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Kinetics and Structure Aspects of the Dissolution of Stainless Steels in Phosphoric Acid

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Abstract

The dissolution of metals in acids is a heterogeneous electrochemical reaction, taking place at the interface between a solid and a liquid, described in terms of energy and configuration of the species involved. The energy of activation for two stainless steels (SSs) in phosphoric acid (PA) was determined from their corrosion rates in the temperature range of 20–120°C, applying the Arrhenius equation. Energy of activation values for the overall process of anodic metal dissolution and cathodic hydrogen release is in the 10–20 Kcal mol⁻¹ range. Metal corrosion is a structure-sensitive process; its mechanism and rate are related to the density of surface defects, based on the Boltzmann expression. A model for the activated complex is proposed based on considerations of energy and configuration. This work is an integration of a theoretical analysis and an experimental investigation of metal corrosion in acids.

Keywords: phosphoric acid, stainless steel, dissolution, kinetics, surface structure

1. Introduction

Acids are broadly applied in many industries: chemical, fertilizer, steel, mineral, water, oil, food, etc. [1]. The acidic properties of their ionized, aqueous solutions are due to the presence of hydrogen ion H⁺ and its complexed form hydronium ion H₃O⁺.

Phosphoric acid (PA), H₃PO₄, is an industrial acid used as an intermediate in the fertilizer industry, for metal surface treatment, and as an additive in the food and beverage industry [2–4]. PA, a polyprotic acid, was selected for this study since it is a nonreductant, nonoxidant acid, to avoid the complication of oxidation and formation of oxides on the metallic surface.

Corrosion rates (r) of austenitic stainless steels (SS) in concentrated PA, in the presence and in the absence of halides, have been determined by weight loss and the corrosion behavior by electrochemical measurements, in the 50–120°C temperature range.

The dissolution of metals in solutions of acids is a heterogeneous electrochemical reaction. Initially, two phases coexist—a solid and a liquid—but as the reaction starts, a third phase appears, hydrogen gas, evolving from the surface of the metal. The kinetics of the dissolution process depends on the collision between the solvated protons and the “active sites” on the metallic crystal surface, promoting

anodic dissolution. The dissolution rate increases with temperature in accordance with the empirical Arrhenius equation:

$$r = A \exp .(-E_a/RT) \tag{1}$$

where r is the metal dissolution reaction rate, A the frequency factor, T the absolute temperature, R the gas constant in calories, and E_a the activation energy. According to the rate process theory [5–7], any process may be described in terms of energy and configuration of the species involved. In the transition from the unstable metallic crystal-acid system to the stable system of solvated metallic cations and anions, the reaction passes through the activated complex which is in dynamic equilibrium with the reactants:

For iron in orthophosphoric acid, the overall reaction is:

The reaction rate, in terms of enthalpy of activation (ΔH*) and entropy of activation (ΔS*), is expressed as:

$$r = (RT/Nh) \exp .(-\Delta H^*/RT) \exp .(\Delta S^*/R) \tag{4}$$

where N is the Avogadro number and h is the Planck constant.

2. Experimental

Laboratory immersion corrosion tests were performed in accordance with the practices recommended in ASTM Volume 03.02 [8]. ASTM G 31 standard [9] was applied for mass loss tests, and the electrochemical parameters were measured and reported following ASTM G 3 [10] and G 5 [11] standards. Reagent grade PA and halide acids were utilized, for preparing PA solutions. Two SS, currently used in PA applications, were tested; their chemical composition is shown in **Table 1**.

Corrosion rates of austenitic SS in concentrated PA, in the presence and in the absence of halides, have been determined by weight loss measurements in the 50–120°C temperature range. The data obtained were plotted in accordance with the Arrhenius equation:

$$\log r = \log A - E_a/(2.3RT) \tag{5}$$

Plots of log r vs. 1/T yield satisfactory straight lines and the values of E_a lie in the range of 10–22 Kcal mol⁻¹, the particular value depending on acid concentration and content of halide.

UNS*	Chemical composition, %			
	Cr	Ni	Mo	C _{max}
S 30400	18–20	8–12	—	0.08
S 31600	16–18	10–14	2–3	0.10

Table 1.
Austenitic stainless steels tested.

UNS	Acid concentration, %	Temperature, °C	Potential, V			Current density, mA cm ⁻²	
			E _{ocp}	E _{pp}	E _p	i _{crit}	i _p
S 30400	70	20	0.14	—	—	—	—
S 31600	70	20	0.15	—	—	—	—
S 30400	70	80	0.17	—	—	—	—
S 30400	85	120	-0.27	-0.04	0.22	12	0.14
S 31600	85	120	-0.19	-0.14	-0.05	0.74	0.20
S 30400	95	120	-0.27	-0.12	-0.05	2.0	0.002

Table 2.
Electrochemical parameters of stainless steel—H₃PO₄.

The kinetics of dissolution was studied also by electrochemical methods. Measurements were made of electrode potential at zero current as a function of immersion time, and the potential-current relationship was determined by potentiostatic and potentiodynamic techniques.

1. The concentrations of the PA tested are 70, 100, and 85% (see **Figure 2** and **Table 2**), and pure PA prepared from PA grade analytical reagent distilled water was used.
2. The halides tested were F, Cl, and Br.
3. Their concentration in PA was 1000 ppm.

3. Results and discussion

3.1 Kinetic and thermodynamic studies

The effect of temperature on the corrosion rate, in accordance with the Arrhenius equation, is shown in **Figure 1**.

Figure 1.
Variation of the corrosion rate of UNS S 30400 and S 31600 with temperature in PA.

The enthalpy of activation ΔH^* and the entropy of activation ΔS^* were calculated by comparison of equations (1) and (4). The free energy of activation ΔG^* was calculated from the expression:

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

(6)

Selected kinetic and thermodynamic values are illustrated in **Table 3**. This table also shows the influence of the halide ions F⁻, Cl⁻, and Br⁻ on the corrosion rate, which was added to PA as halide acids: HF, HCl, and HBr. The halide concentration in PA is 1000 ppm.

The electrochemical behavior of several steels in PA solutions is graphically illustrated by current density-potential plots (**Figure 2**). The following electrochemical parameters are located: open-circuit potential (E_{opc}), critical current density (i_{crit}), primary passive potential (E_{pp}), passivation current density (i_p), passivation potential (E_p), and transpassive potential (E_t) [10, 11].

The corrosivity of pure phosphoric acid solutions increases with the increase in concentration to about 60% PA, and then it is reduced with further increase in concentration. This behavior parallels the H⁺ concentration, which increments with the increase in acid concentration to about 50% PA and then decreases as the

UNS	S 30400				S 31600			
Halide	—	F ⁻	Cl ⁻	Br ⁻	—	F ⁻	Cl ⁻	Br ⁻
Corrosion rate (mdd)*	110	225	2600	110	25	20	70	10
E _a , Kcal mol ⁻¹	22.3	16.8	12.6	10.9	15.4	11.6	15.5	12.2
Activated atoms, atoms cm ⁻²	18.0	4.2 × 10 ⁴	1.8 × 10 ⁷	2.1 × 10 ⁸	3.2 × 10 ⁵	7.4 × 10 ⁷	2.8 × 10 ⁵	1.6 × 10 ⁵
ΔS*, cal deg. ⁻¹ mol ⁻¹	42.0	55.6	63.0	75.0	64.5	75.8	62.1	64.0
ΔG, Kcal mol ⁻¹	36.4	35.7	34.1		37.5	37.7	36.8	34.1

Table 3.
Kinetic and thermodynamic values for corrosion of stainless steel in 70% H₃PO₄ containing 1000 ppm halide at 80°C.

Figure 2.
Anodic potentiodynamic polarization plots in H₃PO₄ at 20°C, showing typical corrosion behavior.

equilibrium in concentrated acid shifts to the left with further increase in acid concentration [12]:

3.2 The energy of activation

The values of activation energy obtained for different SS-PA systems lie between 10 and 22 Kcal mol⁻¹; the values of activation entropy are in the range of -42 to -75 cal deg⁻¹ mol⁻¹ and those of free energy of activation in the range of 34-38 Kcal mol⁻¹.

The energy of activation for the overall process of cathodic release of hydrogen from acids on different metals is in the 10-20 kcal mol⁻¹ range [12, 13]. This indicates that in the dissolution of steel in phosphoric acid, and probably in metals dissolving in strong mineral, non-oxidizing acids, the hydrogen evolution reaction constitutes the rate determining step of the overall dissolution reaction:

3.3 The influence of halides on corrosion

The corrosion activity of S 30400 and S 31600 in 70% PA starts at about 60°C and 80°C, respectively [14]. Up to these temperatures, they exhibit a passive state, but with increase of temperature, breakdown of passivity occurs. The potential becomes active and an intense corrosion process is established. The values of electrochemical parameters indicating corrosion in halide-containing PAs change, in accordance with their respective corrosion rates (**Tables 2 and 3**).

Halogen acids HX were added to PAs to augment their corrosiveness; in particular, addition of HCl results in markedly increased corrosion rates. The corrosivity of these halogen acids and their ions, in strong mineral oxygen acids such as PA, is related to the halogen physicochemical properties, their electronegativity, ion size, and ionic character of the HX molecule, which indicate their chemical reactivity. Cl⁻ ion is adsorbed on metal surfaces and replaces adsorbed oxygen or water molecules. This shifts the metal potential to more active (electronegative) values and causes breakdown of the passive state, mainly in concentration higher than 70% at 120°C (**Table 2**). During attack on SS, chlorides of Fe, Ni, and Cr are formed; they are highly soluble in PA because of its complexing cations of the transition group elements.

The corrosivity of halide ions diminishes in the order F⁻ > Cl⁻ > Br⁻ in 30% and 50% PAs in accordance with their chemical activity. In 70% and 85% PAs, however, the corrosivity of halides is in the order Cl⁻ > F⁻ > Br⁻. This result reflects the formation of stable monofluorophosphoric acid, which complexes F⁻ and decreases its corrosivity. The following equilibrium is established:

3.4 Electrochemical corrosion behavior

Typical types of corrosion behavior shown by anodic polarization plots (1)-(4), locating their electrochemical parameters, are displayed in **Figure 2**.

Active corrosion behavior of carbon steel is shown in plot 1; plot 2 traverses three regions of corrosion behavior: active, passive, and transpassive, the last indicated by the appearance of a yellow color in the colorless PA solution, due to the

presence of CrO_4^{2-} , generated in the oxidative dissolution of SS and corroborated by chemical analysis. Plot 3 starts with passivity; transpassivity appears at E_t about 1.00 V, but a total passive state is maintained in 100% PA (plot 4). The electrochemical behavior of SS in PA is related to acid concentration and temperature. The presence of halide ions in PA accelerates the corrosion, the increase in rate being dependent upon the halide chemical nature and content (**Tables 2 and 3**).

Ta is used for equipment handling hot, concentrated PA due to its high corrosion resistance.

3.5 The activated complex structure

Based on considerations of energy and configuration using the values of enthalpy, entropy, and free energy of activation from equation (6), the structure of the activated complex may be described as an association between the atoms undergoing corrosion on the metal surface and the hydronium ions. This associated configuration conforms to the negative and relatively high values of the entropy of activation which is typical of chemical reactions involving dimerization or association of reactant molecules. This conclusion concurs with the fact that protons and corrosion-promoting ions such as chloride are adsorbed on the metal surface and accelerate the corrosion process. Furthermore, these values are characteristic of slow reactions such as the corrosion of stainless steels in non-oxidizing acids.

Taking into account these considerations, a model for the activated complex of the overall metal dissolution reaction is proposed:

The positive values calculated for the free energy of activation (6) are a measure of the energy required to form the activated complex and its instability. On the other hand, in the corrosion process:

$$\Delta G = \Delta H - T\Delta S \quad (12)$$

where ΔH is the heat of reaction of an exothermic reaction and therefore negative, and ΔS is the entropy of the irreversible corrosion process, which results in an increase in the degree of disorder and therefore is positive. Consequently, the free energy (ΔG) has a negative value expressing the spontaneity of the corrosion process of metal in acids and its acceleration with the increase in temperature.

3.6 Activation and active sites

Experimental values of activation energy for metal dissolution in acid solutions are frequently reported in the literature. For instance, for Ni dissolution [15], the values lie between 10.5 and 21.1 kcal mol⁻¹, and values for other metals are similar [16–20]. It is interesting to speculate why no greater values have been reported. The answer can be found from consideration of the Boltzmann expression [18]:

$$n_a/n = \exp.[-E_a/(RT)] \quad (13)$$

where n is the total number of metal atoms per surface area unit and n_a the number of “activated” metal atoms having energies greater than E_a and therefore able to undergo dissolution. In a metallic crystal, the number of atoms per cm^2 of surface area may be taken as ca. 10^{15} [18], hence:

$$\log n_a = 15 - E_a/(2.3 RT) \quad (14)$$

For instance, at 100°C ,

$$\log n_a = 15 - E_a/1720 \quad (15)$$

and if E_a is $25.8 \text{ kcal mol}^{-1}$, $n_a = 1 \text{ at cm}^{-2}$. Since the density of active sites is 10^8 – 10^{12} cm^{-2} for different cases [18], E_a values of about 25 kcal mol^{-1} or greater are unreasonable.

Metallic corrosion is considered as a structure-sensitive process, and its mechanism and rate have been related to the density of surface imperfections or defects [18, 21–26]. Continuing with calculations based on the Boltzmann expression, the density of active sites n_a in a metal undergoing dissolution with an activation energy of $10.0 \text{ kcal mol}^{-1}$ is $1.3 \times 10^9 \text{ at cm}^{-2}$, and it is $1.7 \times 10^6 \text{ at cm}^{-2}$ when the activation energy is $15.0 \text{ kcal mol}^{-1}$. The similarity between these n_a values and the density of defects in metals—for instance, 10^6 to 10^8 dislocations cm^{-2} in a well-annealed metal [26–28]—strongly suggests a quantitative relationship between metal dissolution and density of surface defects.

4. Conclusion

Corrosion rates and electrochemical behavior of austenitic stainless steels UNS S 30400 and S 31600 in PA solutions, with and without halide ions, have been determined in the 20 – 120°C temperature range. The energy of activation E_a for the dissolution of these SS in PA solutions was obtained in accordance with the Arrhenius equation. The values of E_a for different SS-PA systems lie between 10 and 20 kcal mol^{-1} . Calculations based on the Boltzmann expression, taking into account the activation energy, the total number of metal atoms, and the number of “activated” metal atoms, both per surface area unit, strongly suggest a quantitative relationship between metal dissolution and density of defects in metal’s surface. Based on considerations of energy and configuration, using the values of energy, entropy, and free energy of activation, a model for the activated complex of the overall metal dissolution reaction in acids is proposed.

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