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ADSORPTION ISOTHERM ON FERRITES

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ABSTRACT

The corrosion behaviour of the prepared materials was studied by means of weight-loss technique in stagnant solution of (0.01 M) sulphuric acid in presence of thiourea as an inhibitor. Higher concentration of thiourea reduces the corrosion rate of the samples and protection efficiency of thiourea was found to be 80 % for ferrites Protection is mainly due to adsorption. Corrosion rate increases with increasing temperature. According to Bockris-Swinkels isotherm, one molecule of water is displaced by five thiourea molecules on the surface. Thermodynamic data for the adsorption process $\triangle G^o_{ads}$, $\triangle H^o_{ads}$ and $\triangle S^o_{ads}$ were also calculated and discussed.

INTRODUCTION

Ferrites are of great interest because of their importance in industrial applications as anode material used in solution electrolysis. Ferrite electrode has low electrical resistivity, high corrosion resistance and high mechanical strength. Ferrites were chosen because they extensively used in certain electrical devices, magnetic heads and in electronic circuits, since they exhibit fluorescence, ferromagnetism and ferroelectric properties. Physico-chemical properties of different ferrites were studied[1].

The aim of the present paper is to study the adsorption isotherm on La and Sr-ferrites, because ferrites is of a great industrial application as electronic ceramics.

EXPERIMENTAL

The starting materials ($MnSO_4$. HO_2, $SrCO_3$, La_2O_3 and Fe_2O_3 which are either A.R. (BDH) or E. MERCK (extra pure) grade purity $>$ 99.9 %) are well mixed using an agate mortar.

The product was compressed at 500 Kg / cm^2 and sintered at 1150 C° for 3 hours in an electric muffle furnace.

Chemical and X-ray analyses were performed to ensure correct and complete preparation and to evaluate the phase formed[2],

$$La_{0\cdot5}\ Sr_{0\cdot5}\ [Fe_{0\cdot5}\ Mn_{0\cdot5}]\ O_3.$$

Weight-Loss Technique

The tested sample digressed with acetone, weighted and then each sample was immersed in 100 ml pyrex glass beaker containing 60 ml of the test solution for several days. The samples were then cleaned by brushing under running water to remove corrosion products, then dried and weighted. All the experiments were carried out in an air-thermostat adjusted at temperatures 30, 40 and 50 C°. The solution lost by evaporation during the period of the test was compensated by adding distilled water. Results were duplicated and the mean was calculated.

The surface coverage was calculated from the equation[3].

$$\theta = 1 - W_1 / W_2 \qquad (1)$$

where, W_1 and W_2 are the weight loss with and without thiourea.

RESULTS AND DISCUSSION

Fig. 1 represents the results of weight loss of the samples in the tested solutions. The corrosion rate increases with increasing the time of immersion. The inhibition of the samples in the tested solution at different concentrations is taken to support the adsorption theory, thus thiourea exerts an inhibiting action.

The effect of temperature on the corrosion rate of ferrite in 0.01 M sulphuric acid solution containing 10^{-3} M thiourea was studied. The corrosion rate increased with increase in temperatures (Table 1). In general the surface is invariably hydrated in aqueous solutions l.e. the surface is always covered with adsorbed water dipoles. Thus the adsorption of the organic compound from aqueous solution on the surface is regarded as a substitution reaction between the molecules in solution and the water molecules adsorbed on the surface[4].

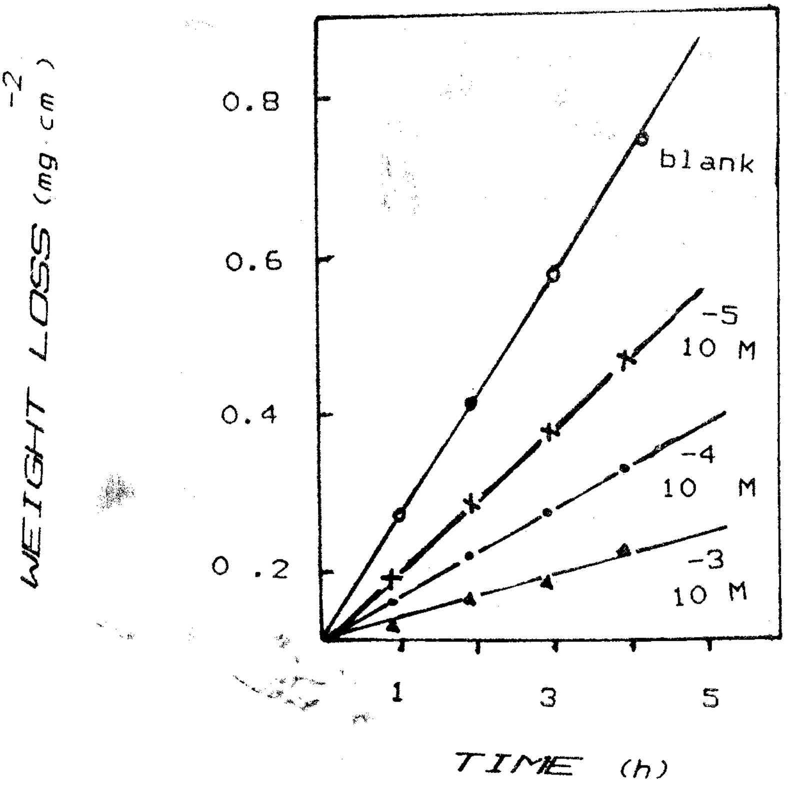


Fig. 1. The relation between weight loss and time for ferrite sample in 0.01 M sulphuric acid with and without thiourea.

Table 1. Corrosion rate and inhibition efficiency at different temperatures in 0.01 M sulphuric acid containing 10^{-3} M thiourea.

Temperature °C	Corrosion rate mg $cm^{-2}h^{-1}$	Inhibition efficiency
30	0.18	80
40	0.29	76
50	0.35	70

TEST OF ISOTHERM

In order to test Bockris–Swinkels isotherm[5]

$$\Delta G = -2.303\ RT \log \{(55.4 \times \theta)/C\ (1-\theta^n) \times [\theta + n\,(1-\theta^{n-1}/n^n] \qquad (3)$$

where C is the concentration of the inhibitor in the bulk of the solution. A plot of the left–hand side of equation (3) against the concentration of thiourea was made to evaluate the exact value of n. Fig. 2 shows the adsorption isotherm for thiourea. The straight line with n = 5 passes through the origin indicating that 5 is the most probable value for thiourea. In an acid solution of thiourea, there are some protonated species in addition to the molecular species. The protonation of thioamide takes place at the S atom giving rise to[6,7].

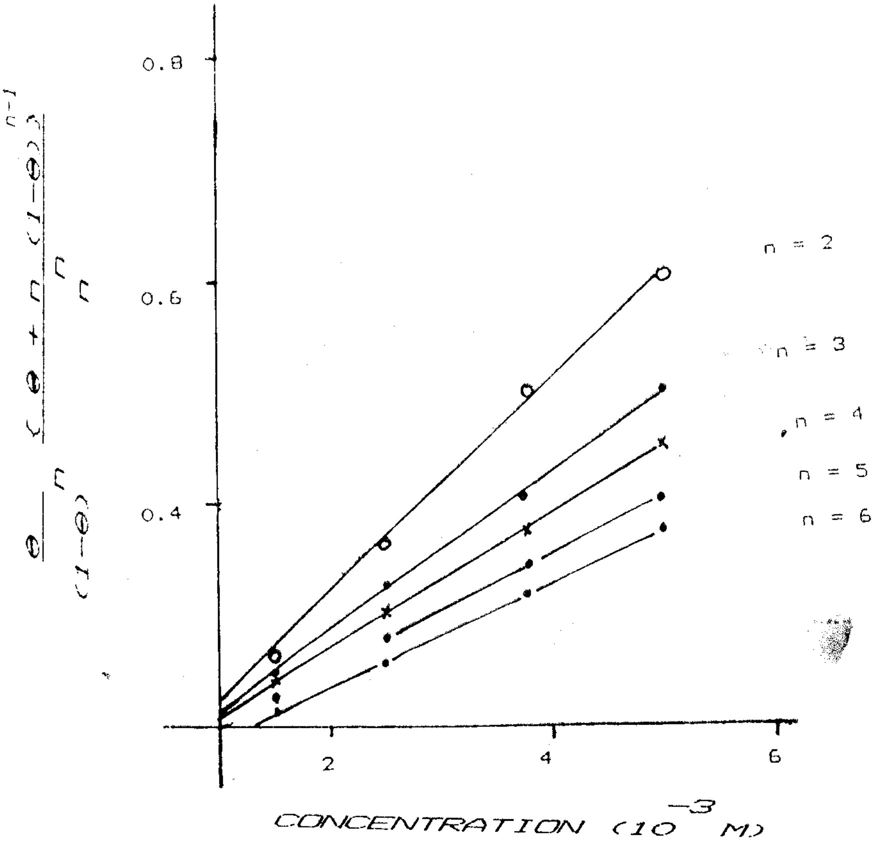
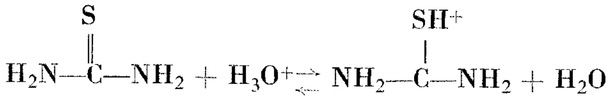


Fig. 2. Bockris–Swinkels adsorption isotherms for adsorption of thiourea on ferrite sample in 0.01 M sulphuric acid at 30 °C.



$$H_2N-\overset{\overset{\displaystyle S}{\|}}{C}-NH_2 + H_3O^+ \rightleftharpoons NH_2-\overset{\overset{\displaystyle SH^+}{|}}{C}-NH_2 + H_2O \qquad (4)$$

The protonation of thiourea has an equilibrium constant of 0.1[8]. Adsorption may be attributed to electrostatic attraction between the surface and protonated forms of thiourea. Thiourea or its protonated forms would be attached to the surface by multicenter adsorption at the sulphur by electrostatic forces. Thus five molecule of water is displaced by one molecule of thiourea.

It has been suggested by Damaskin[9,10] that groups of associated water molecules are displaced off the surface as a result of substitutional adsorption. There is some evidence that at room temperature, water forms groups of five molecules in a tetrahedral arrangement[11]. When such a tetrahedron adsorbs on the surface, it is obvious that its base, i.e. three water molecules, would face the surface. The central molecule would be at a longer distance from the surface base molecules. The area occupied by each water group would thus be about equal to the area occupied by one water molecule[12]. This is the possible explanation of the above finding. Thus, thiourea adsorbs in one particular orientation; **the** planer orientation[13].

Correct evaluation of the standard free energy $(\triangle G^\circ)_{ads}$ has been made by using equation (3).

The values of $\triangle G^\circ_{ads}$ was calculated for thiourea with different θ values. It is seen that for the most probable value of $n = 5, \triangle G^\circ$ is almost independent of θ. The adsorption of thiourea on ferrites has standard free energy of adsorption equal to–38.9 kJ^{-1} mol. The negative values of $\triangle G^\circ_{ads}$ indicate that the adsorption of inhibitor on ferrites is a spontaneous process. Also the increase in the negative values of $\triangle{}^\circ G_{ads}$ with o indicates that there is a lateral interaction between adsorbed inhibitor molecules on the surface[10]. The enthalpy of adsorption $\triangle H^\circ_{ads}$ can be calculated from the following equation

$$\log\left[(K_2/K_1)\right] = -\frac{\triangle H}{2.303\ R}\ \frac{(T_2 - T_1)}{T_1\ T_2} \qquad (5)$$

Change in entropy can be calculated from equation (6)

$$\triangle G^\circ_{ads} = \triangle{}^\circ H - T\triangle{}^\circ S \qquad (6)$$

The results were collected in Table 2.

Table 2. Thermodynamic data for adsorption of thiourea on ferrites surface in 0.01 M sulphuric acid containing 10^{-3}M thiourea at 30 °C.

Concentration of Thiourea	$\triangle G^o_{ads}$ kj mol^{-1}	$\triangle H^o_{ads}$ kJ mol^{-1}	$\triangle S^o$ $Jk^{-1}mol^{-1}$
10^{-3}M	38.9	26.3	41.8

The magnitudes of the values of $\triangle S^\circ_{ads}$ and $\triangle H^\circ_{ads}$ are in accordance of a replacement process during adsorption of thiourea molecules on the ferrites surface[14].

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