) and (ONBA) have a preferred value of (S*), while (5SSA) acid contains two important groups, the hydroxyl group in the ortho position (which can form an intra-hydrogen bond with a carboxyl group that increases the stability of the negative anion), and (SO_3) group as it contains oxygen atoms that can be attached to the clay surface through this position. This bonding, which is formed by physical adsorption from more than one position of this acid, leads to more adsorption efficiency. Since there is a hydroxyl group in the acid, the value of (S*) at the lowest concentration is lower than the acid (ONBA), but is closed to it. So this acid also approaches chemical adsorption on the surface with low spontaneous adsorption of the acid (ONBA) through the value of (AAE), but it is more spontaneous than the acid (OABA) at a high concentration. It is closed to a mixture of physical and chemical adsorption; the spontaneity is greatly reduced, and it is close to the positive value. Thus, one can conclude that the effect of (S *) values is less than the effect of substituted groups according to the following sequence:

Acids	OABA > 5SSA > ONBA
S*	$0.0125 > 142\times10^{-7} > 611\times10^{-9}$
AAE	$-7.423 > -21.10 > -29.48$
Ka	$1.6\times10^{-5} > 1.12\times10^{-5} > 670\times10^{-5}$

5- A- In general, the adsorption process of the acids under study is inherently exothermic and converts with increasing concentration into an endothermic.

B- To clarify the effect of the adsorption system components on the mechanism and type of adsorption (physical or chemical) which consequently affecting the values of (S *) and (AAE), it can be illustrated as follows:

The components of the adsorption system are three: the liquid phase that includes both acid molecules, ions, and the solid phase, which represents the adsorbent substance (clay). In the liquid phase, there are positive and negative ions of the acid as well as water that possesses polarity. As for the solid phase represented by the clay, it contains a number of metal oxides that carry negative charges on the oxygen atoms to which they belong and are considered polarization sites for positive charges, especially aluminum oxide , which is more responsive to polarized acids compared to other oxides [13][14]. The main effect on the adsorption system is water as a solvent that contains acid ions of positive and negative charges; when adding the absorbent substance to the solution with the negative charge it carries, it mixes easily with water. The first step of the adsorption process will begin by transferring the positive hydrogen ions with water molecules to the clay surface to convert it from a negative polarized surface to a positive polarized surface. The negative anions can move and transfer to the surface and adsorb onto it as a second step in the adsorption process [15][16][17]. The concentration of the acid solution and the nature of substituted group affect this process.

These steps can be represented as follows:

Surface of metal oxides = $\mathbf{M}\text{-}O^{-}$

$\equiv M\text{-}O^{-} + H_2O \rightarrow \equiv M\text{-}OH$ --------1 **(First step)**

$\equiv M\text{-}OH + H^{+} \rightarrow \equiv M\text{-}OH_2{}^{+}$ -------2

The presence of acid anions (RL^{-}) for carboxylic group after ionization gives the second step of adsorption:

$\equiv M\text{-}OH_2^{+} + HL^{-} \rightarrow \equiv M\text{-}OH_2{}^{+}$ ------ ^{-}LR -----3 (second step)

Where RL^{-} = anion

The second effect of water as a solvent is the interference with acid ions and its molecules by forming hydrogen bonds, especially in concentrated solution [12]. The adsorption steps from solution to surface are important in studying the interaction between organic molecules and the solid surface (clay) as an inorganic surface [17].

C- Studying the effect of the acidic function shows that the acidity function at a concentration of (0.005) M for (ONBA) is less than (5SSA) with a small value ($\Delta pH = 0.04$), as the it is illustrated in table (6) . For both acids, there are (H+) ions in their solutions that contribute with water molecules in the first step of the adsorption process interacting with the oxygen atoms of metal oxides that carry the most negative polar charge on the clay surface. This leads to converting the clay surface into a positive surface charge; so an increase in the acidic function occurs after adsorption. Therefore, there is an increase in the acidic function after adsorption due to the transfer of hydrogen ions from the solution to the clay surface. The value of (ΔpH) represents the difference in acidity function before and after adsorption . The high value for (ΔpH) refers to a high transition for (H^{+}) ions from solution to surface of the clay . This transition of hydrogen ions affects the first step of adsorption process by increasing the positive charges on the surface of the clay which in turn affect the number of acidic anions which move from solution to surface of the clay in the second step of adsorption process . The (ΔpH)values of (5SSA) and (ONBA) acids at dilute solution (0.005)M are larger than (ΔpH) for (OABA) acid; these values affect the (S^{*}) values of acids (5SSA) and (ONBA) which have negative values that are less than zero and high negative values for (AAE). For these reasons the efficiency of adsorption is very high. All these results indicate a high transition of hydrogen ions and anions of acids from solution to surface of clay. The results also indicate that the values (S^{*}) of (OABA) were more than zero and the values of (AAE) were low negative. For this reason the efficiency of adsorption for (OABA) acid is less than acids (5SSA) and (ONBA). This means that there is a low transition of hydrogen ions and anions of this acid (OABA) from solution to surface of clay. These results are listed in table (3-5) and table(6).

It becomes obvious that the acidic function of the solution plays an important role in the values of (S*) and (AAE). As for the highest concentration in (0.013)M, the acidic function of the solution will decrease, which means an increase in hydrogen ions. However, this increase does not lead to an increase in the adsorption efficiency but increases the value of (S*). Converting the value of (AAE) from a high negative value to a low negative one approaching the positive value of (zero) is due to that the adsorption system needs more energy to overcome the ionic interference in the solution and allow a limited number of hydrogen ions and anions from the acid molecule to transfer to the clay surface. After the adsorption process, the acidic function increased by low values. This means that the acid function, before and after absorption (ΔpH), varies slightly, due to the low number of hydrogen ions involved in the first step of the adsorption process, where the positive site is on the surface. For this reason, the transfer of anions to the surface will decrease, and therefore the adsorption efficiency will decrease, for example the adsorption efficiency was (94.72%) at (0.005) M while it was (49.54%) at (0.013) M.

The previous results have indicated that the concentration of the acid solution affects the values of (S*) and (AAE) because it affects the values of the acid function. The substituted groups (NH_2, NO_2 , OH , SO_3) on aromatic ring of carboxylic acids have a little effects on the values of (S^*) and (AAE) at a high concentration of acid solution .For the purpose of comparison, the effect of substituted groups in the acids under study as well as the effect of the groups substituted in acids (5SSA) and(ONBA) is more than the effect of substituted group in acid (OABA). From the above, it can be said that the effect of the concentration of the acidic solution on the (S^*) and (AAE) values is greater compared to the effect of the substituted groups in the carboxylic acids at high concentration.

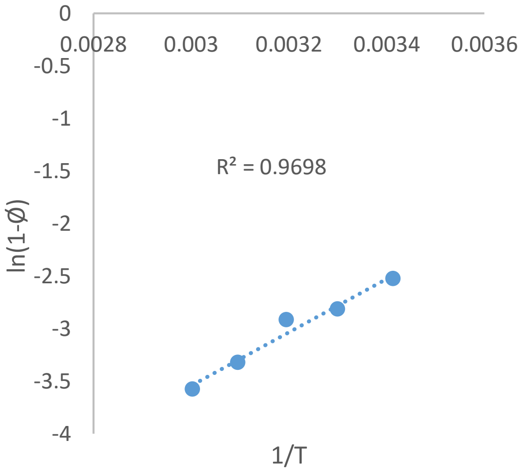
Table (6) Acidity functions before and after adsorption for acids at (0.005) M and 25°C

Acid	pH before adsorption	pH after adsorption	Δ pH	% adsorption
5SSA	2.81	4.58	1.77	94
ONBA	2.77	4.45	1.68	92
OABA	3.60	5.17	1.57	76

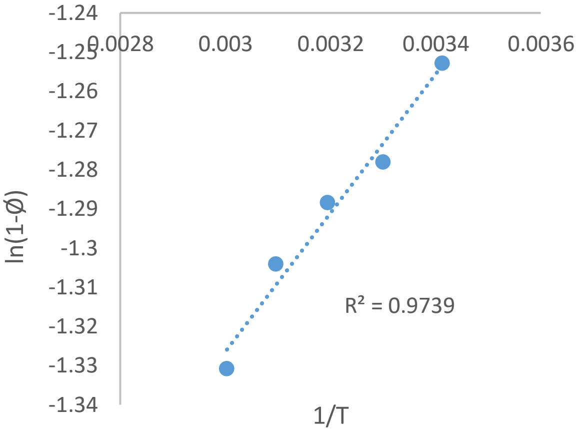
d-In this study we tried to choose a simple way to describe the adsorption mechanism and its steps using the developed Arrhenius equation.

Figures (1-3) represent the relation between Ln (1 – θ) and 1 / T for (5SSA), (ONBA) and (OABA) at different concentrations .

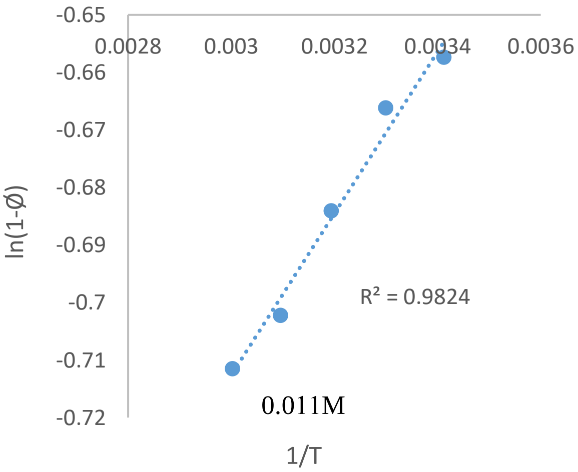
Figure (1) is for (5SSA) at different concentrations:



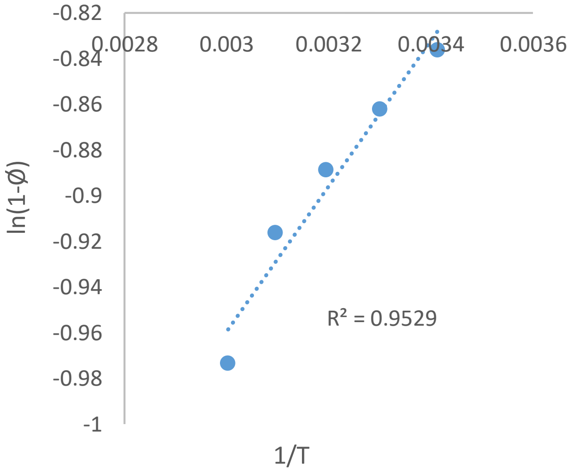
0.005M

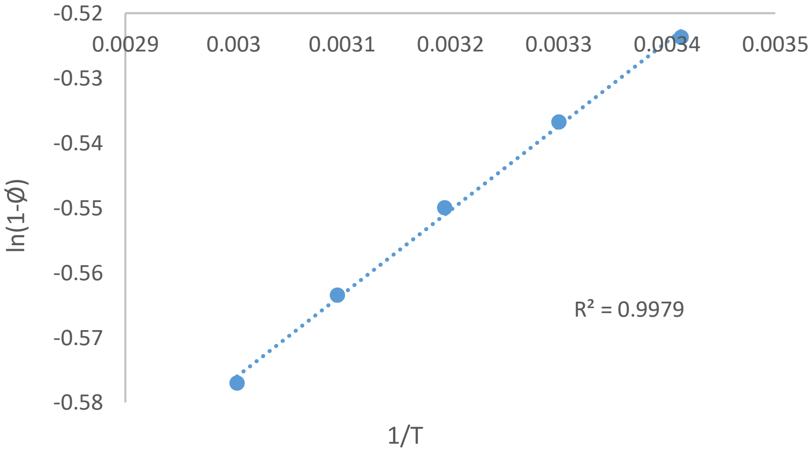


0.007M



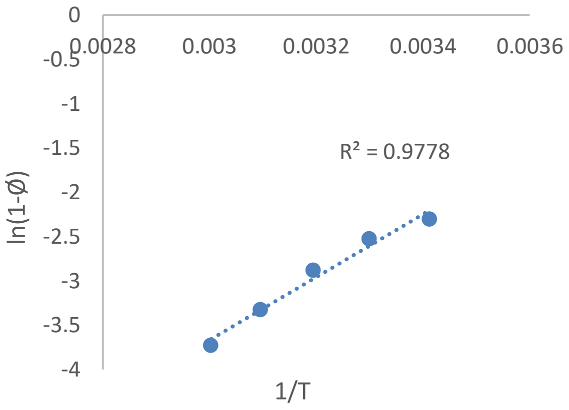
0.011M



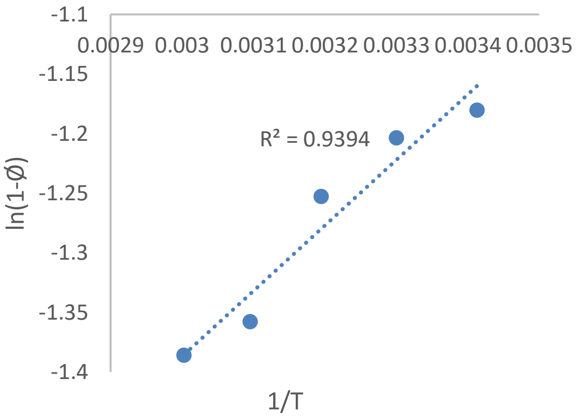


0.013M

Figure (2) is for ONBA at different concentration:



0.005M



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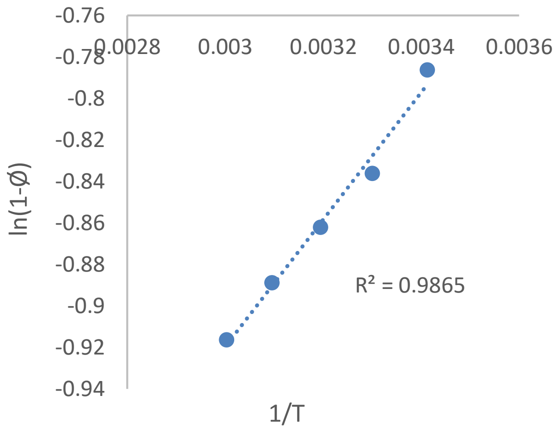
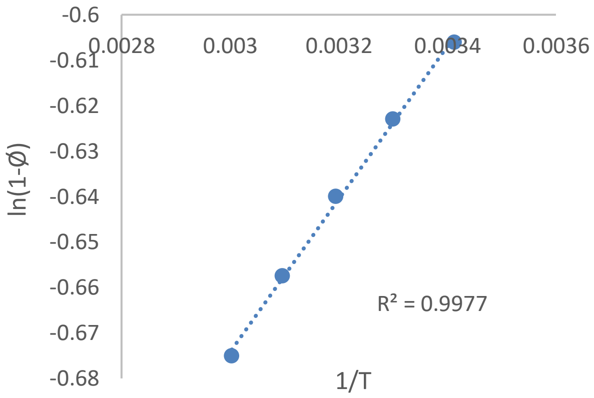
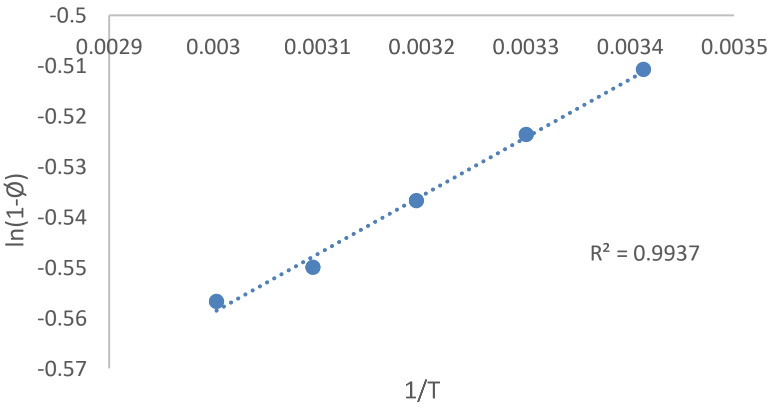


0.009M

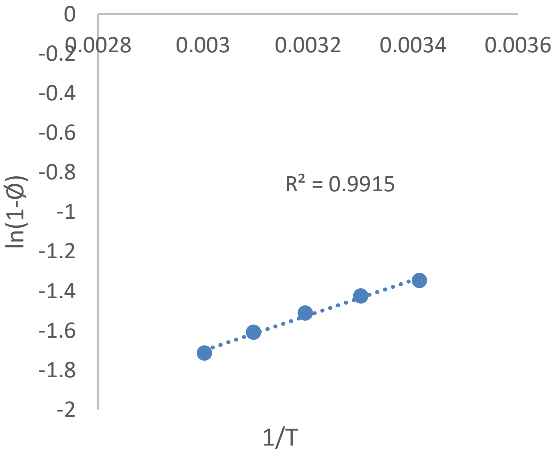


0.011M

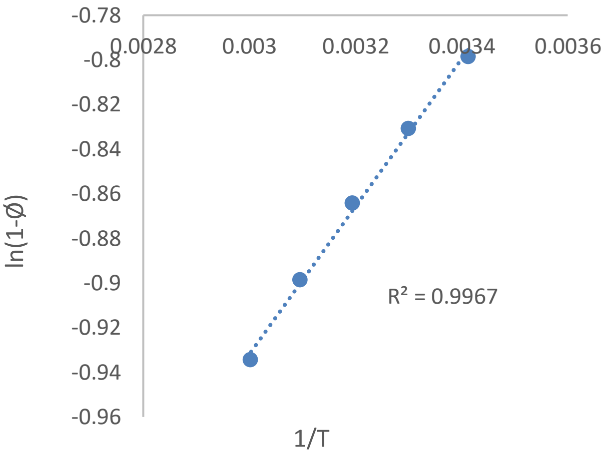


0.013M

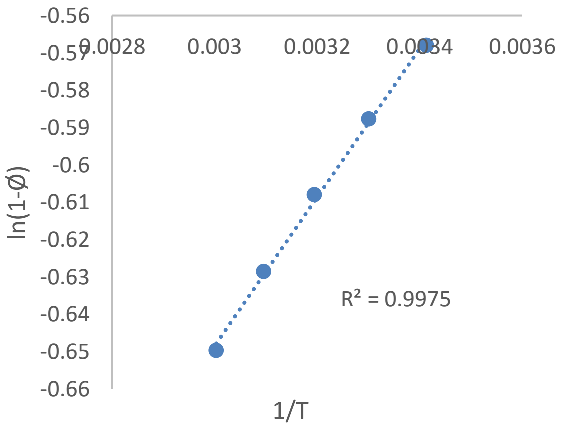
Figure (3) is for OABA at different concentration :



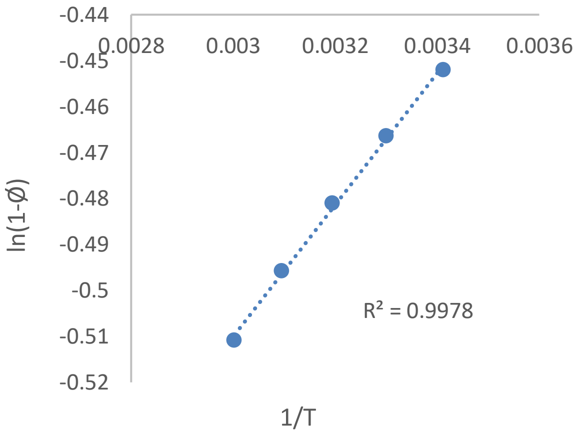
0.005 M



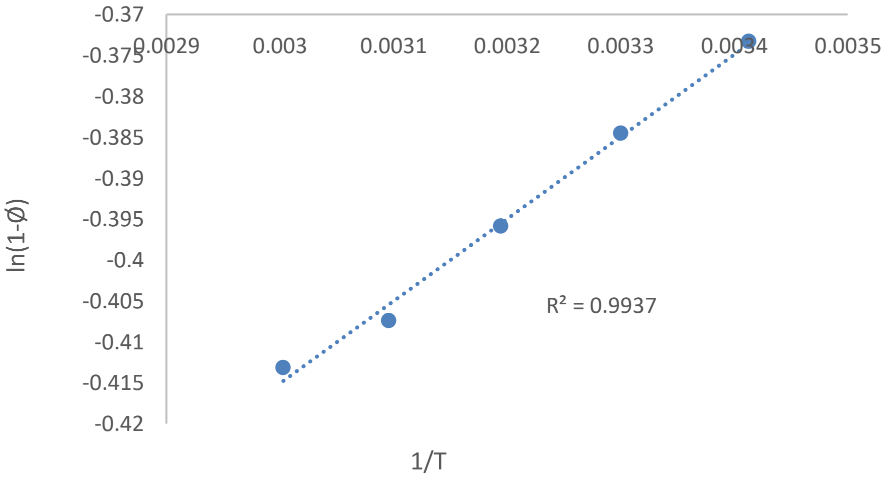
0.007 M



0.009M



0.011M

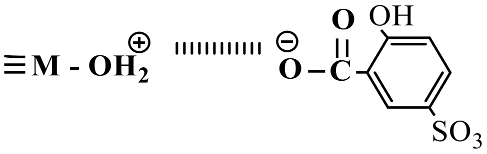


0.013M

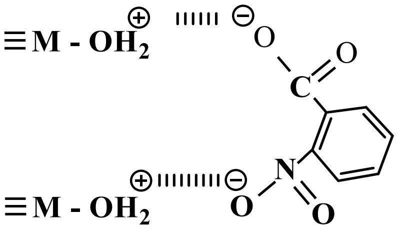
The following shapes of bindings between acid anions of carboxylic acid and surface of the clay clarify the effect of the structural formula of the acid and the effect of the presence of the substituted groups (NH_2,OH,NO_2,SO_3) on the adsorption mechanism. These bindings give different models of surface complexes:

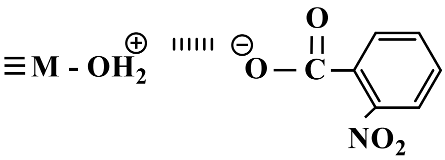
The shapes of the surface complex models (scm) formation for acids and clay.

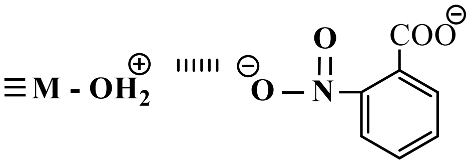
1 – 5SSA: The main shape of (scm) is produced from a physical adsorption as follows :



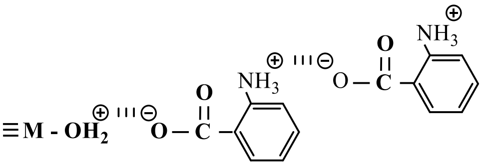
2- ONBA: This acid has a (scm) with two-polarity positions.

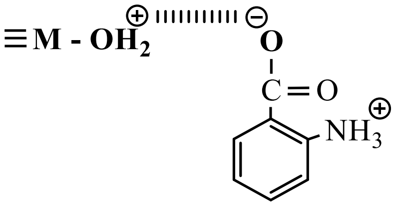




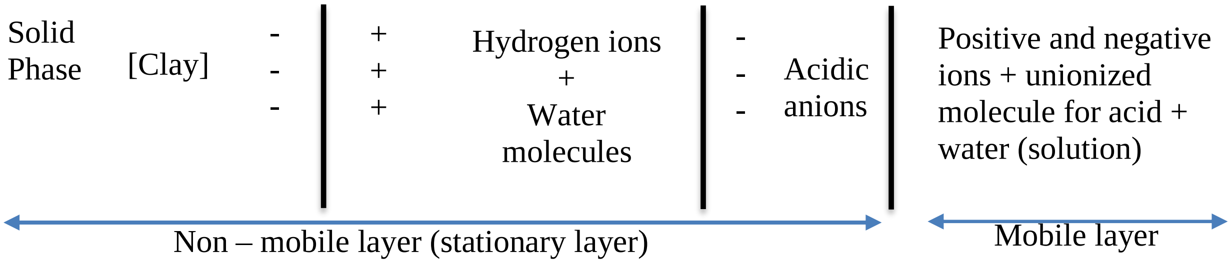


3- OABA: this acid contains two groups after ionization in solution (acidic) and (basic) (Dipole) with the following mechanism:





Finally, the arrangement of the adsorbed ions from the clay surface as a solid phase to the solution as a liquid phase as follows:



Conclusion:

The modified Arrhenius equation is useful for obtaining (S *) values which represent the surface potential stickiness. These values are preferred within (0 <S <1), and can describe the type of adsorption dominant in the adsorption process (physical, chemical or a mixture of both).

The value of (AAE) represents the thermodynamic condition of the adsorption process. It can be spontaneous or non-spontaneous, endothermic or exothermic system through the positive or negative value of (AAE). Increasing the concentration of the acid solution increases the values of (S *) and (AAE). And the substituted groups in the acidic molecule affect the values of (S *).

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