# THEORETICAL STUDY FOR THE ADSORPTION OF LINEAR PROPADECYL BENZENE SULFONATE (LAS) ON BENTONITE WHICH MODIFIED BY THREE SURFACE ACTIVE MATERIALS

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## Abstract

The study included the using of semi-empirical method to calculate the Molecular Orbitals Energies, This calculation let to suggest the best surface active material can be used to modified the adsorption efficiency of LAS (Alkyl benzene Sulfonate) on Iraqi Bentonite by comparison the theoretical results with experimental results which achieved in previous experimental studies between LAS and modified Bentonite by 1-Hexadecylpyridinium bromide (HDPYBr). The theoretical calculation showing the good Efficiency of Hexadecyltrimethyl ammonium chloride (HDTMACl) and 1,12-dipyridiniododecane dibromide ($DPYDDBr_2$), to modified adsorption of LAS on Bentonite.

Also a theoretical calculation was made to (HDPYBr) which was studied in previous experimental studies.

This study shows that the adsorption efficiency of LAS as the following:-

$HDPYDDBr_2$ > HDPYBr > HDTMACl

The study including also of the comparison of the stability of the four substance according to the enthalpy of formation which calculated from the theoretical solution, and from the different between the energy of HOMO and LUMO energies levels for the four sub starts.

**Keywords : AM1 semi-empirical method, adsorption, solid-state chemistry.**

## Introduction

Nowadays, the removal of toxic substances from aqueous medium such as effluents is of great interest for environmental and human healt purposes. For this reason , the control and treatment of these effluents have become one of the most important steps of the productive process. In this scenario, the application of solid phase extraction (SPE) procedures has increased in last few years, specially due to its efficiency and low requirements in terms of cost[1] .

Clay minerals have been proposed as host rock and as a principal component of barrier and back fill materials (Pusch and Karnland, 1990; Muurinen, 1994; McCombic et al., 1995; Madsen, 1998). They are characterized by high plasticity, Low hydroulic conductivity and excellent adsorption capabilities for cations, but are generally ineffective in adsorbing anions. The weak adsorptive capabilities of clays for anionic species Like Linear propadeccyl benzene sulphonates (LAS) can be improved substantially by replacing the natural inorganic interlayer cations of the clay minerals with organic cations of certain chemical structures.

The resulting organo-clay minerals are capable of adsorption LAS[2].

Bentonite clay is widely used in many field of technology including adsorption of dyes and surfactants, and the wide use of bentonte may be attributed to its high surface area, high chemical and mechanical stability and to a variety of surface and structural properties. Bentonite modified by surfactants was reported to be efficient in the treatment of various pollutants [3].

The pollution by detergents is the major problem of industrial progress, since a large amount of those detergents are disposed into the environment and specifically into the rivers and lakes.

Linear Alkyl benzene Sulfonate (LAS) is the major anionic surfactant used world wide in detergents and household cleaning product

formulations. The main disadvantages of LAS are their effect on the skin and hence they cannot be used in personal care formulations.

Semi-empirical methods have a long useful history in solid-state chemistry, spanning several decades [4]. Indeed a approximate molecular orbital calculation laid the foundation for subsequent ab initio methods at time when computing resources did not permit more accurate techniques to be applied. Jon K. west [5], et.al, study the molecular modeling of adsorption of poly-L-lysine onto silica glass by using two approaches: an AM1 semi-empirical molecular orbital method and an MM2 molecular mechanics method to investigate the structural configuration for poly (L-lysine).

Jon K. West [6] study the chemical binding of proteins with bioactive surfaces theoretically using Semi-empirical molecular orbital theory

(AM1). The model calculates the optimized molecular structures of an amino acid (L-alanine) interacting with a cyclotetrasiloxane silica cluster (a four-membered hydrated silica ring)

Joao B. L. Matins[7], et .al .investigated the adsorption and heterolytic dissociation of $H_2O$ and $H_2$ molecules on a $(ZnO)_{22}$ cluster corresponding to ZnO(0001), (000(OVERBAR)1), and (10(OVERBAR)10) surfaces using MNDO, AM1 and PM3 semiempirical procedures .

The major objective of this research is to compare between experimental adsorption results for the adsorption of LAS on Iraqi bentonite which modified by a cationic surfactant (cetyl pyridinum Bromide (HDPYBr) and theoretical study using AM1semi-empirical method for three cationic surfactants.

## Method

As computers become ever more powerful, we may wonder if there is any need to pursue semi-empirical methods. For now it is, argnably, worthwhile, as there are always problems which are still too large for first principles. Techniques or situations where qualitative answers are needed on a short timescale. From a chemist's point of view, three semi-empirical methods have been predominantly applied to solid-state problems :extended Huckel theory[4],CNDO(complete neglect of differential over lab) and INDO (intermediale neglect of differential overlab). Despite the dramatic simplifications that are made to the Hamiltonian, these approaches have been successful in tackling many problems in oxide and halide chemistry.

However, in many cases this has only been achieved by tuning some of the adjustable parameters for specific materials, thus reducing transferability. Given that fitting can often be time consuming in its own right, this surrenders some of the advantage gained over more accurate methods. If we study the literature within the organic community then this field is dominated by methods based on the modified neglect of differential diatomic overlab (MNDO). In addition to the original formulation, there have been some modifications of the core- core repulsions which have led to two subsequent reparametrisations, AM1 and PM3.

These methods are generally superior in the reproduction of molecular properties and have a number of desirable features, such as the ability to model the stereo- chemical activity of lone pairs, as demonstrated by calculations on the water dimmer.

Within the NDDO approximation, all integrals are retained provided they involve pairs of orbitals on the same atom. Hence, all three- and four-centre integrals are neglected, but the majority of the largest two-centre integrals are retained. The elements of the fock matrix are thus given by the following expressions[9],

$$F_{\mu\mu} = U_{\mu\mu} + \sum_{B} V_{\mu\mu,B} + \sum_{\nu}^{A} P_{\nu\nu}\left[(\mu\mu,\nu\nu) - \frac{1}{2}(\mu\nu,\mu\nu)\right] + \sum_{B}\sum_{\lambda,\sigma}^{B} P_{\lambda\sigma}(\mu\mu,\lambda\sigma)$$

$$F_{\mu\nu} = \sum_{B} V_{\mu\nu,B} + \frac{1}{2} P_{\mu\nu}\left[3(\mu\nu,\mu\nu) - (\mu\mu,\nu\nu)\right] + \sum_{B}\sum_{\lambda,\sigma}^{B} P_{\lambda\sigma}(\mu\nu,\lambda\sigma)$$

$$F_{\mu\lambda} = \beta_{\mu\lambda} - \frac{1}{2}\sum_{\nu}^{A}\sum_{\sigma}^{B} P_{\nu\sigma}(\mu\nu,\lambda\sigma)$$

Where μ and ν are orbitals on atom A and λ and σ are orbitals on atom B.

If we consider the application of the above expressions to a periodic system we need to handle correctly the two-centre terms in the long-range limit.

Taking first the terms that arise in the off-diagonal blocks between two distinct atoms $F_{\mu\lambda}$, the two-centre one-electron core resonance integrals $F_{\mu\lambda}$ are calculated from the overlap integral multiplied by a combination of one-centre terms:

$$\beta_{\mu\lambda} = \frac{1}{2}\left(\beta_{\mu} + \beta_{\lambda}\right)S_{\mu\lambda}$$

The overlap integrals are calculated analytically for Slater orbitals and, therefore, this term decays exponentially in the long-range limit and can be readily converged in real space within ca.10 Å, depending on the exponents. For the on-diagonal blocks, the sum of the two-centre one-electron core attraction and two-electron repulsion integrals represents the electrostatic-potential contribution. These contributions are slow to decay and cannot be truncated readily as, in the long-range limit, it takes the form of a Coulomb interaction. Consequently, care must be taken to evaluate these terms using a suitable lattice sum. In an earlier attempt to produce a solid-state program for MNDO calculations, called MOSOL,[18] these terms were handled by summing over complete unit cells. While this approach of the evjen type may lead to approximate convergence it has a number of undesirable characteristics. One of the primary difficulties is that atoms which are equivalent by symmetry may not end up with the same charge distribution, as they may be in different positions relative to the cut-off boundary. Also, difficulties will be encountered if the unit cell has a non-zero dipole moment.

In order to discuss how these terms can be handled in the long-range limit it is necessary to describe how the integrals are evaluated in the MNDO scheme. Rather than using exact integrals based on the Slater orbitals, which is expensive, the integrals are approximated by a set of multipole-multipole interactions

$$(\mu\nu, \lambda\sigma) = \sum_{l_1}\sum_{l_2}\sum_{m}\left[M^{A}_{l_1 m}, M^{B}_{l_2 m}\right]$$

For an sp basis, all charge distributions can be represented by combinations of suitable monopoles, dipoles and quadrupoles, where each multipole moment is generated by a series of point charges distributed about the atomic centre. Full details of these configurations can be found elsewhere[9].

The interactions between the point charges are evaluated using the Dewar-Sabelli-Klopman (DSK) formula:

$$I(r_{AB}) = \frac{1}{\left[r^2_{AB} + \left(\rho^{A}_{l_1} + \rho^{B}_{l_2}\right)^2\right]^{1/2}}$$

This has the correct behaviour, in that it tends to a pure Coulomb potential in the long-range limit and, by suitable choice of the ρ parameters, can be made to tend to the one-centre limit as well. At intermediate distances, the magnitudes of integrals calculated in this fashion are lower than for the exact expression, which reflects the empirical inclusion of correlation effects.

The DSK formula for the integrals can be directly manipulated into a long range sum by performing a Laplace transform in the same way that is used for the Coulomb operator in the Ewald sum(19). Unfortunately, the outcome of the Laplace transform is a Bessel function which leads to series expansions in both real and reciprocal space which are not guaranteed to be rapidly convergent. A simpler approach to the problem is to start from a series expansion in the limit of large distance:

$$a = \left(\rho^{A}_{l_1} + \rho^{B}_{l_2}\right) \text{ ; where } I = \frac{1}{\left(r^2 + a^2\right)^{1/2}}$$

for r>>a;

$$I \approx \frac{1}{r} - \frac{a^2}{2r^3} + \frac{3a^4}{8r^5} - \frac{5a^6}{16r^7} + O\left(r^9\right)$$

Based on this series expansion, we can calculate the integrals in the limit of large distance, using the more straightforward transforms of inverse powers of the distance. The leading term is just the standard Ewald summation, while the term involving the third power of inverse distance is given below (higher-order terms can be found elsewhere)[20]:

$$V(3,r)=\frac{1}{2}\sum_i\sum_j{}'C_{ij}\sum_d\frac{1}{r^3}\left[\begin{array}{l}\operatorname{erfc}\left(\eta^{\frac{1}{2}}r\right)\\ +2\left(\frac{\eta}{\pi}\right)^{1/2}r\exp\left(-\eta r^2\right)\end{array}\right]$$
$$+\frac{1}{2}\left(\frac{2\pi}{V}\right)\sum_G\sum_i\sum_j C_{ij}\exp(iGr)E_1\left(\frac{G^2}{4\eta}\right)$$
$$-\frac{1}{2}\left(\frac{4\pi}{3}\right)\left(\frac{\eta}{\pi}\right)^{3/2}\sum_i C_{ii}$$

Unfortunately, the lattice sum for the inverse third power of the distance is still a conditionally convergent series. Although there is no restriction that the coefficients must be separable into one-centre terms which sum to zero, as is the case for charges in the Ewald sum, there is the condition: $\sum_i\sum_j C_{ij}=0$

In this case the coefficients are functions of the *a* parameters from the DSK equation and the charges on the atoms: $\therefore\sum_i \rho_i q_i = 0\ C_{ij}=a_{ij}^2 q_i q_j=\left(\rho_i+\rho_j\right)^2 q_i q_j$

As a simplification, it is generally the case that, when the above criteria are satisfied, the contribution of the quadrupoles to the long-range potential is small, at the level of the accuracy of the method, and their contribution to the forces is even smaller. Hence, initially, we have only fully implemented the method for terms up to and including the dipole-dipole interaction. Quadrupolar terms can be included for the energy, but not yet for the derivatives.

The parameters for all methods used are the standard ones derived from the geometries, enthalpies of formation, dipole moments and other properties of gas-phase species. As yet, we have made no attempt to reparametrise for the solid state and one of the issues to be examined in this work is whether this is necessary or not. Based on the above formulation we will now examine a number of problems in the solid state to investigate the utility of the method[4].

## Results and Discussion

The adsorption of LAS over Iraqi bentonite was studied in previous experimented study[8] by using different LAS concentration and at different temperatures and range of pH. The modification of bentonite clay has been a accomplished to activate the surface of it, and to get better adsorption process for LAS molecules in the solution, the 1-Hexadecyl pyridinum bromide (HDPYBr) was adsorbebed on the surface of bentonite clay in the form of $CP^+$ which attached to the Bentonite, while for the sorption (adsorption + absorption) of LAS molecules on the surface of bentonite. The molecules orient themselves in a pattern that is completely different, and the adsorption was expected to be taken place at the external and internal surfaces of the modified bentonite clay. The sorption percentage of LAS on the modified bentonite has significantly increased, due to the strong interaction between the LAS molecules and the modified surface and the sorption percentage exceeds 81%, while the sorption of LAS on free bentonite clay at 298K is about 36%, so the modification process is profitable, and was increased the capacity of bentonite clay to accommodate LAS molecule on the surface of bentonite. In this study we use the AM1 semi-empirical method[9] to calculate :-

a-Electronic density.
b-Geometrical optimizing shape .
c-Molecular orbital energy .
d-Dipole moment (μ) .
e-Enthalpy of formation $\Delta H_f^{\circ}$ for the three modifier molecules and for LAS molecule.

The modifier molecules are :-

1-[1-Hexadecyl pyridinium bromide (HDPYBr)] which was used in the experimended study .
2-[1,12-dipyridiniododecane dibromide ($DPYDDBr_2$ )].
3-[Hexadecyl trimethyl ammonium bromide (HDTMA )].

Figs.(1-5) show the structures of Bentonite, LAS, HDPYBr, $DPYDDBr_2$ and HDTMA respectively.

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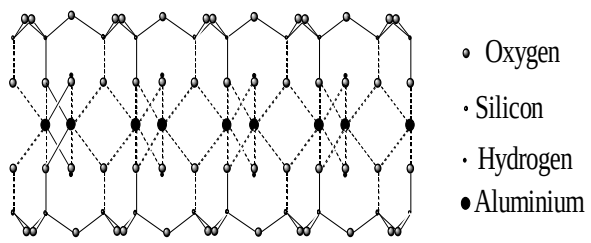



***Fig. (1).***

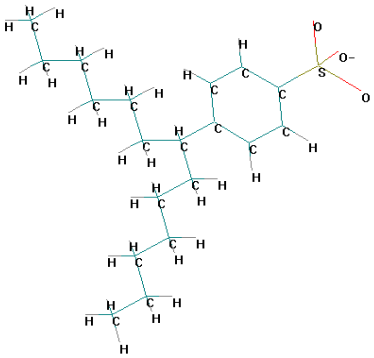
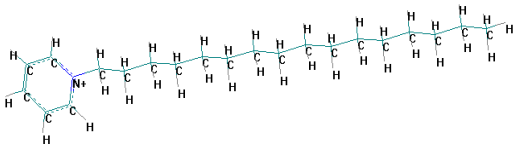


*Fig. (2).*



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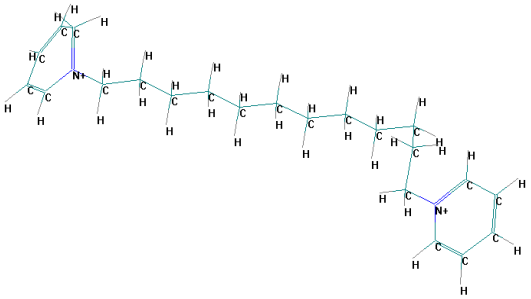

*Fig. (4).*

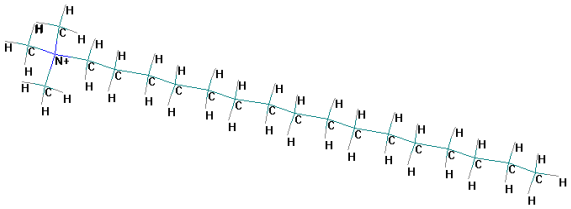

*Fig. (5).*

Figs.(1-5) show the structures of Bentonite, LAS, HDPYBr, DPYDDBr$_2$ and HDTMA respectively.

## Experimental

The work system specifications are:-

a-Microsoft windows XP Pack 2.
b-Hard Disc : 40 GB.
c-CPU : 1.72 GHz.
d-RAM : 128 MB.

By using AM1 semi-empirical implemented in the program package Hyperchem version 7.1 [Hypercube Inc. Gainsville FL.].

The geometrical structures and the distribution of electronic density of the four molecules [LAS,HDPYBr,DPYDDBr$_2$ and HDTMA] are shown in Figs.(6-9), the dark regions in the distribution of electronic density Fig.(B) due to the highly distribution of electronic density, while the bright regions are due to the lowest distribution of electronic density.

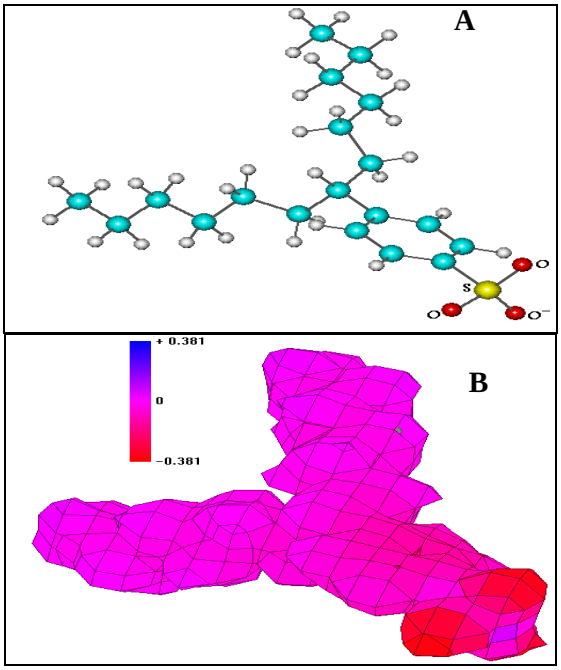


***Fig.(6) : A.Geometric shape B.distribution density for (LAS).***

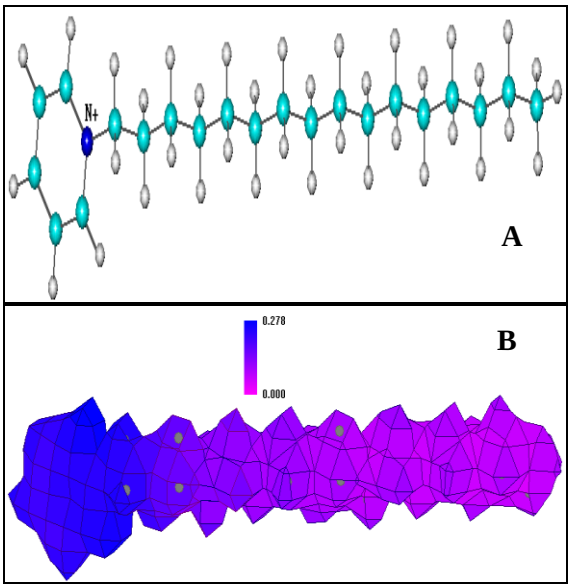


***Fig.(7): A.Geometric shape B.distribution density for (HDPYBr).***

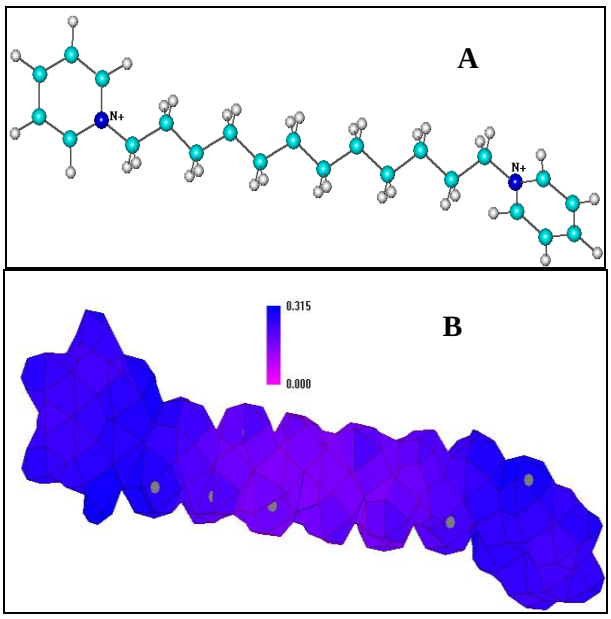


***Fig.(8) : A.Geometric shape***
***B. distribution density for ($DPYDDBr_2$).***

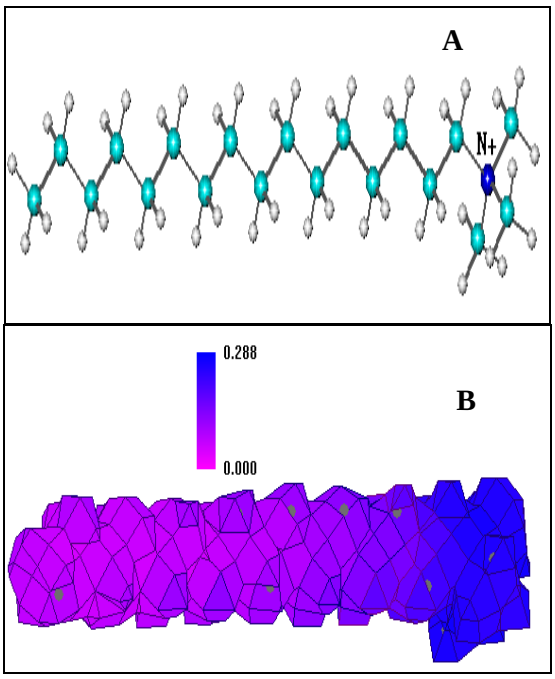


***Fig.(9) : A.Geometric shape***
***B.distribution density for (HDTMA).***

Table (1) gives the structure, molecular weight, enthalpy of formation $\Delta H_f^{\circ}$ and HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital) for the four molecules.

The $\Delta H_f^{\circ}$ data[10] reflect the stability of the four molecules as following :-

$$\Delta H_f^{\circ}(LAS) > \Delta H_f^{\circ}(HDTMA) > \Delta H_f^{\circ}(HDPYBr > \Delta H_f^{\circ}(DPYDDBr_2)$$

So the LAS molecule have the highest stability[$\Delta H_f^{\circ}$(LAS)=-216.23Kcal/mol] and the seriousness of LAS depend on its stability and the hardness to dissociated it by biodegradation or catalytic degradation or by light degradation, so LAS is very dangerous pollutant. $DPYDDBr_2$ gives the lowest stability [ $\Delta H_f^{\circ}$=324.77 Kcal/mol ].

***Table (1)***
***Values of calculated parameters for the four surfactants.***

| Substance | Formula | M . Wt (g/mol) | $\Delta H_f^{\circ}$ (Kcal/mol) | μ (D) | HOMO eV)( | LUMO (eV) | ΔE= (LUMO-HOMO) eV)( |
|---|---|---|---|---|---|---|---|
| **LAS** Linear Alkyl benzene Sulfonate | $C_{19}H_{31}SO^{-}_{3}Na^{+}$ | 352 | -216.23 | 26.85 | -6.3428 | 3.4649 | 9.8077 |
| **HDPYBr** 1-hexadecylpyridinium bromide | $C_{21}H_{38}N^{+}Br^{-}$ | 283.9 | 81.13 | 37.2 | -11.9547 | -5.4242 | 6.5305 |
| **$DPYDDBr_2$** 1,12-ipyridiniododecane dibromide | $C_{22}H_{34}N_2^{+}Br_2^{-}$ | 486.34 | 324.77 | 0.07 | -14.7146 | -6.2918 | 8.4228 |
| **HDTMA** Hexadecyltrimethyl ammonium bromide | $C_{19}H_{42}N^{+}Br^{-}$ | 320.01 | 51.81 | 38.50 | -11.9747 | -3.9823 | 7.9924 |

Fig.(10) show the HOMO and LUMO energy level for LAS and the three modifiers.The different energy between HOMO and LUMO leveles (ΔE) for each molecules reflect the energy require to translate electron to excited state(from HOMO to LUMO)[11,12]. The ΔE values are given in table(1)and the sequence became as:-

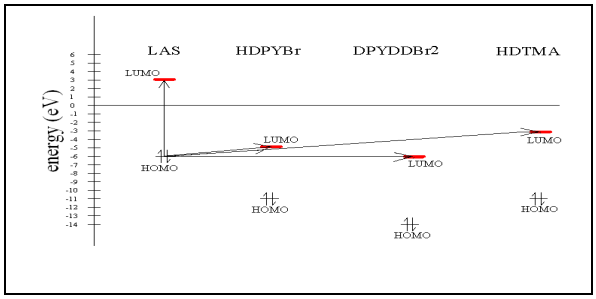


***Fig.(10): Correlation digram of HOMO and LUMO levels for LAS and the three modifiers.***

( LAS ) > ΔE ( $DPYDDBr_2$ ) > ΔE ( HDTMA ) > ΔE ( HDPYBr )

The ΔE values for the four molecules reflect the different in physical and chemical activity of the different four molecules, that's mean the higher value of ΔE reflect the lowest activity against light and chemical reaction[11,12].According to the HOMO and LUMO leveles for LAS and the three modifiers Fig.(10) the sequence energy required to translat electron for HOMO of LAS to the LUMO of the three other molecules was as :-

$DPYDDBr_2$ < HDPYBr < HDTMA 0.0510 eV < 0.9186 eV < 2.3605 eV

So the efficiency of the three modifiers was as :-

$DPYDDBr_2$ > HDPYBr > HDTMA

From experimental adsorption results we found that HDPYBr give 81% efficiency to modified bentonite clay and by compare this efficiency with the different energy leveles in Fig.(10), the expected efficiency for $DPYDDBr_2$ was reached to 1300 time more than HDPYBr.

The LAS molecule can be bonded with two $N^+$ groups in $DPYDDBr_2$ (Figs.(4,8)). The efficiency of HDTMA expected to reach to 29.09% according to the different between (LAS) HOMO and (HDTMA) LUMO Fig.(10 ).

## Conclusion

Certain conclusions can be derived from the results and discussions as in following :-

1-Semi-empirical method calculation gives good information to study the adsorption of any organic or inorganic polluants on any surface after using modifier molecules like anionic or cationic surfactant and the best modifier can be selected theoretically.

2-It can be used the theoretical data to study the photodegredation of different polluants and there chemical stability and comparison this data with the experimental study.

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**الخلاصة**

تتضمن الدراسة استخدام الطرق شبه التجريبية (Semi–empirical method) في حساب طاقات الاوربتالات الجزيئية لاقتراح أفضل مادة فعالة سطحياً يمكن إن تستخدم لتحسين امتزاز مادة Linear propadecyl benzene Sulfonate (LAS) على طين البنتونايت العراقي بمقارنة النتائج النظرية مع نتائج عملية سابقة أجريت بين LAS وطين البنتونايت المطعم أو المبلمر مع 1-Hexadecylpyridinium bromide (HDPYBr).

وتبين من الحسابات كفاءة كل من Hexadecyltrimethyl ammonium chloride (HDTMACl) ومادة 1,12-dipyridiniododecane dibromide ($DPYDDBr_2$) كمحسنات للطين في امتزاز مادة (LAS) .

كما تم أجراء حسابات على مادة HDPYBr المدروسة عملياً وتظهر النتائج أن كفاءة الامتزاز على النحو التالي :-

$HDPYDDBr_2 > HDPYBr > HDTMACl$

كما اشتملت الدراسة على مقارنة أستقرارية المواد الأربعة اعتمادا على حرارة التكوين المستحصلة من الحلول النظرية وكذلك من خلال حساب الفرق الطاقي بين مستويات HOMO و LUMO للجزيئات الأربعة.

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