

Effect of Substituents Type on the Adsorption of Aromatic Carboxylic Acids and their Relation to Concentration, Temperature and pH

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ABSTRACT

The study involved investigation of the adsorption of aromatic carboxylic acids carrying various substituents such as OH, NH₂ and SH. The effects of concentration, temperature and pH were induced. The results indicated that increasing the temperature from 15 to 30 °C reduces the adsorption ratio, while dilution of carboxylic acid solution to a little value showed high adsorptivity. This point is of a valuable interest because most of carboxylic acids as pollutants present in a minute amounts.

Effect of pH showed that the natural pH is the best condition for the removal which is arreptable for the treatment of industrial water. According to the literature we assumed that after one hour of extraction the system will be in equilibrium. Therefore, from this point we determined the thermodynamic functions for each system under investigation. The study revealed that the hydrogen bond present in the system and other attraction forces with the resonance have great effect on the adsorption.

–SH –NH₂ –OH

° 30-15

INTRODUCTION

Adsorption can be defined as the collection of substance onto the surface of adsorbent solids or, a removal process where certain particles are bound to an adsorbent particle surface by chemical or physical attraction (Robert, 1996). Adsorption is often used as a method for treating aqueous solution to remove dissolved contaminating organic compounds. Organics are of a great concern in water treatment because they react with many disinfectants, especially chlorine, and cause the formation of disinfection -by- products (DBP's) (Robert, 1998). These DBP's are often carcinogenic and highly toxic and undesirable. Therefore, the removal of such organics is very important task. Various sorbents were used for this purpose. The most conventional adsorption system being activated carbon (McKay, 1982). Adsorption by activated carbon is proved to be a desirable technology to remove dissolved organics from waste water flows that contains a significant quantities of industrial waste (EPA, 2000). The water industry used activated carbon in several forms, typically powdered and granular, to deal with a variety of undesirable aspects in raw water. Granular activated carbon adsorption has been used successfully for the advanced treatment of municipal and industrial waste water. This type of carbon is used to adsorb the relatively small quantities of soluble organics, and inorganics such as nitrogen, sulfides, and heavy metals remaining in waste water following biological or physio-chemical treatments (EPA, 2000).

The reason for the use of activated carbon in the removal of dissolved substances from water by adsorption process is that it is an effective adsorbent due to its large number of pores. These provide a large surface area to the size of the actual carbon particle and its visible exterior surface (Robert, 1996). Adsorption efficiency decreases over time and eventually activated carbon will need to be replaced or reactivated (Robert, 1996). It is therefore, affected by temperature and concentration. The extent of adsorption decreases with the increase of temperature. The variation of the extent of adsorption with concentration is given by empirical isotherms (Kikic *et al.*, 1996). Isotherms are relations used to predict how much solute can be adsorped by activated carbon. The most three known isotherms are those suggested by Freundlich, Langmuir and Linear. In environmental engineering and specifically drinking water treatment was conducted by the application of the most commonly used Frenldlich isotherm (, Daniel, 1966).

This isotherm is represented by the equation:

$$\chi / m = K C^{1/n}$$

Where χ and m are masses of substance adsorbed and adsorbent respectively.

C; is the equilibrium concentration of adsorbed substance in the solution, K and n are empirical constants which depend on the nature of the adsorbate, adsorbent and temperature. Taking logarithms of this equation gives:

$$\text{Log } \chi / m = \text{log } K + 1/n \text{ log } C$$

This equation implies that a plot of $\text{log } (\chi/m)$ versus $\text{log } C$ should be a straight line with a slope of $1/n$ and intercept of $\text{log } K$.

A theoretical description of recently published paracetamol adsorption data on a series of non-modified commercial activated carbon is presented by Terzyk (Terzyk, 2003). In this study, nineteen of the most wide spread adsorption isotherm equations were analysed, and the resulting maximum adsorption values were compared on the basis of the results obtained. The importance of the functional groups in the adsorption of paracetamol were emphasized. Nouri *et al.* (Nouri *et al.*, 2003), studied the adsorption of three types of aromatic hydrocarbons having different functional groups on untreated carbon. The study involved effect of pH and concentration on the nature of adsorption. It showed that the maximum adsorption is varied according to the size and nature of functional group, on the other hand, the adsorption on such carbon was found to be heterogeneous to a certain extent. Adsorption on activated carbon also appeared to be a good alternative for the removal of dyes in the effluents of the textile industries (Nawar and Doma, 1989; Waters, 1979). The decolorization of prepared aqueous solutions of three reactive azodyes used in textile processing by adsorption on different types of powdered activated carbon was investigated, and the colour removal efficiency and equilibrium adsorption isotherms for these dyes were studied using five commercial powdered activated carbons (Pala *et al.*, 2003).

Adsorption and removal of five commercial dyes were studied in aqueous suspensions with a sandy clay soil of low organic matter content (Al-Banis *et al.*, 2000). The experiments were carried out at equilibrium conditions for concentrations of dyes between 5 and 60 mg.L^{-1} . The logarithmic form of Freundlich equation gave a high linearity. The removal of dyes from adsorption on column decrease with the increase of the solution concentration showing the process to be highly dependent on concentration of the solution. In another study (Farere *et al.*, 1998), the adsorption of some anionic dyes on a certain type of polymer was investigated, employing the Langmuir isotherm. The results showed that the adsorption capacity is dependent on pH. In acidic medium the amino groups of the polymer are protonated and the polymer chain positively charged, with a predominance of adsorption through ion exchange. Vander Waals adsorption, as well as adsorption through hydrogen bonding was found to occur to some extent. The temperature increase reduces adsorption capacity by polymeric materials, due to enhancement of the adsorption step in the mechanism. The value of ΔH (< 40 KJ/mole) proved the physical nature of the adsorption by these dyes. The adsorption of solute of a solution onto a solid adsorbent is very important, but inspite of the extensive application both in laboratory and industry, and treatments, the process is still little understood and current theories of surface reactions are still often loosely supported.

The purpose of this work is to study the removal of benzoic acid and some of its selected ortho substituents from its solutions by adsorption on activated carbon of a commercial grade.

EXPERIMENTAL

1. Preparation of stock solution for carboxylic acid and substituted aromatic carboxylic acid:

Exact weight of pre-purified carboxylic acid was dissolved in 100ml volumetric flask. Ethanol was added to the solution for clarification and complete solubility. The prepared sample was kept in a reagent bottle for the study (0.1 M).

2. Adsorption of carboxylic acid from aqueous medium:

Exact weight of activated carbon (commercial grade), ca. 0.1 gm was transferred to a conical flask containing previously 5.0 ml of the stock solution. 10, 15, 20, and 25 ml were added to the same amount of activated carbon. The series under study was shaken at constant temperature for 1 hr. The sample was then filtered and used in the determination of the residual carboxylic acid.

The adsorption of the same carboxylic acid was carried out at various temperature and different pH in addition to different concentrations.

3. Determination of the removal unadsorped carboxylic acid:

The stock solution concentration was determined using standard sodium hydroxide solution (0.1 M). the filtrate from step 2 was used for the determination of the remaining acid.

4. Variation of determination conditions.

Using suitable buffer and pH solution was conducted to indicate the effect of other parameters on the determination. Each parameter such as concentration, temperature was kept constant and different pH and different functional group type and position were investigated, as illustrated later.

RESULT AND DISCUSSION

A great efforts have been directed toward the understanding of adsorption and removal of carboxylic acids and their derivatives (Kikic *et al.*, 1996; Al-Banis *et al.*, 2000; Madras *et al.*, 1993) and substituents from polluted water, sediments, soil, and some times combustion products.

Its very important to purify water from toxic, colored and heavy metals from the quality point of view in the industrial products, especially those of nutrients and medical products (Safarik *et al.*, 1998). The presence of acids and their substituents may divert the application of the medicals into others forms, also their presence may cause instability towards heat and sun light. Carboxylic acids in general cause a certain type of corrosion in the metallic type and the machinery system and may inhibit some enzymes in the body. Therefore, their complete removal or at least reduce their amount is a vital task, and necessary to product quality.

In our study, we aimed to investigate the removal of benzoic acid and some of its substituents such as OH, NH₂ and SH by adsorption using activated carbon of a commercial grade (BDH-grade). The study involved variation of the experimental parameters such as concentration, temperature and pH. The effect of varying the concentration when other reaction parameters are constant are give in Table (1).

Table (1): Effect of Concentration on Adsorption efficiency of A.C when other parameters are constant. (Temp= 30°C, natural pH).

Compound	Weight before adsorption	Wt of adsorped acid	% of adsorption
Benzoic acid (BA)	0.061	0.0066	10
	0.122	0.0105	8.6
	0.183	0.0131	7.15
	0.244	0.0142	5.7
	0.302	0.0166	5.4
Salicylic acid (SA)	0.069	0.003	4.4
	0.138	0.0039	2.8
	0.207	0.00534	2.5
	0.376	0.00345	1.8
	0.345	0.00165	0.48
Anthranilic acid (AA)	0.068	0.0030	4.4
	0.137	0.00411	3.0
	0.2055	0.0053	2.5
	0.2740	0.0063	2.2
	0.342	0.00465	1.3
Thiol benzoic acid (Th.A)	0.07707	0.0099	12.8
	0.15414	0.0189	11.0
	0.23121	0.0234	10.1
	0.30828	0.0283	9.2
	0.380	0.03329	8.6

The results in Table (1) shows that the forces control the adsorption of benzoic acid using activated carbon are very little, and the factors affecting the adsorption when all the parameters are constant except the concentration indicate that the adsorption is very active at low concentration and start to reduce at almost one-third or one-fourth, and decreases by almost 50% at high concentration. This may indicate that the pores available for the adsorption which are energetically unbalanced are poisoned or saturated at high concentration (Al-Banis *et al.*, 2000).

Looking at the salicylic acid in which the OH group is in ortho position, and at the same molarity of the benzoic acid, the results showed a reduction by about 55% compared to the unsubstituted acid. Increasing the concentration showed a decrease in the adsorption in the same manner as in the benzoic acid. The reduction reached to almost a neglected amount at higher concentration. This may be due to the presence of intra hydrogen bonding in the salicylic acid which affects the adsorption and the forces through the carboxylic group that lead to adsorption and removal. This clearly appeared when the concentration increased which means high concentration of hydrogen bonding and low ability to adsorption.

When anthranilic acid (which contain NH₂ group in the ortho position) is used as and compared with the benzoic and salicylic acids, at low concentrations adsorbent anthranilic and salicylic acids act in the same manner as the unsubstituted benzoic acid, but when a higher concentrations are employed, anthranilic acid showed better

adsorptivity than salicylic acid. This may be due to the power or the strength of the hydrogen bonding in the anthranilic acids compared to salicylic acids, but overall adsorption of salicylic and anthranilic acids showed a systematic reduction with the increase of concentration that could be due to saturation and adsorption failure due to the strength of hydrogen bonding.

The study of thiolbenzoic acid that contains SH group in the ortho position showed a slight increase in the adsorped amount compared with same concentrations of benzoic acid and with a difference which exceeds 200% compared to salicylic and anthranilic acids. The results are showed clearly in Table (1). This could be explained by weak hydrogen bonds formed between the carboxylic group and the thiol, also very little effect of concentration on the hydrogen bonding is observed.

The overall adsorption process for the removal of aromatic acids from their aqueous solutions depends mainly on the type and strength of the hydrogen bonding present in the molecule when other parameters are constant.

Investigation of the effect of varying the temperature on the adsorption process for the acids under study between 15-40°C indicates that the adsorption decreases in all cases of the acids no mater what type of substituents on the aromatic ring is present (Farere *et al.*, 1998) (See Table (2)). This observation leads to a conclusion that adsorption of the acids are mainly exothermic over activated carbon.

Table (2): Effect of temperature on adsorption of carboxylic acids on activated carbon.

Comp.	% of Adsorption at Temperature				
	15°C	20°C	25°C	30°C	40°C
BA	21.84	17.35	12.79	10.8	3.66
SA	21.82	17.28	12.73	4.4	3.6
AA	17.30	12.68	8.15	4.4	0.89
Th.A	30.22	26.37	21.83	12.8	8.19

Effect of pH on the adsorption of the acids under study indicate that; in the acid medium the benzoic acid adsorped relatively high due to intensifying the positive charge on the system while decreasing the acidity to a neutral case diminishes the adsorption (Farere *et al.*, 1998). This could be attributed to adsorption poisoning. On the other hand, increasing the pH to (9) indicates alittle adsorption when compared to that in the acid medium. This could be due to the conversion of the carboxylic group to a carboxylate which result in intensifying the anion character that may not enhance the adsorption. In case of salicylic and anthranilic acids, they showed almost the same behaviour at different pH values. Great values are obtained in acid medium and moderately low values at neutral pH, while in a basic medium the difference from the acidic medium is slightly low and this may due to the engagement of the carboxylic group by hydrogen bonding formation and rather than salt formation.

The thiolbenzoic acid showed high value of adsorption in the acid medium, and moderate value in the neutral medium (table (1)). However, the adsorped amount in the basic medium is slightly low, this could be attributed to charge intensifying in the acid medium and carboxylate formation in the adsorption of the basic medium.

The overall conclusion for the adsorption of the aromatic carboxylic acids indicate that; the process is exothermic, concentration dependent, temperature variable and finally pH type. Since the carboxylic group in the acid and its substituents could be changed to salt in the basic medium, therefore, the removal of the polluted acid from the polluted water require strong acid medium to intensify the positive charge and hence increases the removal and adsorption. The temperature required from the investigation is below the room temperature which is beneficial of economic point of view. However, most methods of the removal require to be sensitive at slight low concentration to be detected and in our case and from the conditions fixed the procedure is quite suitable for doing the job.

The study included the determination of atom charges, bond length, bond angles and molecular geometry of the system under investigation by employing the parameters available in the theoretical programme “Chem Office of Cambridge University- Version 1999”. The results obtained are given in Tables (3-5). The results indicate that the charge on the system and heteroatoms have great effect on the adsorption. The size of the electronegative atoms and the availability of electrons and also their ability to form hydrogen bonding have a direct relation to the adsorption. The intramolecular hydrogen bonding increases the stability and decreases the steric energy in the anthranilic and salicylic acids when compared to the thiol-benzoic acid. The repulsion force that resulting from the high steric interaction in the later acid increases the length of the bond (C₇-O₈) due to the increase of the electron density on this bond (i.e., the repulsion reduces the charge on the (O₈) atom). In the same time, the repulsion increases the value of the angle (C₅-C₆-C₇) in this acid (look at the structures in figure (1)). The results of the theoretical calculations explain the experimental data in the investigation.

Table (3): The atom charges of the system under study

Atom	Charges on compounds			
	BA	SA	AA	Th.A
C ₁	-0.008	-0.006	-0.005	-0.005
C ₂	-0.027	-0.089	-0.146	-0.079
C ₃	-0.008	-0.005	-0.008	-0.10
C ₄	-0.027	-0.119	-0.147	-0.079
C ₅	-0.007	0.285	0.200	0.080
C ₆	-0.004	-0.089	-0.140	-0.070
C ₇	0.571	0.569	0.552	0.562
O ₈	-0.157	-0.164	-0.158	-0.154
O ₁₀	-0.671	-0.689	-0.710	-0.691
O ₁₁	-	-0.218	-	-
N ₁₁	-	-	0.048	-
S ₁₁	-	-	-	0.098

Table (4): Molecular geometry deformations of the acids studied in term of energy (Kcal/mole).

Comp.	Bond stretch	Angle bending	Torsion	Non bonded 1,4- interaction	Steric energy	Heat of formation
BA	0.194	0.985	-7.194	-0.473	-2.612	-68.06
AA	0.240	1.345	-8.254	-0.695	-4.136	-70.51
SA	0.292	1.541	-7.187	-1.030	-3.630	-108.97
Th.A	0.337	1.979	-7.193	0.467	0.428	-60.85

Table (5): Selected bond length and bond angle of the acids under investigation.

Comp.	C ₆ -C ₇	C ₆ -C ₅	C ₇ -O ₈	C ₅ -C ₆ -C ₇
BA	1.467	1.400	1.367	121.245
AA	1.462	1.413	1.350	124.474
SA	1.464	1.409	1.362	123.126
Th.A	1.469	1.401	1.367	125.817

The adsorption was also studied at various pH. The variation of the pH was aimed in our case to show which form of the acid could be adsorped stronger compared to the others. The results obtained are listed in table (6).

Table (6): The variation of adsorption with pH.

Comp.	% adsorption at natural pH		% adsorption at pH=7	% adsorption at pH=9
BA	10.8	(4.2)	0.2	2.19
AA	4.4	(5.2)	2.62	3.93
SA	4.4	(3.5)	2.18	3.4
Th.A	12.8	(2.8)	3.60	2.1

The results presented Table (6) show that the free acid form in all cases is the most preferable form.

The relationship of Freundlich is used to test the adsorption isotherm mathematically. The value of $\log \chi / m$ is plotted versus $\log C$. A straight line is obtained in all cases with an intercept equal to $\log K$ and slope of $1/n$. the values of the empirical constants K and n are given in Table (7). The results of Table (7) show that the value of K decreases in the presence of intramolecular hydrogen bonding. The values of the correlation coefficients and standard deviations indicate that all of the models give good fits on the data.

Table (7): Results of application of the Freundlich isotherm on the system studied.

$$\log \frac{\chi}{m} = \log K + \frac{1}{n} \log C$$

Comp.	K	n	Correlation coefficient	Standard deviation
BA	0.968	2.27	0.9997	1.36×10^{-2}
AA	3.2×10^{-5}	1.677	0.9995	2.05×10^{-2}
SA	2.64×10^{-5}	-4.950	0.9327	0.210
Th.A	3.767	-0.259	0.9996	2.18×10^{-2}

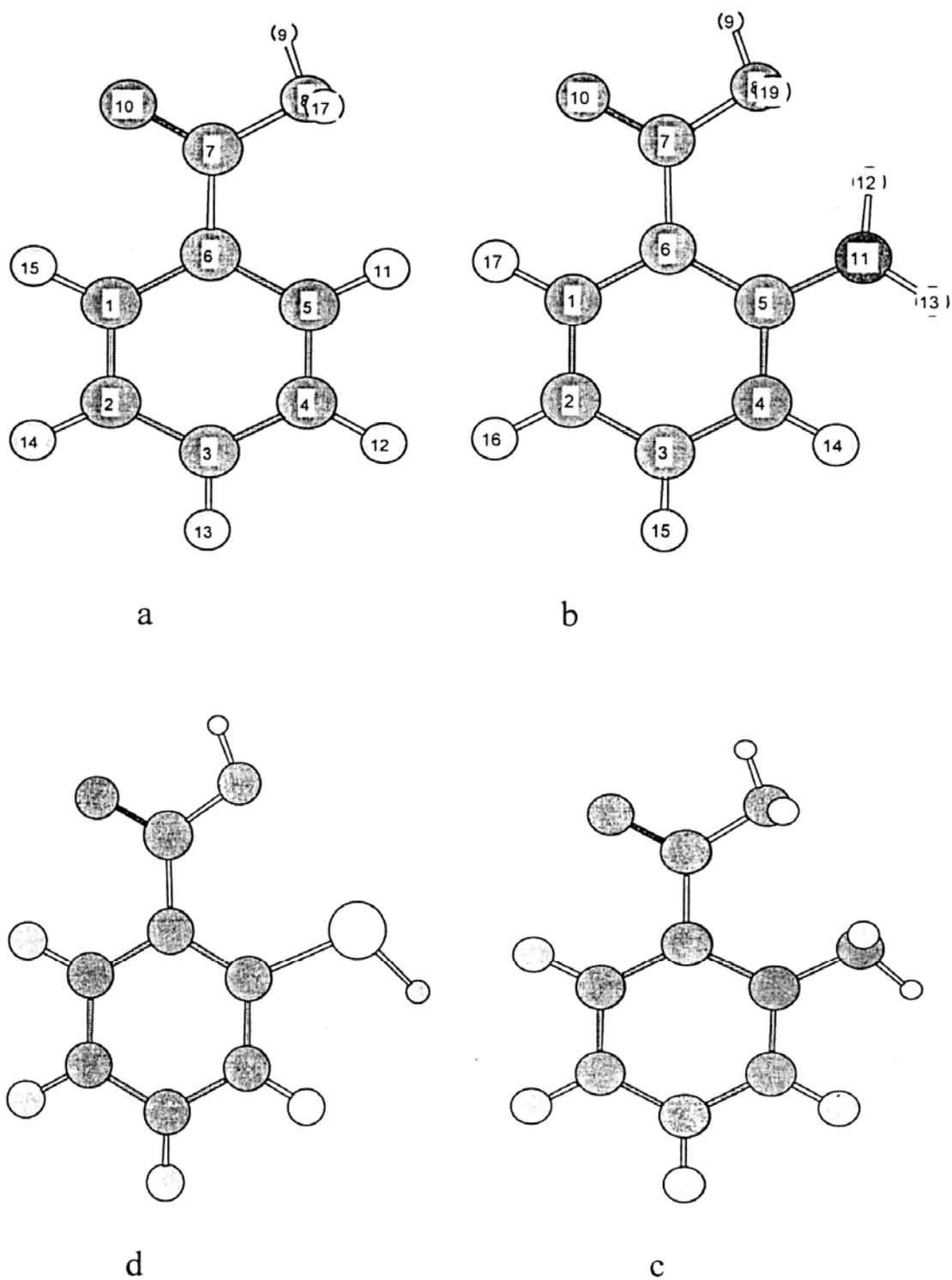
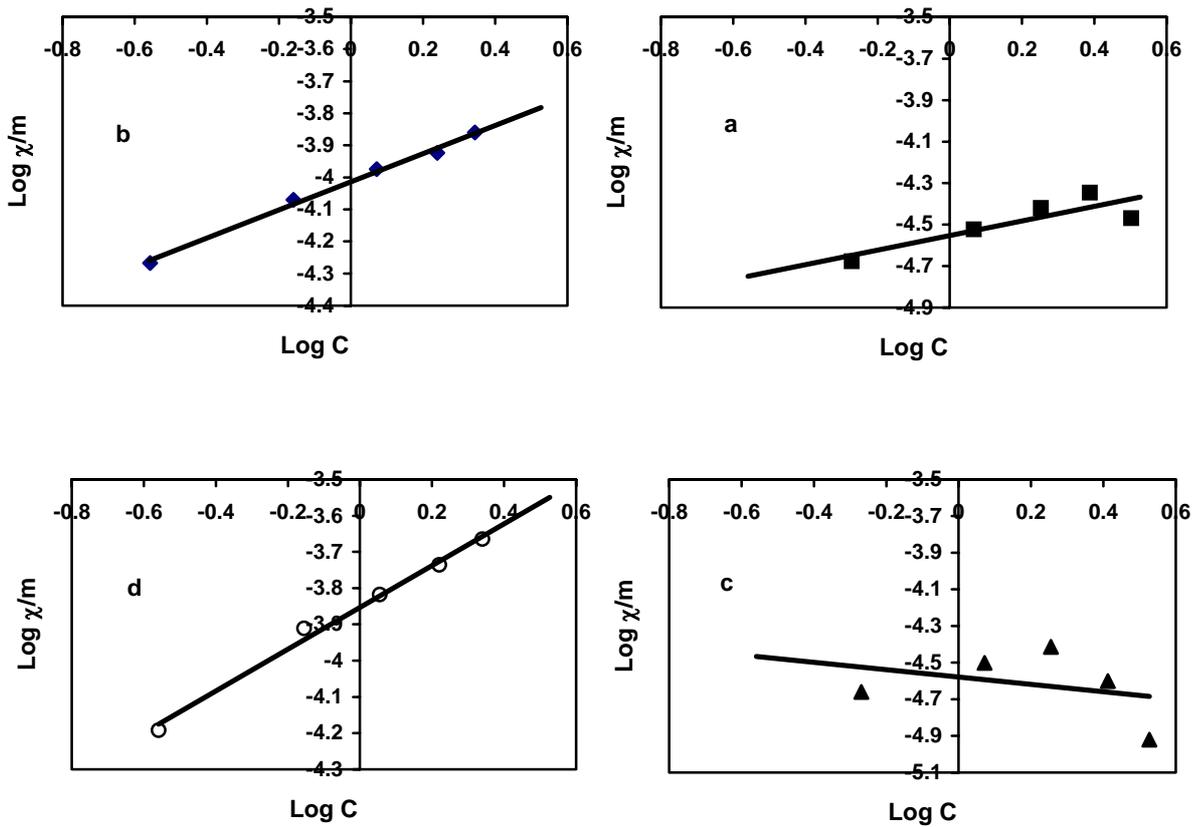


Fig. 1 A: Structure of the acids considered in this study.
a- BA b-AA c-SA d-ThA



**Figure (1)B: Plot of the relationship between log x/m inverse log C
BA, b. AA, c. SA, d. Th.A**

The investigation was extended to calculate the thermodynamic parameters depending on the adsorption isotherm knowledge, variation of temperature and variation of concentration. The calculations were carried out by assuming that, there is a thermodynamic equilibrium between the adsorbed and remained after adsorption, which could help to calculate the adsorption equilibrium constant for each case. Gibbs free energy is calculated from the relation:

$$\Delta G = -RT \ln K$$

The heat of adsorption (ΔH) is calculated from the Vanit Hoff equation which relates the adsorption equilibrium constant to the temperature by supposing that, the adsorption equilibrium constant obeys the Vanit Hoff equation:

$K = K_0 e^{-\Delta H/RT}$, then algorithmic plot of the adsorption equilibrium constant as a function of the reciprocal temperature is linear. The value of ΔH is calculated from the slope of this line. The value of ΔS is calculated from the equation $\Delta G = \Delta H - T\Delta S$. The results of the calculated thermodynamic functions are given in Table (8).

Table (8): The calculated thermodynamic parameters of the acids under study.

Comp.	Temp. °K	K	ΔG cal/mole	$-\Delta H$ cal/mole	$-\Delta S$ C.H.
BA	288	1.236	-121.24	18557.78	64.015
	293	0.7605	159.39		63.88
	298	0.467	450.860		63.78
	303	0.326	674.82		63.47
	313	0.10035	1429.87		63.85
AA	288	1.042	-23.54	34251.906	118.84
	293	0.7426	173.258		117.49
	298	0.357	609.90		116.98
	303	0.282	762.11		115.55
	313	0.021	2402.66		117.10
SA	288	1.2007	-104.66	11127.2	38.27
	293	0.7387	130.25		38.42
	298	0.461	458.51		38.87
	303	0.309	707.06		39.05
	313	0.257	845.004		38.24
Th.A	288	1.362	-176.800	11332.65	38.73
	293	1.085	-47.495		38.5
	298	0.920	49.37		38.19
	303	0.869	84.53		37.68
	313	0.357	640.00		38.25

The results of Table (7) indicate that the adsorption of the acids studied is a spontaneous process at low temperature and as mentioned before, it decreases by increasing temperature.

Looking at the entropy, which are almost similar in all cases, this may indicate that the adsorption process and the forces responsible for the attachment are physical in nature. The value of ΔS is completely in line with the Gibbs free energy of the system. The enthalpy indicate that there is another factor beyond the seen which affect the values and increase it in case of anthranilic acid to unexpected value and decrease it to another value for thiolbenzoic acid. The variations of the enthalpy in such a way may indicate that the strength of hydrogen bonding in the molecular structure of the acids under study have a great effect and direct relation to the values of ΔH . These values are similar to previous estimate from supercritical adsorption of solid solutes (Madras *et al.*, 1993). From these values of the adsorption heat (enthalpy). (<40 Kcal/mole), we can conclude that the adsorption of acids onto activated carbon is a physical adsorption (Chern and Chim, 2001).

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