

Multilayer Adsorption of Poly Donor Organic Molecule on Heterogeneous Steel Surface from Inhibited Pickling Acid Solutions as a Function of the Adsorbate, and Acid Concentrations

A.R. Ismaeel*

Chemistry Dep., Faculty of Science, Garyounis University, Benghazi, Libya

*Corres.author: riadbasha2003@yahoo.co.uk

Abstract: The adsorption of, the large molecular size non electrolyte 1-(3- amino-4-phenylazopyrazol -5 yl)-3-benzoylthiourea (PSU) on heterogeneous steel surface from sulfuric acid solutions was studied in the light of the fact that (PSU) is consider as poly dentate adsorbate having seven nitrogen, one sulfur, and one oxygen electron donor atoms in addition to eleven pi bonds suitable for planar adsorption of the molecules on the solid heterogeneous steel surface.

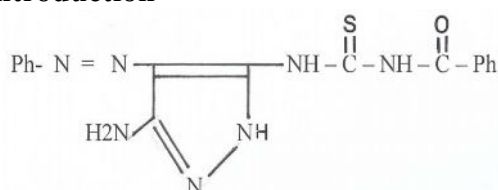
The electrochemical, weight loss study, and application of the Ismaeel adsorption isotherm which is suitable and applicable to our results, indicate multilayer adsorption by illustrating more than one adsorption equilibrium constant for each layer. The isotherms give us the adsorbate concentration satisfying the formation of each layer after which the formation of the second layer start, this concentration depends on acid concentration as it increased by increasing acid concentration due to withdrawing of water molecules adsorbed on metal surface by acid ions during formation of its primary hydration sheath, which enhancing (PSU) adsorption by replacement of water molecule. At certain higher acid concentration salting in process of organic non electrolyte molecules (PSU) by acid ions started for forming acid secondary solvation sheath, as acid ions prefer (PSU) molecules on water due to (PSU) higher dispersion dipole moment, leading to decreases of free (PSU) molecules in solution bulk leading to the decreases of its adsorption.

The adsorption free energy change was calculated for each adsorption layer at each acid concentration indicating chemisorptions of high spontaneity, but at higher acid concentrations the adsorption free energy change of the upper layer indicates low spontaneity of the adsorption due to the decrease of concentration of (PSU) in solution bulk, as a result of salting in processes acting on the upper layer.

We postulated that the high efficiency of (PSU) as a steel corrosion inhibitor, is due to the thickness of its multilayer non electrolytic barrier against acid ions which indicated by high polarization resistant, and concluded that the pickling acid concentration must not exceeding the maximum value to get maximum inhibition efficiency, and to save both the un effective acid and inhibitor coasts.

Key words: Multilayer, Adsorption, Isotherm, Poly Donor, Heterogeneous, Corrosion, Pickling.

Introduction



The non electrolyte of large molecular size 1- (3-amino-4-Phenylazo Pyrazol-5yl) -3-benzoyl thiourea (PSU) [1-3] was used as corrosion inhibitor for low carbon steel in sulfuric acid solutions where it acts by

surface coverage adsorption on heterogeneous steel surface making use of its large molecular size and poly donor atoms, nitrogen, oxygen, and sulfur in addition to its eleven pi bonds [1-3]. This processes was used in determination of the primary hydration number of sulfuric acid [1] where the adsorption processes considered as a replacement of water molecule adsorbed on steel surface by (PSU) molecules, as the concentration of sulfuric acid increase it withdraw water molecules from metal surface to form its primary hydration sheath, which increasing the chance of (PSU) to replace water by adsorption on metal

surface. The surface coverage increase till the complete formation of acid primary hydration sheath at certain acid concentration [1], at higher acid concentration the (PSU) molecules is used in completing of acid secondary solvation sheath due to the salting in of (PSU) molecules by the acid ions preferring it on water molecules due to the higher dispersion dipole moment of (PSU) than that of water [1,4,5], which leads to the decrease of free (PSU) in solution bulk which lead to decrease of its adsorption on metal surface by more increase of acid concentration.[1]

So the sulfuric acid ions has two opposite actions on the adsorption processes one is the enhancing (PSU) in replacement of water molecules and adsorption on metal surface at low and moderate acid concentrations, the other opposite actions is its competing with (PSU) molecules for replacement water molecules or for adsorption on metal surface, in addition to its action at higher acid concentration by decreasing (PSU) free molecules in solution due to (salting in) processes of (PSU) [1,4,5].

Ismaeel [6, 7] predict adsorption isotherm concerning the dual competing and enhancing actions of acid ions on the adsorption of organic molecule on heterogeneous steel surface represented by the equation

$$\text{Log}[\theta / (1 - \theta)] = \log(r_{12} / m C_2) + C_1 C_2 r_{12} m \log K \dots\dots (1)$$

where θ is the surface coverage fraction, C_1 is (organic molecule) concentration, C_2 is acid concentration, r_{12} is the size ratio of organic molecules to that of acid anions, m is the heterogeneity parameter of the surface, and K is the adsorption equilibrium constant. Ismaeel isotherm is applicable to adsorption of benzotriazol from hydrochloric [6] and sulfuric acid [7] solutions

The aim of our work was to study the effect of large molecular size non electrolyte (PSU) with structure having poly donor atoms and sites on its adsorption, expecting planer chemical adsorption of high spontaneity, and to find the suitable applicable adsorption isotherm.

Experimental Methods

All chemicals are of analytical grad, water used for solutions preparations, and for electrodes and samples final washing was of conductivity 4×10^{-6} S. Sulfuric acid solutions of concentrations C_2 equals 0.5, 0.75, 1.0, 1.25, 1.5, and 2.0 M containing (PSU) of concentrations C_1 equals 0.5, 1.0, 1.25, 2.5, 4.0, and 5×10^{-4} M in each of the acid concentration C_2 at 30 °C was prepared

The needed precautions of preparation of the specimens for the mass loss, and electrodes for the polarization techniques as, isolation, polishing,

degreasing, washing, and drying was taken into account [1, 6 – 9,].

The Galvanostatic polarization technique [9 – 14] was followed on steel electrode in sulfuric acid of 0.5 M containing C_1 (PSU) Concentrations at 30 °C.

The mass loss technique was applied on specimens in the form of circular discs has cross-sectional area of 5 cm², and thickness of 4 mm completely isolated from test solution with a thick layer (3 mm) of araldite resin except one of its circular surfaces for exposure to test solutions of (500 ml) pure and inhibited sulfuric acid solutions for exposure time 2 hours during which specimen rotate magnetically acting as self stirrer for test solution. The surface coverage θ was calculated from the equation (2) where W_1 , and W_2 represents the corrosion rates (mass loss per unit time per unit area) in pure and inhibited acid solutions respectively

$$\theta = (W_1 - W_2) / W_2 \dots\dots\dots (2)$$

Taking into account that the metal density is the same in the two cases, the mass loss was calculated by indirect and accurate analytical method, by titration of the dissolved iron ions in solution (corrosion product) using standard 0.01M potassium dichromate solution [6 - 9, 15]. The mass loss = mass of dissolved Fe x 100 / %Fe, where the %Fe in the sample was determined by digital Quantometer for (emission spectroscopy).

In both the Galvanostatic and mass loss technique air was removed from the test solution by passing argon gas for (1 hour) just before exposure. The temperature was maintained at 30 °C using air thermostat

Results and Discussion

From the Galvanostatic results, the Tafel lines represent the relation between Log polarization current density (A / Cm²), and the corresponding polarization over potential (V) for pure 0.5M sulfuric acid and that contain different (PSU) concentrations C_1 are parallel and only shifted by the increase of C_1 indicating no change in cathodic hydrogen evolution mechanisms where the slope of all cathodic Tafel lines are (bc = 104 mV / decant) The values of surface coverage θ are calculated at any polarization potential from the shift of Tafel lines of the inhibited solution from that of pure acid solution.

The polarization resistance R_p (Ohm. Cm²) is increases as C_1 increases. with the same trend of increase of surface coverage θ (as it will seen in figure of isotherm) this confirm that the inhibition is due to surface coverage by (PSU) molecules.

From the results of mass loss technique the values of the surface coverage θ were calculated, the variation of θ with the increase of acid concentration C_2 containing different (PSU) concentrations C_1 is

shown in figure(1) where % efficiency = $\theta \times 100$, the figure indicate

The effects of sulfuric acid concentration C_2 on the adsorption of the non electrolyte of large size molecules (PSU) on solid heterogeneous steel surface is summarized as:

- As acid conc. C_2 increase its ions withdraw water molecules adsorbed on the steel surface to complete acid primary hydration sheath, which enhance the adsorption of (PSU) by replacing water (θ increased).
- At higher C_2 values the adsorption of non electrolyte decreases due to the decrease of its free molecules in solution bulk as a result of (PSU) salting in processes by acid ions to complete acid 2nd solvation sheath. (θ decrease).
- So sulfuric acid has opposite dual effects on (PSU) adsorption.

On applying different adsorption isotherm as Temkin, frumkin, hennery, and Langmuir,s, which shows physical adsorption of low adsorption spontaneity where $-\Delta G$ values ranged from 11.0 to 22.0 KJM⁻¹ while that of chemical adsorption are in the rang from 40 to more than 80 KJM⁻¹ [16,17]. So the results from the mentioned isotherms are not in agreement with the high values of θ and high corrosion inhibition efficiency of (PSU) reached 98%, and not expected as

a result of adsorption of such poly donor large size molecule expecting to undergo planer chemical adsorption on steel surface. Also these isotherms did not indicate multilayer formation.

Ismaeel adsorption isotherm[6,7] represented by equation (1), is applicable on the results where the size ratio of (PSU) molecule to that of sulfate anion r_{12} calculated from bonds lengths and angles [6,7,18] to be $r_{12} = 11.8747$.

The relation between (PSU) concentration C_1 and $\text{Log} [\theta / (1 - \theta)]$ give straight line of **slope** = $C_2 m r_{12}$ **Log K**, and **intercept** = $\text{Log} (r_{12} / m C_2)$. From the value of intercept, (m) is calculated, substituted m , r_{12} , and C_2 in the value of the slope, **Log K** is determined. The Gyps free energy change $\Delta G = -2.303 R T \text{Log K}$ where **R** here is the gas constant, and **T** = **303.15 Kelvin** for all solutions.

Effect of (m),&(C₂) on the Spontaneity of Adsorption processes:

- 1- The Slope indicate that $[\log K \propto 1/m]$, or $[\text{adsorption spontaneity} \propto 1/m]$
- 2-The intercept value indicate that $[C_2 \propto 1/m]$, so $[C_2 \propto \log K]$ this represents the enhancing effect of the acid at its low concentration.
- 3-The values of \dot{C}_2 in the slope represent the competing effect of the acid at higher concentration at which acid solvated by (PSU) $[\log K \propto 1/\dot{C}_2]$.

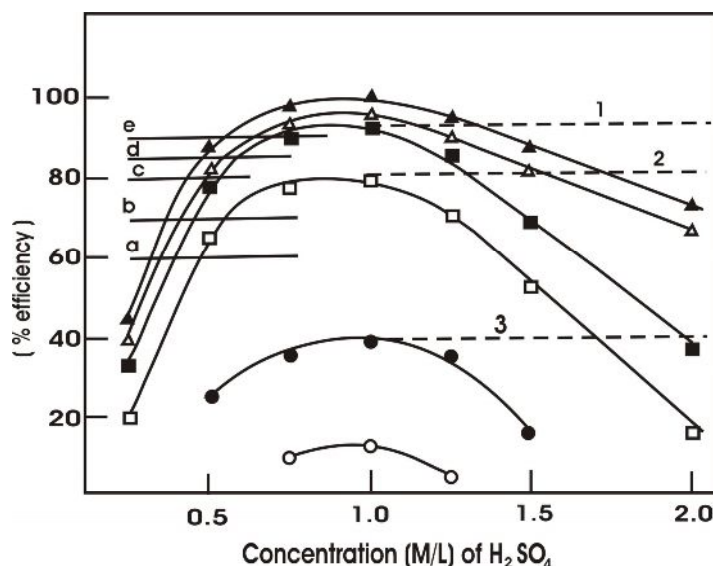


Fig. (1) Relation between % Efficiency of (PSU) As corrosion Inhibitor of Carbon Steel at Conc. Of $[1 \times 10^{-5} \text{ M} \circ, 5 \times 10^{-5} \text{ M} \bullet, 1.25 \times 10^{-4} \text{ M} \square, 2.5 \times 10^{-4} \text{ M} \blacksquare, 4 \times 10^{-4} \text{ M} \triangle, 5 \times 10^{-4} \text{ M} \blacktriangle]$ and Conc. Of H_2SO_4 solutions at 25 C°

Fig.(1) Represents the relation between % efficiency of (PSU) as corrosion inhibitor of carbon steel at Conc. of $[10^{-5}, 5 \times 10^{-5}, 1.25 \times 10^{-4}, 2.5 \times 10^{-4}, 4.0 \times 10^{-4}, 5 \times 10^{-4} \text{ M}]$ and the Conc. of sulfuric acid solutions at 25 C°

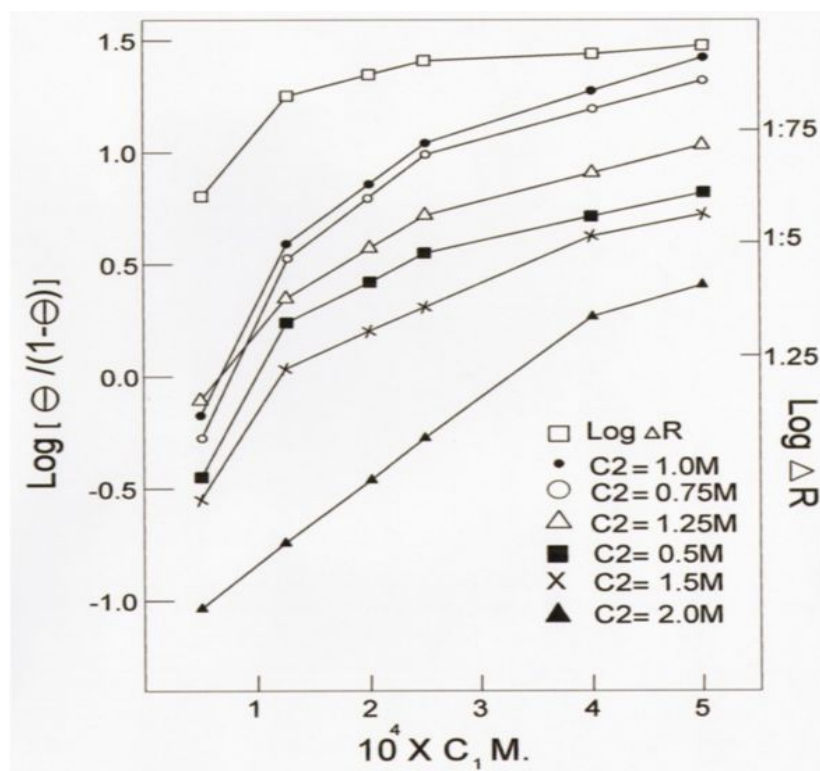


Fig. (2) Ismaeel adsorption isotherm at 30C° indicating the multilayer adsorption of (PSU) on heterogeneous steel surface from solutions of different acid C_2 , &(PSU) C_1 Conc. Showing the variation of $[\text{Log } \Delta R_p]$ verses C_1 with the same trend as that of $\text{Log } \theta / (1 - \theta)$

Figure(2) show that Ismaeel adsorption isotherm [6,7] is applicable for all sulfuric acid solutions of concentrations C_2 each containing (PSU) concentrations C_1 . The isotherm illustrate multilayer adsorption lines with different slopes and intercepts leading to different values of (m), ($\text{Log } K$), and (ΔG) for each layer. Since the line of the second layer started after the 1st layer had been completed [19,20]. Accordingly:

1- The (PSU) concentration ($C_1 = 1.25\text{M}$) at the end of the 1st layer is the concentration needed for the formation of the 1st layer

2- The value of ($C_1 = 2.5 \times 10^{-4} \text{ M}$) at the end of the 2nd layer give the concentration needed for the formation of the 1st + the 2nd layers, at which the 3rd layer started.

At low and moderate values of acid concentrations C_2 (from 0.5 to 1.25 M) , The values of concentration C_1 in 1, and 2 didn't affected by increasing the acid concentration C_2 .

3- At ($C_2 = 1.5 \text{ M}$) the (PSU) concentration C_1 needed to form the 1st + the 2nd layer at which the formation of the 3rd layer started equal ($4 \times 10^{-4} \text{ M}$) [instead of 2.5×10^{-4} at lower C_2], Due to the previously mentioned salting in of (PSU) with the acid ions at high concentrations

4- At ($C_2 = 2.0 \text{ M}$) of C_1 needed to form the 1st layer only at which the formation of the 2nd layer started and didn't complete, equal ($C_1 = 4 \times 10^{-4} \text{ M}$) instead of ($1.25 \times 10^{-4} \text{ M}$) at low C_2 , due to the previously mentioned salting in processes.

5- Fig (2) also illustrate that the variation of $\text{Log } \Delta R_p$ with the increase of (PSU) concentration C_1 at $C_2 = 0.5 \text{ M}$ increase with the same trend as that of $\text{Log } [\theta / (1 - \theta)]$, (where ΔR_p is the change of the cathodic polarization resistant in (PSU) solution from that of pure acid solution), and show the same definite adsorption layers which Confirmed the surface coverage inhibition, and the formation of multilayer's.

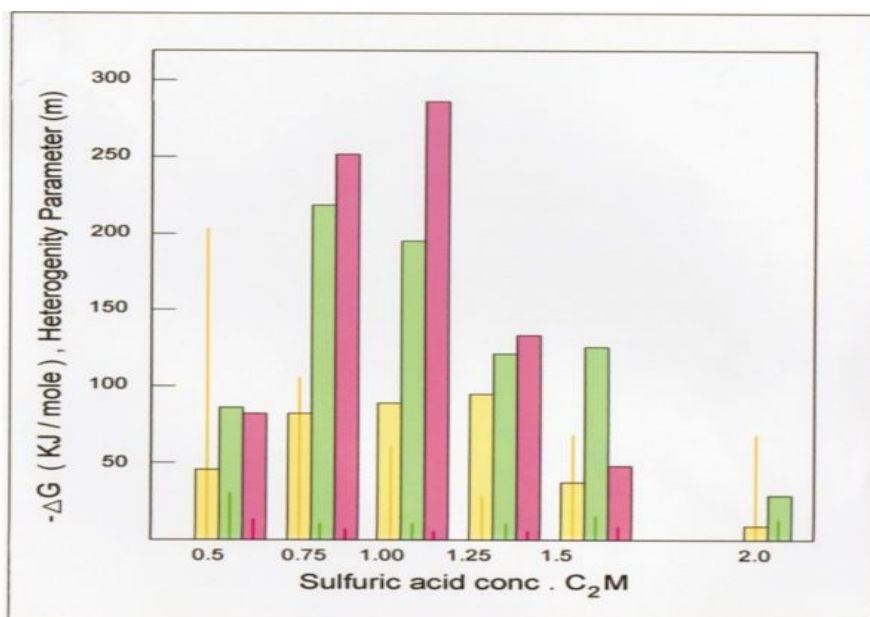


Fig. (3) A diagram represent the values of free energy change ΔG of the 1st layer (yellow column), 2nd layer (green column), & 3rd layer (pink column) at different acid conc. C_2 with heterogeneity parameter (m) represented by the lines in the middle of each column

In figure (3) the values of the adsorption free energy change $-\Delta G$ of each layer at different acid concentration C_2 represented by the columns, and the values of the heterogeneity parameter (m) indicated by lines in the middle of each Column. The figure indicate that the spontaneity of the 3rd layer is greater than that of the 2nd layer which is greater than that of the 1st layer which explained to be due to the effect of the nature of the surface at which the layer adsorbed represented in its heterogeneity parameter (m) as it has high values in the 1st layer where the steel surface have high heterogeneity due to containing cathodic, and anodic sites in addition to atoms of alloying elements as carbon, sulfur, manganese, silicon, and ect. with some parts of the adsorbed water molecules on the surface which are not suitable to adsorption of (PSU) molecular size, at equilibrium and the end of 1st layer, the heterogeneity parameter of the 2nd layer has less value because (PSU) molecules were adsorbed on the planar homogeneous (PSU) 1st layer of identical molecules suitable for forming chemical adsorption on its identical molecules. The 3rd layer had the minimum values of (m) in all acid concentration C_2

because the 1st layer formed on heterogeneous steel surface but the 2nd layer formed on the surface of the 1st layer having more homogeneity than metal heterogeneous steel surface but not completely homogeneous because it is still affected by its steel base, so the 3rd layer formation has the lower values of heterogeneity parameter (m).

The results also indicate the increase of spontaneity of adsorption processes represented by the ($-\Delta G$) value of the 1st layer with the increase of acid concentration till $C_2 = 1.25\text{M}$ due to the withdrawing of water molecules from metal surface by acid ions to form its primary hydration sheath enhancing (PSU) water replacement, then spontaneity decreases by the increase of C_2 to 1.5, and 2.0 M. as a results of salting in processes of (PSU) taking place at higher acid concentrations. The same maximum spontaneity behavior occurred to the second layer at lower $C_2 = 1.0\text{ M}$, and occurred in the 3rd layer at $C_2 = 0.75\text{ M}$ because as acid concentration C_2 increase it needs more (PSU) for salting in processes. The results are illustrated in table (1)

Table (1) Summaries the resulted heterogeneity parameters (m) and spontaneities of each layer with explanation of reasons of the change of its values from layer to another .

1-The resulted value of the Heterogeneity Parameter (m) of:	The reason explaining the results
The 1st layer has the highest value of (m)	Its adsorption is on heterogeneous steel surface contain cathodic ,and anodic sits in addition to alloying elements as Mn, C, p, Si,ect., adsorbed water molecules, HSO ₄ ⁻ , H ⁺ , and H ₂
The values of (m) of the 1 st layer decreases as the acid concentration C ₂ increases	Because as C ₂ increases, the adsorbed water on the solid surface decreases leading to the decreases of the surface heterogeneity which affect that of the following layers
The 2nd layer has lower (m) than the 1 st layer	Its adsorption is on the 1st layer formed only of (PSU) molecules having more homogeneity but still affected by the heterogeneity of its base metallic heterogeneous surface
The 3rd layer has minimum value of (m)	Its adsorption is on the 2nd layer formed of the more homogeneous identical (PSU) molecules
The adsorption spontaneity of the 3 ^{ed} layer is grater than that of the 2 nd which is grater than that of the 1 st layer	As a result of the decrease of (m) with the same order [spontaneity \propto (1/m)]

Conclusions

- 1) In studies of the adsorption of large size none electrolytic molecules from solution contain electrolyte, on solid surface we have to tack into account the effects of electrolyte concentration on the adsorption of the non electrolyte.
- 2) In using electrolytic pickling acid solution with non electrolytic inhibitor, we have to considering both the inhibitor and acid concentrations that give maximum efficiency for saving the coasts of the harmful higher acid concentration, and the desorbed inhibitor due to salting in processes at this concentrations.
- 3) To apply Ismaeel adsorption isotherm which considering the effects of heterogeneity of the solid surface, and the electrolyte concentration, the mode of adsorption suitable for molecular structure, the size ratio of the two adsorbate, and multilayer formation, on the adsorption processes
- 4) In case of multilayer adsorption, To make use of Ismaeel adsorption isotherm to give the adsorbate concentration needed to complete the formation of

each layer, and its adsorption spontaneity indicated by the value of the free energy change.

Acknowledgment

Special thanks and appreciation to Dr. Mohamed Helmi Elnagdi, distinguish Professor of heterocyclic chemistry, Chairman of Chemistry Department - Faculty of Science-Cairo University, and, in Kuwait Univ.), for suggesting, and introducing this compound for acting as very good adsorbate on steel surface.

Acknowledgment to the Souls of Dr. Mohamed Saber El Basiouny, and Dr. Badre Ghazi Atya, Professors of Physical Chemistry, Chemistry Department , Faculty of Science , Cairo University for continuous encouragement and enhancing.

Acknowledgment to Dr. M.N. Ibrahim, Professor of organic chemistry, Garyounis University, for confirming my postulate for (PSU) planar adsorption on steel surface through its electron donor atoms and pi bonds.

References

- [1] A. R. Ismaeel, International Journal of Chem. Tech. V(2) NO. 2 [Apr.– Jun.] 2010
- [2] A.R. Ismail, M.M. Hefny, A. Elkot. And M.S. El – Basiouny; Asian J. Chem. Vol. 4, No 3, pp469 – 480 (1992).
- [3] M.H. Elnagdi, and Sanoa, O. Abd Allah., J. Prackt. Chem. 315 (6), 1009 (1973).
- [4] John O'M Bokris, and Amulya K.N. Reddy, Modern Electrochemistry Vol. (1) , second edition chapter (2) P. 173 –175 .
- [5] Raymond Chang, Physical Chemistry for the Chemical and Biological Sciences, edition 2000 chapter 8 P 274 (By university science books California).
- [6] A.R. Ismaeel , Asian Journal of Chemistry, Vol.18,No.3 (2006), 2081 – 2088
- [7] A.R. Ismaeel , Asian Journal of Chemistry, Vol. 19 ,No. 5 (2007), 3688 – 3696
- [8] A.R. Ismaeel, S.S. Abdelrhim, and A.E. Abdou, , Asian Journal of Chemistry, Volume 19, No. 6(4665 - 4673).
- [9] Annual Book of ASTM Standards, PART 10,G31-72,876(1980)
- [10] A.R. Ismaeel, S.S. Abdelrehim , and A.E. Abdou, Proceeding of the 6th Libyan Corrosion Conference, Tripoli, Libya, 12 – 14 / 11 /2007
- [11] A.R. Ismaeel, Proceeding of the 6th Libyan Corrosion conference, Tripoli, Libya,12 – 14/11/2007.
- [12] Lyon.s., & El Sahli, H.A.A., Libyan corrosion society, the 5th Libyan corrosion conference and Exhibition, Benghazi, Libya, P161-165. 2005.
- [13] Bereket, G.,yurt, A., kandemir, S.U., Baluaban, A., and Erk, B., Advanced Battaries and Accumulations-ABA,2004
- [14] Fontana, M.G. Corrosion Engineering, pp499-503.Mc-Graw-HILL-Singapore,1987.
- [15] A.I. Vogel, A Textbook of Quantitative Analysis, Longman Green and Co., London, edn.2,p 296(1973).
- [16] A.W. Marczewski Practical Guide to Isotherms of Adsorption on Heterogeneous Surfaces,2000,AWM,s adsorption page, site (isotherm.adsorption.org)
- [17] Karatschmer, W.; Rathousky,J. ;Zukal,A., Carbon,1999,37,301.
- [18] Vilkov.L.V., Mastryukov.V.S., Sadova. N .I., Determination of the Geometrical Structure of Free Molecules, English translation, Mir publishers,Moscow1983..
- [19] Leszek Czepirski, Mieczyslaw R.Balys, Ewa Komorowska – Czeprska., Some Generalization of Langmuir Adsorption Isotherm., Internet Journal of Chemistry,2000,3,14[ISSN; 1099-8292] Article 14.
- [20] Multilayer Adsorption of Ions , and Non Electrolyte from electrolytic and Non Electrolytic Solutions , Site [glossary.sorption.org)]
