

Determination of Primary Hydration Number of Sulfuric Acid by Taking "Salting In Processes" of Nonelectrolyte by Acid Ions as A monitor for Following the Acid Hydration Processes

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Abstract :The nonelectrolyte of large molecular size 1- (3 - amino - 4 - Phenylazo pyrazol-5-yl)-3-benzoylthiourea (P.S.U.) was used as inhibitor of corrosion of low carbon steel in sulfuric acid solutions where acting by surface coverage adsorption on metal surface. The change of its percent inhibition efficiency (% surface coverage) with increasing acid concentration shows a maximum values at critical acid concentration of (IM./L) for all (P.S.U.) concentrations .

The increase of (% efficiency) before the maximum was explained to be due to increase of adsorbed (P.S.U.) molecules on metal surface replacing water molecules which desorbed to from the primary hydration sheathe of acid ions. After the maximum the decrease of (% efficiency) is due to processes of "Salting In" of (P.S.U.) molecules by acid ions. From the values of rate of desorption of water molecules by increasing acid concentration , the (P.S.U.) Concentration at which primary hydration layer is completely formed, and the critical acid concentration, the primary hydration number of sulfuric acid was calculated to be 21.84 Mole of water / gram Mole of sulfuric acid .

Key words: Primary Hydration Number, Salting In Processes, Nonelectrolyte, Acid Hydration Processes

Introduction

The nonelectrolyte of large molecular size 1- (3 – amino – 4 – Phenylazopyrazol – 5 – yl) – 3 – benzoylthiourea (PSU) [1],[2] has 11 pi bonds, 7 nitrogen atoms, and 1 sulfere atom presented the molecule as good adsorbate. It has also asymmetric structure, expected to has a roll with the solvation processes.

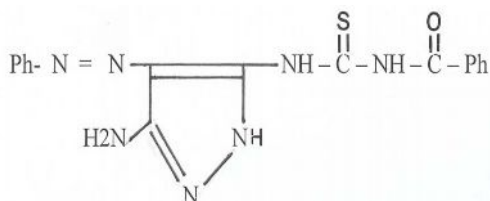
Bockris [3] proposed the term "primary solvation number for the number of molecules near to an ion which lost their translational degree of freedom and move as an entity with ion during its Brownian motion , accordingly, the primary solvation number is a definite quantity while the secondary solvation caused by electrostatic interaction beyond the first solvation shell depends on the type of property observed.

There are various methods for investigation of solvation or hydration number (Nh) of electrolytes [4], which show different values for the same electrolyte [5,6].

Although sulfate and mono hydrogen phosphate ions has the highest hydration power in Hofmister series [7]. $[SO_4^{2-}, HPO_4^{2-} > \bar{F} > \bar{Cl} > \bar{I} \cong ClO_4^- \cong NO_3^- > SCN^-]$, No investigation of hydration number of neither sulfate anion (SO_4^{2-}) nor sulfuric acid is present in literatures [4-6]

As most of thiourea derivatives, which was repeatedly recommended as inhibitors for metallic corrosion in acid solutions specifically adsorbed on metal surface [8 – 11] (P.S.U.) acting as corrosion inhibitor for low carbon steel in sulfuric acid solutions

making use of its large molecular size . [11],[12] Non electrolyte of large molecular size and non symmetric molecule has high dispersion forces, when dissolved in aqueous electrolytic solution of high concentration, the non electrolyte are suffering "Salting In" Process by the ions of electrolyte which prefer it on water molecules due to the higher dispersion dipole moment of the nonelectrolyte [12-14].



Experimental Methods

The used chemicals :-

1 – All chemicals used were of the analytical reagent grade .

2 – Water used to prepare test solutions and for final washing was of conductivity grade, its specific conductance ranged from 2×10^{-6} to 4×10^{-6} ohm⁻¹ cm⁻¹

3 – The nonelectrolyte (PSU) was prepared and recrystallized several times and its purity was checked by measuring its melting point (m.p. 220 C°) [1]

Test solutions :-

A set of sulfuric acid solutions of concentrations 0.25M, 0.5 M , 0.75 M, 1.0 M , 1.5 M , and 2.0 M was prepared , another set of inhibited acid solutions with (P.S.U.) Were prepared from each of the previous acid solutions with concentrations 1×10^{-5} M, 5×10^{-5} M, 1.25×10^{-4} M, 2.5×10^{-4} M, 4×10^{-4} M, and 5×10^{-4} M (P.S.U.).

Steel specimens :-

Specimen of low carbon steel in the form of a disc which has cross-sectional area of 5 cm², and thickness of 4 mm , was completely isolated from test solution with a thick layer (3mm) of Araldite resin (ciba – production , switzerland) except one of its circular surface for exposure to test solutions .Specimen was reused after polishing and cleaning so we were shore of the same exposed area and structure in each test .

Specimens exposed to test solutions at 25 C ° by using air thermostat for fixed time of 60 minutes during which specimen rotate magnetically in test solutions acting as self stirring

The mass loss corrosion test technique :-

This technique was followed in determining the effectiveness of (P.S.U.) as (corrosion inhibitor) [3,4,10,12],[15-18] as specimens exposed surface was polished by metallurgical emery papers (120 to 800) , water washing , acetone washing , and drayed. After exposure time 60 minute to test solution , specimens was washed with hot conductivity water during brushing by hard plastic brush till complete removal of corrosion products, the washing water was added to test solution for determination of dissolved iron. nearest 0.0001 gram by volumetric determination of iron using standard solution of 0.01 M. K₂Cr₂O₇ where

1 ml of 0.01M K₂Cr₂O₇ = 1.675×10^{-3} gram Fe

Mass loss of steel = mass of iron determined x (100 / %of iron in steel)

The % of iron in steel samples was determined by technique of emission spectroscopy using ARL quantemeter (model 31000-292 IC)

The mass loss per unit area per unit time for pure acid solutions (W1) and for the same concentration inhibited acid solutions (W2) were determined

The effectiveness of (PSU) as corrosion inhibitor is given by the relation

$$\text{The \% effectiveness} = [(W_1 - W_2) / W_1] \times 100$$

Results and discussion

The results are given in Fig. (1) which shows the relation between sulfuric acid concentrations, (P.S.U.) concentrations and the effectiveness (% efficiency) of (P.S.U) as inhibitor of corrosion of Low carbon steel by acid solutions. The relations indicating the increase of % efficiency with the increase of (P.S.U.) concentration and with the increase of sulfuric acid concentration to reach a maximum values at sulfuric acid concentration of 1M/L for all (P.S.U.) concentrations .This behavior (before reaching the maximum) was explained in the light of the fact that the increase of acid concentration decrease the adsorbed water molecules on metal surface through the formation of the primary hydration layer of the acid ions , these water molecules is replaced by (P.S.U.) molecules adsorbed on metal surface which increasing percent surface coverage , and so the percent inhibition efficiency increase [8,12 ,20 ,21], till maximum values where there is no further water molecule able to be desorbed from metal surface, and an equilibrium is reached between the adsorbed inhibitor molecules and the desorbed water molecules .

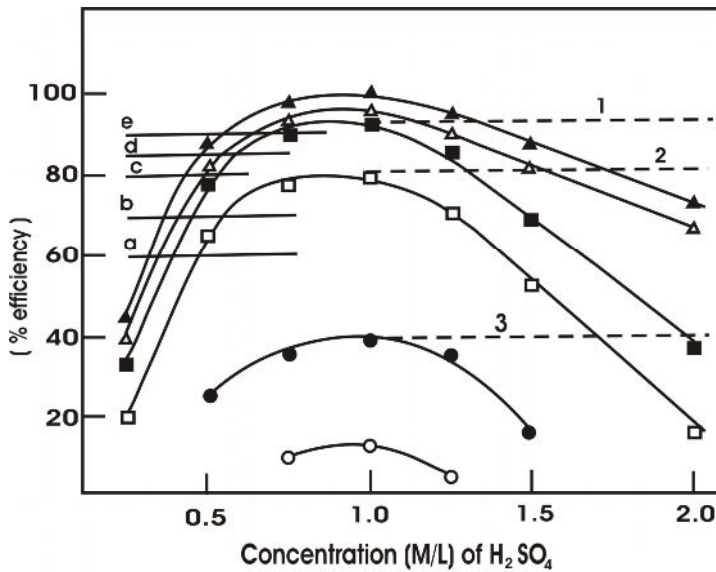


Fig. (1) Relation between % Efficiency of (P.S.U.) As corrosion Inhibitor of Carbon Steel at Conc. Of [1×10^{-5} M \circ , 5×10^{-5} M \bullet , 1.25×10^{-4} M \square , 2.5×10^{-4} M \blacksquare , 4×10^{-4} M \triangle , 5×10^{-4} M \blacktriangle] and Conc. Of H_2SO_4 solutions at $25^\circ C$

From Fig. (1) the inhibitor concentration needed to give certain effectiveness value decrease with the increase of acid concentration as shown by the horizontal lines a, b, c, d, and e at effectiveness 60% , 70% , 80% , 85% and 90% respectively this relations is indicated in fig.(2) as straight lines parallel to each other with slope equal $(-27.3 \times 10^{-4} \text{ M/L inhibitor})$ per (1 M /L increase in sulfuric acid) , i.e. the inhibitor

concentration needed to give certain inhibition efficiency decrease by $27.3 \times 10^{-4} \text{ M/L}$ with increasing acid concentration by (1M/L) which in turn represent the total amount of water molecules desorbed from metal surface to shear in forming primary and secondary hydration layer per 1M increase in sulfuric acid.

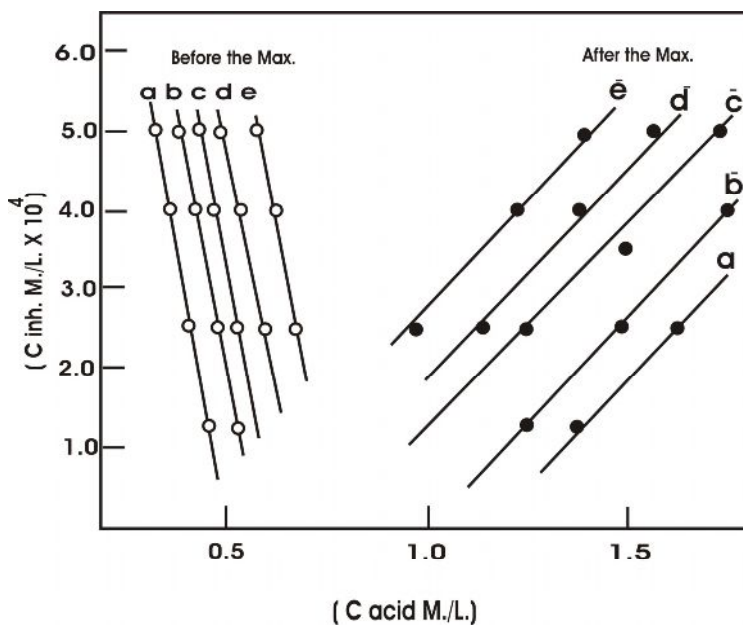


Fig (2) Relation between Concentration of H_2SO Solutions and Concentration of (P.S.U.) Inhibitor needed to give inhibition efficiency 60% a , 70% b, 80% c, 85% d, and 90% e

After the maximum, the effectiveness of (P.S.U.) decreases with the increase of sulfuric acid concentration Fig. (1) , and Fig.(2) , we explained this behavior on the light of the fact that the nonelectrolyte (P.S.U.) molecule has high dispersion dipole moment due to its large size and non symmetrical structure [12-14]. So when the concentration of the electrolyte (sulfuric acid) increases after the maximum where primary hydration layer is formed its ions tends to form second solvation layer through "Salting In" of the nonelectrolyte (P.S.U.) molecules due to its higher dispersion dipole moment than the dipole moment of water molecules, accordingly the free inhibitor molecules (P.S.U.) decrease in solution bulk , so its adsorption on metal surface decreasing leading to decrease in its effectiveness ,and the inhibitor concentration needed to give certain effectiveness increase as shown by parallel lines \bar{a} , \bar{b} , \bar{c} , \bar{d} , and \bar{e} after the maximum for efficiencies values to 60 % , 70% , 85% , and 90% with slope equal (5.4×10^{-4} M/L inhibitor concentration) per (1M/L) increase in sulfuric acid concentration) which represent the rate of salting in of (P.S.U.) with increase of acid concentration .

From Fig. (1) lines (1) , (2) , and (3) started at the maximum effectiveness 93 % , 80 % , and 40 % of (P.S.U.) solutions concentrations 5×10^{-5} M , 1.25×10^{-4} M , and 2.5×10^{-4} M respectively .

Fig.(3) represent the relation between the change of sulfuric acid concentration (M/L) (measured from the maximum , position) (ΔC acid) and the corresponding increase in (P.S.U.) concentration needed to give certain effectiveness (measured from the maximum position) (ΔC inh.) . The relation is indicated by 3 parallel straight lines (1) , (2) , and (3) which show the line (2) started at (P.S.U.) concentration of 1.25×10^{-4} M/L, only pass through the origin , i.e. , when (ΔC inh. = 0) and (ΔC acid = 0) or at the beginning of "Salting In" process which start at the end of formation of primary hydration layer of acid ions, this means that the primary hydration process is completed at (P.S.U.) concentration 1.25×10^{-4} M /L which represent the amount of water molecules desorbed from metal surface to shear in forming secondary hydration started to complete the secondary hydration layer with P.S.U molecules .

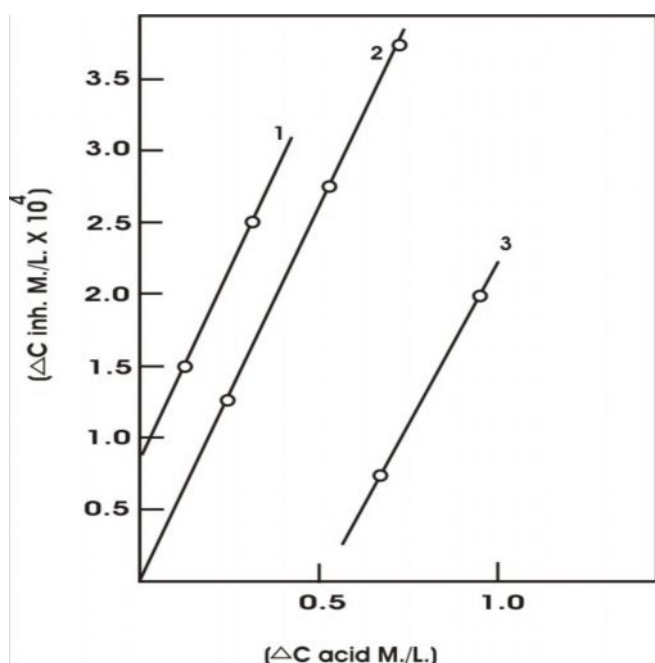


Fig (3) Relation between increase in concentration of H_2SO_4 solution (ΔC acid) and the decrease in corrosion inhibitor (P.S.U.) concentration (ΔC inh.) , (measured from the maximum) , needed to give the same effectiveness 93 % line (1) , 80 % line (2) , and 40% line (3) .

Calculations of primary hydration number (Nh): -

A) From fig(2) , it follows that the total number of water molecules desorbed from metal surface per one mole increase in sulfuric acid concentration to form primary and some of secondary hydration layer were represented by 27.3×10^{-4} M change in (P.S.U)concentration .

B) From fig(3) the number of water molecules sheared in forming some of secondary hydration layer is represented by 1.25×10^{-4} M change in (P. S. U.) conc. / 1M change in H_2SO_4 concentration. Consider,

1 – Number of H_2O molecules desorbed to form primary hydration

Layer / 1M change in H_2SO_4 Conc. = X_1 mole of H_2O / M H_2SO_4

2- Number of H_2O desorbed to shear in forming the secondary

Hydration layer / 1M change of H_2SO_4 concentration =

X_2 mole of H_2O / mole H_2SO_4

So we have from (A) 27.3×10^{-4} M (PSU) \propto (X_1 mole water / mole sulfuric acid) . (X_2 mole water / mole sulfuric acid)

Also we have from (B) 1.25×10^{-4} M (PSU) \propto X_2 mole of water / mole acid

$$27.3 \times 10^{-4} / 1.25 \times 10^{-4} = (X_2 \cdot X_1) / X_2 = X_1$$

X_1 is the (primary hydration Number Nh.)

$$Nh = 27.3 \times 10^{-4} / 1.25 \times 10^{-4} = 21.84 \text{ mole of } H_2O / 1 \text{ mole } H_2SO_4$$

Conclusions

This study is useful in determining the critical acid concentration in inhibited pickling solutions to avoid the loss of inhibitor effectiveness in electrolytic prison by “Salting In” process, in addition to determining the primary hydration number of the electrolyte and , indicating secondary solvation by Monitoring “Salting In” process .

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References

- [1] Ibrahim, N.S., Preparation and spectroscopic Measurement of heterocyclic thiourea derivatives, **Ph.D. Thesis , Faculty of Sciences , Cairo university, Egypt (1978).**
- [2] Elnagdi M.H. and Sanoa, O. Abd Allah, Modified procedure for preparation of diamino (phenylazo) – porazoles, **J. Prakt. Chem., 315 (6) 1009 (1973).**
- [3] ASTM, part 10 G 4 , U.S.A (1980).
- [4] Conway ,B.E., and Bockris, J.O.M., **Modern Aspects of Electrochemistry No. 7** chapter (1) P. 30-36 (Published by Butter Worth and Co.(publishers) Ltd. England Lodon (1972) .
- [5] Bockris, J.O'. M. and Amulya K.N. Reddy, **Modern Electrochemistry VOL (1),** second edition, chapter (2) P. 50 – 87 (Plenum pres. New York and London on (1998).
- [6] Antropov, L. **Theoretical Electrochemistry second edition 1977 ;** chapter translation Chapter 3 , P. 95-96 (Mir publisher Moscow 1977
- [7] Mason P.E.; Nilson, G.W.; Dempsey, C.E.; Bames, A.C.; and Cruickshank , J.M., the hydration structure of guanidinium and thiocyanate ions (**PANS) Apris 15, 2003 , VoL. 100, No 8, P. 4557 – 4561** (proceedings of the American National academy of science) united state of America 2003.
- [8] Ateya B.G. , EL-Anadoul B., and El-Nizamy F. , The adsorption of thiourea on mild steel, **Corros , Sci. , 24 , 509 , (1984).**
- [9] Azim, S.S.; Muralidharan, S., Maralidharan , B.; and Vasudevan, T. , Synergistic influence of iodide ions on inhibition of mild steel in H_2SO_4 by N- phenyl thiourea, **British Corrosion Journal pag. 297 – 301 (1988).**
- [10]- Gad Allah, A.G.; Girgis, N.N.; Mostafa, HCl.; and Mikhail, T.F., Corrosion inhibition of Helwan mild steel in Ho media by urea and thiourea derivatives at higher temperatures, using weight- loss and polarization measurements, **Hung. J. Ind. Chem. volume (23) P.11 (1995).**

- [11] A.R. Ismail, M.M. Hefny, A. Elkot. And M.S. El –Basiouny; Asian J. Chem. Vol. 4, No 3, pp 469 – 480 (1992).
- [12]*A.R. Ismaeel, Multilayer adsorption of poly donor large size organic molecule on heterogeneous steel surface from inhibited pickling acid solutions, **International journal of Chem. Tech.,V(2) , No. (2), Apr. – Jun. (2010)**
- [13]Bockris, J.O'. M. and Amulya K.N. Reddy, **Modern Electrochemistry VOL (1)**, second edition, chapter (2) P. 173 – 175 (Plenum pres. New York and London on (1998).
- [14]Raymond Chang, **physical chemistry for chemical and Biological Sciences, edition 2000** chapter (8) P274 (By university science books California) (2000).
- [15]**Annual Book of ASTM Standards**, Wear and Enrosion Metal Corrosion , Valum 03,02 U.S.A. Aug. 2004.
- [16]Muralidharan, S.; Madhavan, K.; karthikeyan,S.; and Venkatakrishna S. Lyer Indian, Influence of anions on Corrosion inhibition and hydrogen permeation through mild steel in acidic solution in presenle of p – tolyl thiourea, **Indian Journal of chemical technology volume (9). (2002)**
- [17]A.R.Ismaeel,,Asian Journal of Chemistry, Vol.18,No.3 (2006), 2081 – 2088
- [18]A.R. Ismaeel, Asian Journal of Chemistry, Vol. 19 ,No. 5 (2007), 3688 – 3696
- [19]Bockris, J.O'. M. and Amulya K.N. Reddy, **Modern Electrochemistry VOL (1)**, second edition, chapter (3) P. 293 – 294 (Plenum pres. New York and London on (1998).
- [20]Conway, B.E.; and Bockris, J.O'.M., **Modern Aspects of Electrochemistry No. 7**, chapter (3) p. 149 – 150 (published by Butter worth and Co. (publisher) Ltd. England London 1972).
- [21]Stupnioek – lisac; Ademovi, Zahida , Heterocyclic organic compounds as iron Pickling Inhibitor's, **Proceedings of 8th European symposium of Corrosion inhibitors, ferrara, jtaliy (1995) p. 257 – 265.**
