Adsorption study of ionic surfaces active agents from aqueous solution on the surface active alumina

دراسة امتزاز منشطات السطوح الأيونية من محلولها المائي على سطح الالومينا الفعال

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الخلاصة:

تهدف دراسة امتزاز منشطات السطوح الفعالة الأيونية والتي هي هبتيل بنزين كبريتيت الصوديوم Hebtyl benzene sodium sulfonate ($C_7H_{15}phSO_3Na$) والاوكتيل بنزين كبيرتيت الصوديوم ($C_8H_{17}phSO_3Na$) على سطح اوكسيد الالمنيوم المنشط Al_2O_3 الى معرفة ميكانيكية عملية الامتزاز بدرجات حرارية 25°م، 35°م، 45°م لهذين المركبين، علماً ان الامتزاز الحاصل لكلا المركبين يحصل من الجهة القطبية حيث ان الصلب، يمتلك الصفة الحامضية وقيمة الاس الهيدروجيني pH لـAl_2O_3 في الماء ما يقارب 5. كما تم حساب الخواص الثرموديناميكية ابتداء من تركيز المستحلب الحرج.

Abstract

The aim of the study is to investigate the adsorption of ionic surfaces active agents such as Heptyl benzene sodium sulfonate ($C_7H_{15}SO_3phNa$) and octyl benzene sodium sulfonate ($C_8H_{17}phSO_3Na$) on the surface of

active aluminium oxide, which lead to the understanding the mechanism. of adsorption process as a result of interface interaction between solid and solution, the isotherms adsorption was obtained at 25 ° C, 35 ° C, and 45 ° C for both compounds.

The adsorption occurred from the polar side, because the solid process the acidic property and the pH value for AL_2O_3 in water is 5. Thermodynamic properties have been calculated from the critical micilar have concentration (CMC).

Introduction:

The use of ionic surface active agent is of economic benefit from the industrial sense. As their solutions are used in the regrouping of oil inside the well also in the process of attracting metallic materials as if they are to the all of cruising on the surface of collector of flotation of such materials, several studies have been conducted to determine mechanism of adsorption [1-4] of the polar part Amphiphyles on the surfaces of solids.

The properties of chemical and physical for adsorbent and adsorbat. important in terms of knowledge of mechanism adsorption, especially when concentrations arc very low-lying. And also in the case of high concentrations that are after the concentration Critical Micelle Concentration (CMC) because of the possibility to configure several layers between the surface interface.

Gaunin And Fuekstrnau but theory for Hemimicelle [5, 6] of water with a volwne (V) contains the asorbed. As this system is at a temperature (T) and under external pressure (P) and can be represented by the free energy of the system the following equation:

$$G_{11} = G_a + N_s\mu_s + G_c \quad \text{...}(1)$$

Where

N_s is the number of ions or molecules that suffer adsorption within aqueous solution.

μ_s represents the chemical potential of the molecule in solution.

G_c represents the free energy of the solid.
G_a represents the free energy for adsorbed phase.

G_{11} represents the free energy of the system and now are trying to build initial phase of the system before adsorption, considering that $N_a >> N_a$ and this effort is the chemical fonn in the following:

Where: $\mu_{s.l} \approx \mu_{s.ll}$

$\mu_{s.l}$ represent the chemical potential in initial state.
$\mu_{s.ll}$ represent the chemical potential in final state.
N_a is the number of molecules adsorbat.

$$G_1 = (N_a + N_s)\mu_s + G_c \quad \text{(2)}$$

The change in free energy ΔG be identical to the process of adsorbtion is therefore:

$$\Delta G = G_{11} - G_1 = G_a - N_a \mu_a \quad \text{(3)}$$

Can be written in the free energy G_a for adsorbat phase as the following:

$$Ga = Na - KT\left[Na \log Za + \log \frac{N_o!}{N_a!(N_0 - N_a)!} \right] \quad \text{(4)}$$

The expression of $\log \frac{N_o!}{N_a!(N_0 - N_a)!}$ represent the integral entropy

(S_c) (model of Bragg- William)
N_o number of surface sites.
If we use the Stirling approximation as
$\theta = N_a/N_o$ with $\log N! \approx N \log N - N$
Integral entropy can be written as the following:
$S_c = KN_o[\theta \log \theta + (1 - \theta) \log (1 - \theta)]$ ......(5)
In fact, could write a function retail Q_a adsorbat phase as the following:

$$Q_a = Z_a^{N_a} \sum_i g_i \exp^{-(N_{a,i}KT)} \quad \text{(6)}$$

Where Z_a represents the total number of cases or each molecule.

Thus we find that the law of the Boltzmann distribution plays an important role in the process of adsorption, as noted in the equations mentioned above. Provided there is no interfacial interaction of molecules.

Experimental and technical materials experience

We have been processing material C_7phSO_3Na and C_8phSO_3Na of the laboratories at the Faculty of Science - University of Montpellier France.

The aluminum oxide activated AL_2O_3 has been Processed by the placed where the amount of 0.5g alumina activated in aq test tube and add to the solution and shake for a three hour period of time sufficient to reach equilibrium. Separated from the solid result for the solution by centrifuge (4000 rpm) for ten minutes difference in focus before and after the centrifuge is the amount of adsorbat on the 1mg of alumina. The device for measuring the focus when adsorption is a UV/ V is type Pu 8800 device has been used to measure the pH meter for each acid concentration after adsorbtion. When the curve is drawn between the quantity of the isotherm adsorbat and focus at equilibrium.

Results and discussion

1. Adsorption C_7phSO_3Na on the surface of activated Al_2O_3:

I've been getting isotherm adsorption of the compound at 25 ° C, 35 ° C and 45 ° C and shown in Figure (1, 2 and 3), respectively. It was noted that the effect of temperature, albeit a little on the amount of material adsorbat and at the level of the plateau. In fact, the increase in temperature is accompanied by a decrease in the quantity of adsrobat at the level of the plateau, and applies to the ionic surface active agent on the surface of silica gel [7]. When a high temperature that the location of the CMC oriented high concentrations [8], Note Isotherm and find after reaching the CMC adsorption continues to rise slightly until it reaches the level of the plateau [9-11].

In practice we find that the pH value measured after adsorption and at equilibrium change from 4.5 to approximately 8 as the pH- f(C) where C represents the concentration at equilibrium, and when drawing the curved note by the pattern vertically when concentrations of low-lying and at the concentration (0.5) we find The value of pH increase slightly.

The pattern of adsorption, the first mechanism represents the vertical curve and this explains that in the beginning of the adsorption get there contact is weak with Al_2O_3 means that the ions adsorbat be individually at concentrations of low-lying [12] in terms of the existence of electric power between ionic surface active agent and adsorbent, and when it reaches the dergree of coverage of the surface of (0.4) show mechanical Second Stabi1ity of molecules at the surface interface, and when we increase the quantity of the adsrobat at a concentration of balancing high note so that the particles will be adsorbed in a collaborative manner (cooperative) between the alkyl chains composed half-micelle at the interfacial surface (4) the Mechanical been clarified be Schechter and Wade [13].

2. Adsorption $C_{8ph}SO_3Na$ on the surface of activated Al_2O_3

Forms the figure (4-5) represents isotherm Adsorption C_8phSO_3Na on alumina at 35 ° C and 45 ° C it appears from the figure that the level of the plateau be comparable to the CMC and is similar to that in the case of C_7phSO_3Na it appears from this that mechanical adsorption be identical. We note that there is a clear difference in the quantity of Adsorbat at the level of the plateau for each regular $C_8phSO_3Na/\ Al_2O_3$ and $C_7phSO_3Na/\ Al_2O_3$ as shown in table (1).

Table (1)

Adsorbat quantity in maximum for the $C_7$and C_8 at Interfacial surface at temperature 35 ° C

	C_7	**C_8**
Adsorbat quantity Γ_{max} mol g^{-1}	3.75×10^{-1}	3.16×10^{-1}

As the lengths of those ions and C_7phSO_3Na and C_8phSO_3Na were 15.4 Å and 16.6 Å . If we consider Hemimicelle radius equal to the length of the ion drive, the space occupied by Hemimicelle case C_7phSO_3Na is a 745 $(Å)^2$. and 1866 $(Å)^2$ C_8phSO_3Na. Case assuming that the number of clusters be the same on both cases. It is possible to calculate the maximum number of moles of C_7phSO_3Na adsorbat of the information of the C_8 and the expulsion of ions C_7 and C_8.

Thermodynamic properties for micelle

Thermodynamic values can be calculated for each of the two system of knowledge of CMC for both systems as shown in the following equations where we can find the value of ΔG at 25 ° C, 35 ° C, 45 ° C, note that the value of the CMC at temperature 25 ° C is 11×10^{-3} mol/ kg for C_8.

ΔG_{mic} = RTln CMC ....(7)

Note Isothermal and can learn the values of CMC for each of the C_7 and C_8 at three temperature and this can be calculated ΔH°_{mic} and ΔS°_{mic} the relationship of the following:

$$\Delta\left(\Delta G^{\circ}_{mic}\right)/\Delta T = -\Delta S^{\circ}_{mic} \quad \text{..........}(8)$$

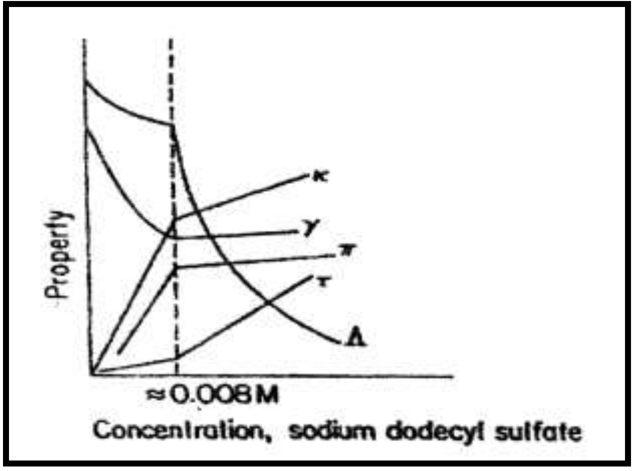
Where they were taken ΔG_{mic} values in the equation (8) at temperature in 25 ° C and 45 ° C and from the relationship of the following value is calculated ΔH°_{mic} at temperature in 25 ° C.

$$\Delta H^{\circ}_{mic} = \Delta G^{\circ}_{mic} + T\Delta S^{\circ}_{mic} \quad \text{..........}(9)$$

When we the Note Table (2) we find that the values ΔS°_{mic} for both systems are addressed and that which indicates the arbitrary arrangement of molecules in the process of composition at the surface the micelle interface. The negative values shown by the values ΔH_{mic} at 25 ° C clear indication of the adsorption of ions C_7 and C_8 on the surface effectively owned sites adsorption effectively have a direct impact on the ions adsorbed, leading to release the amount of heat that the amount be close for both system C_7 and C_8.

Micelle and the Critical Micelle concentration

Figure shows the schematic following the change in orientation that occurs when the concentration of low- lying it was also noted that the solube nature polar which include both ionic and non ionic show a sharp change in properties in addition to identify behavioral dissolved attributed these phenomena to the process of input molecul;es dissolved in the formation of micelle called the micelle concentration that occurs the critical micelle concentration and symbolized by the symbol CMC.The figure shows the conformity of the curves for a number of physical properties compared to the focus to solutions sodium dodecyl sulfate.



And signs that are pointing A, τ, π, γ,k the curves represented a connectivity, surface tension, osmotic pressure, the degree of disturbance, connective quality, and the contribution of molecular nature polar a space to configure Micelles is special significance to the surfaces and chemistry colloids and some of those compounds that show effectiveness of the surface is lower than the CMC has which the molecule form the colloid with a range of more than this focus and can use the following equation is applicable to solutions containing the micelle.

$$\frac{H\left(C - C_0\right)}{\tau - \tau_0} = \frac{1}{M} + 2B\left(C - C_0\right)$$

Where C, τ_0 represents the focus and the degree or disturbance, respectively, in the solution at the CMC.

M represents the molecular weight of micelle.

H represents the shipment Micelle.

As the electric power that arise between the ion - ion as a result of interaction between the groups polar so you can describe the properties thermodynamic these regimes using the equation Poison-Boltzmann these include quantities such as osmotic pressure, the effectiveness of ions, and changes in the CMC with the salt concentration and chain length alkyl of activated surface and particular party, we find that the surface is activated body ball or spherical clusters and through these groupings, we find that a little bit of water molecules permeate the spherical assembly process gives an idea of the influence of water miccllairc hydration. There are two important consequences First, it combines a number of molecules of the surface of the polar on the CMC, which reduces value, leading to an overall increase in the concentration of activated surface. Second, the proportion of the non-polar, which is one of the anti-ions are related to the number of parts of the composition of the polar micelle be fixed in a wide range of concentrations.

Increase in the portion Hyderovobi reduces the value of CMC in aqucous media that the focus critical for ionic surface active agent is divided into two parts and that when you start a group $-CH_2-$ a molecule with the same added $-CH_2-$ for the stimulant surface of the non-ionic reduces the value of the CMC and the general relationship exists between a focus the micelle critical and the number of carbon in the chain Hyderovobi [14-15] for the doping surfaces ion that a shipment ion has an important role in participating ion example sodium dodecyl sulfate, magnesium, lead or zinc to the value of focusing the micelle critical 2mM and sodium or potassium is 8mM at a heat in 20 ° C. In terms of the impact of Ionic Force plays a major role in the Solutions electrolytic processes strong and have an impact on the value of the CMC, leading to reduction of that value, as is clear from the following equation:

$$\text{Log CMC} = -a \text{ Log (CMC} + C) + b$$

Where a and b are constants and connected to the doping the surface, the nature of the salt affects the concentration of activated surface (C). That is, they collect the particles in a narrow area. We have also launched by the concentration of the micelle critical [16]. This consists of a new phase and above the CMC, we find that the effectiveness of catalytic surface increases slightly with increasing concentration and this is what is observed in Tonic surface active agent, there is a difference in the effectiveness of the polar and non-polar as it happens overlap between the polar groups [17].

Table (2)

Thermodynamic properties

	tC°	$-\Delta G^{\circ}_{mic}$ **kJ/mol**	$-\Delta H^{\circ}_{mic}$ **kJ/mol**	ΔS°_{mic} **kJ/mol**
C_7phSO_3Na	25	9.367	2.463	0.013
	35	9.679		
	45	9.994		
C_8phSO_3Na	25	11.173	2.543	0.029
	35	11.523		
	45	11.897		

Conclusion :

Through the study of systems C_7 and C_8 on the surface of Al_2O_3 found that isotherm adsorption at temperature 25 ° C, 35 ° C and 45 ° C are nearly identical, showing that there is a mechanized battalions of adsorption clearly, as it is at the beginning of adsorption are there the overlap due to the presence of attraction electrostatic power between the adsorbat particles and the adsorbent and be followed by Hemimicelle at interfacial surface and then consists of the plateau at relatively high concentrations, were calculated thermodynamic values.

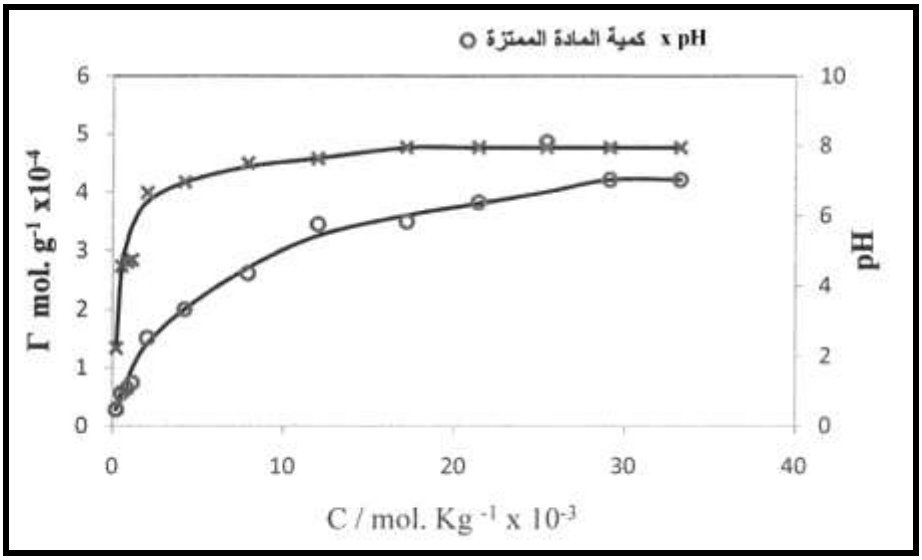


Fig. (1): *Adsorption isotherm of* $C_7H_{15}phSO_3Na$ *on the activated surface of* Al_2O_3 *and pH as a function of concentration at equilibrium at 25 °C.*

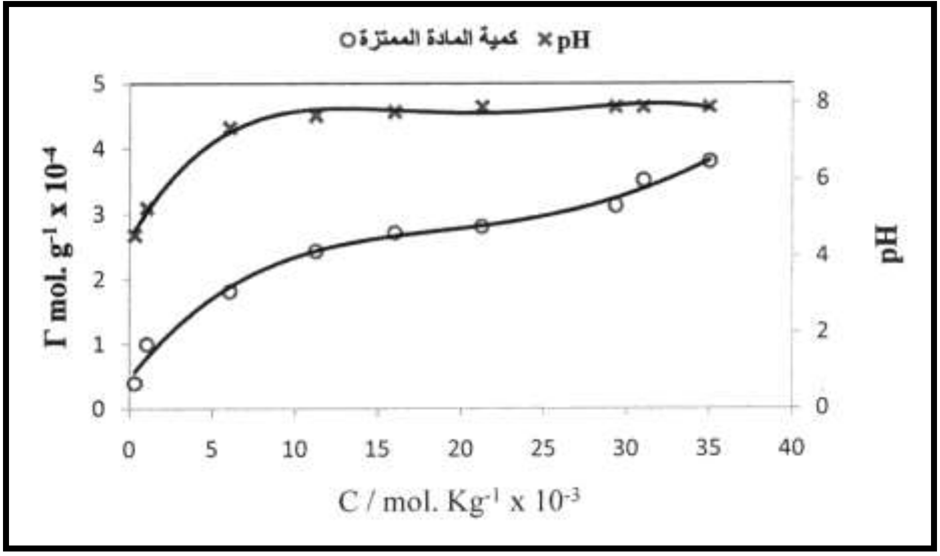


Fig. (2): *Adsorption isotherm of* $C_7H_{15}phSO_3Na$ *on the activated surface of* Al_2O_3 Γ *and pH as a function of concentration at equilibrium at 35 °C.*

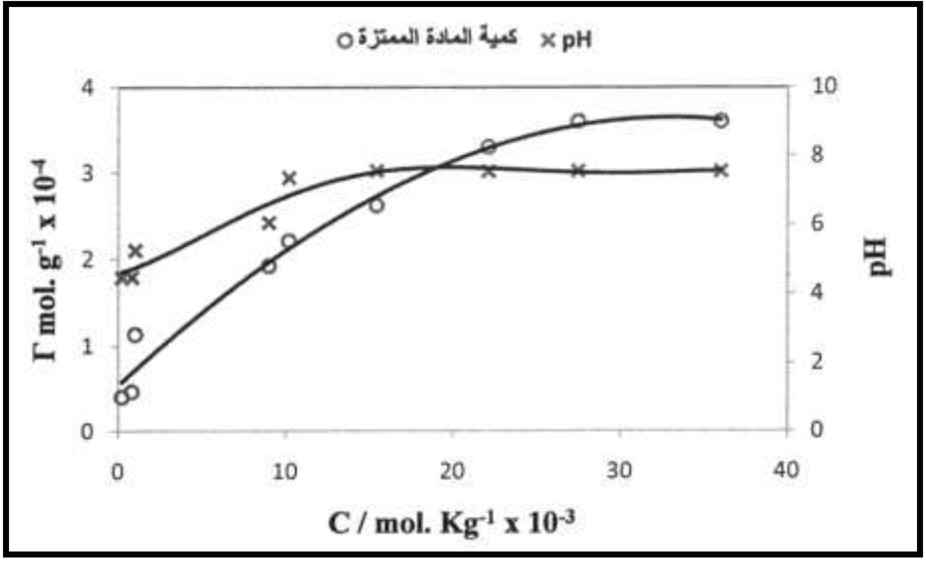


Fig. (3): *Adsorption isotherm of* $C_7H_{15}phSO_3Na$ *on the activated surface of* Al_2O_3 *and pH as a function of concentration at equilibrium at 45 °C.*

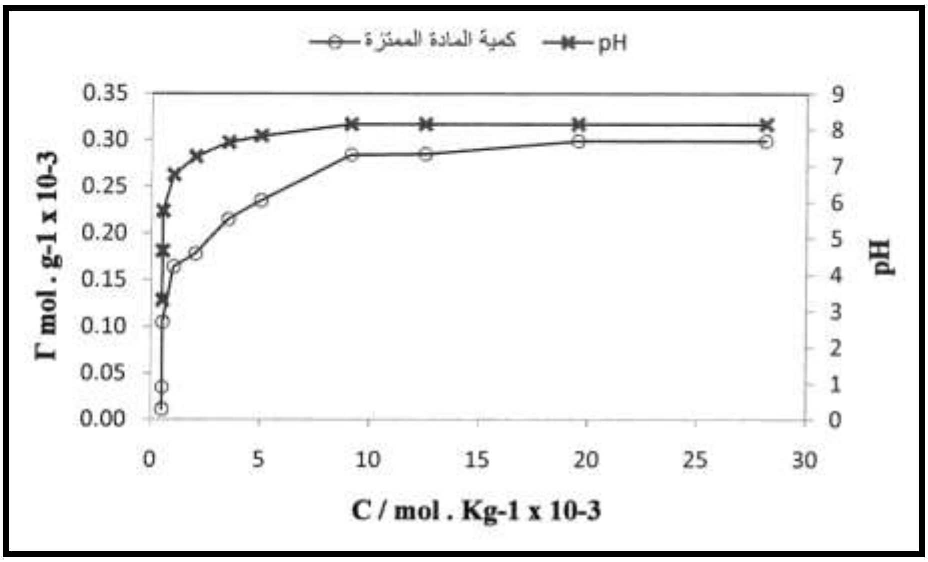


Fig. (4): *Adsorption isotherm of $C_8H_{17}phSO_3Na$ on the activated surface of Al_2O_3 Γ and pH as a function of concentration at equilibrium at 35 °C.*

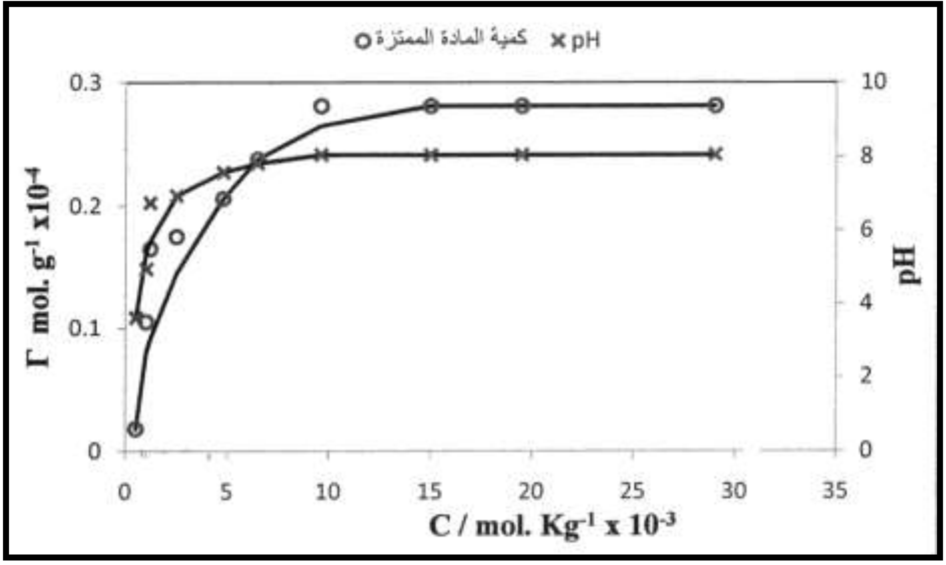


Fig. (5): *Adsorption isotherm of $C_8H_{17}phSO_3Na$ on the activated surface of Al_2O_3 and pH as a function of concentration at equilibrium at 45 °C.*

المصادر

1- Brasquetc., Bourges., etal Sci. & Technol., 33, 4226-4231 (1999).
2- Cases, J.M., Trans. A.I.M., 247.123-128 (1970).
3- Douglask., Luddlow., J.Am.chemical society, 2006.
4- fuerstenan, D.W. and Aplan, F.F., in Forth Flotation, 50th Aniversary Volume, A.I.M.E, Ed., New York P. 170. (1962).
5- Fuerstenan, D.W. and Raghavan, S. in M.C.Fuerstnan (Ed). Flotation, A.M.Gaudin Memoriat < A.I.M.E., New York, 1,21-64(1979).
6- Fuerstenan, D.W., in xxint. congo Of pur and applied Chemistry. plenary lectures. butterworths. London, P.135 (1970).
7- Gaudin, A.M. and Fuerstenan, D.W., Trans. of A.I.M.E., 202,985962(1955).
8- Gaudin, A.M., Flotation, 2nd Ed. MacGraw-Hill Book Co.NewYork, 1957.
9- Martin and Weightman, Surface Sci, 450, 171-180 (2000).
10- Mary gane shultz., Cheryl Schnitze., international Review in physical Chemistry 19, 12153, (2000).
11- Pandou, M. Thesis of state. France (1982).
12- Scahehph, J.F., Schechter, R.S. and Wade, W.H., J. colloid interface sci, 85, 2, 463 (1982).
13- Smani, S., Blazy, P. and Cases, J.M., Trans. Of S.M.E., 258.768-787 (1975).
14- Somasundaran, P. and Fuerstenan, D.W., J.phy.chem., 70,90~96 (1966).
15- Somasundran, P. in P.Somadran andR.b.Grieves (Ed.), Advances in interfecial phenomema of particulate/solution/gas systems,application to flotation reseach. AlChe symposium series, 150, 71, 7- 15.(1975).
16- Stepher. b., Johson., etal, Langmiur, 20, 299665006 (2004).
17- Zaini, S.J. and Malkhasian, A.Y.S. Adsorption of NNAlkyl I-betaine on Silica gel Accepted in J. of Iraqi Chern. Soc. (1988).