Studies on Inhibitor of Aluminum in Alkaline Medium. III.

Aminophenols as an Inhibitor of Aluminum in Alkaline Medium

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Studies on the inhibitive actions of aminophenol inhibitors for aluminum in alkaline medium were made with the experimental measuring corrosion potential with lapse of time and observing polarization characteristics.

In pH 11.8 medium, a chelate film of *o*-aminophenol was supposed to form on the aluminum surface, but the inhibitive action was not appreciable. *m*- and *p*-aminophenols and toluidine which can not have structure to form chelate showed inhibitive effect due to sorption by polarity of amino-radical.

In pH 13.2 medium, corrosion was promoted due to high alkalinity, and any chelate film was not observed even in the addition of *o*-aminophenol.

It was concluded that *o*-aminophenol showed inhibitive action but inhibitive action was not due to forming chelate compound with aluminum even in alkaline medium.

Introduction

The mechanism of inhibitive action by organic inhibitors has been studied in the direction of sorption since about 25 years ago. Mann¹⁾ suggested that the organic substance which can form onium ion forms cation in acidic solution and it would be adsorbed on the cathodic portion of metallic surface and then hydrogen ion cannot pass through the film. Hackerman²⁾ concluded that there is another case than physical adsorption, due to the chemical sorption between the metal and the lone pair electron in nitrogen atom of amine. But Hayakawa et al.^{3,4)} considered that there is the third case where the stronger combination, i.e. chelation, between metal and organic substance than physical or chemical sorption plays its role in inhibition.

In the previous papers, the authors found that *o*-hydroxyazo compounds³⁾ and 8-hydroxyquinoline derivatives show inhibition effect on aluminum just in alkaline medium, and concluded the mechanism of inhibitive action was due to the chelate formation between aluminum and the substances. In this paper, the experiment on aminophenol inhibitors was carried out along the same way presented in the previous reports.

Experimentals

Apparatus used in this experiment was the same as shown in the previous paper.³⁾ Metallic aluminum of 99.8% purity, 0.3 mm thick and 2×3 cm² wide, was treated as shown in the previous paper and used as specimen.

Additive reagents *o*-aminophenol was used as a reagent having a structure which is able to form metal chelate compound with aluminum, and in order to compare with them, *m*- and *p*-aminophenols and toluidine were used as reagents having a structure which is unable to form any chelates.

Surface active reagent An anion activator, $C_6H_5O-\text{C}_6H_4-O-(CH_2\cdot CHO)_9H$, was used only in case of toluidine. In case of aminophenols any activators were not used, because aminophenols are soluble in alkaline solution.

Measurement of corrosion potential Using N/10 KCl calomel electrode, potential-time curve was obtained with the same method described in the previous paper¹⁾.

Measurement of corrosion current density After 3 hrs. from the immersion of aluminum speci-

men into alkaline medium and when the current was almost steady, current density-potential curve was obtained by using platinum electrode with the same method described in the previous paper³⁾.

Results

1) **Corrosion potential** The results obtained are listed in Table 1, and an example of the relation between potential and time is shown in Fig. 1. In case of pH 8.7, by addition of additives the potential shift to baser potential side was seen and the corrosion increased with addition of additives.

Table 1 Corrosion Potential of Aluminum

pH	Addition	Amount	Corrosion potential (V)		
			1 h	2 h	3 h
NaOH pH 8.7	no addition	—	-0.43	-0.39	-0.38
	<i>o</i> -aminophenol	0.1	-0.47	-0.45	-0.42
	<i>m</i> -aminophenol	0.1	-0.52	-0.49	-0.47
	toluidine	0.1	-0.55	-0.52	-0.48
NaOH pH 10.5	no addition	—	-0.69	-0.64	-0.65
	<i>o</i> -aminophenol	0.1	-0.66	-0.62	-0.61
	<i>m</i> -aminophenol	0.1	-0.63	-0.59	-0.56
	<i>p</i> -aminophenol	0.1	-0.82	-0.72	-0.62
	toluidine	0.1	-0.69	-0.65	-0.59
NaOH pH 11.8	no addition	—	-1.15	-1.14	—
	<i>o</i> -aminophenol	0.025	-1.14	-1.07	-1.06
	"	0.05	-1.12	-1.07	-1.06
	"	0.1	-1.09	-1.08	-1.08
	"	0.2	-1.14	-1.14	-1.14
	<i>m</i> -aminophenol	0.05	-1.10	-1.08	-1.05
	"	0.1	-1.08	-1.06	-1.05
	"	0.2	-1.09	-1.09	-1.09
	<i>p</i> -aminophenol	0.05	-1.15	-1.10	-1.08
	"	0.1	-1.09	-1.07	-1.06
	"	0.2	-1.12	-1.12	-1.13
	toluidine	0.1	-1.13	-1.14	-1.12
	"	0.2	-1.14	-1.13	-1.12
	"	0.25	-1.26	-1.26	-1.25
	"	0.5	-1.21	-1.20	-1.19
NaOH pH 13.2	no addition	—	-1.26	-1.26	-1.27
	<i>o</i> -aminophenol	0.05	-1.13	-1.14	-1.17
	"	0.1	-1.14	-1.13	-1.14
	"	0.2	-1.04	-0.97	-0.98
	"	0.25	-1.22	-1.20	-1.15
	<i>m</i> -aminophenol	0.05	-1.26	-1.26	-1.26
	"	0.1	-1.08	-1.13	-1.14
	"	0.2	-1.00	-0.97	-0.97
	<i>p</i> -aminophenol	0.05	-1.24	-1.25	-1.25
	"	0.1	-1.13	-1.14	-1.15
	"	0.2	-1.00	-0.96	-0.99
	toluidine	0.1	-1.01	-0.95	-0.95
	"	0.2	-1.01	-0.95	-0.95

While in case of pH 10.5, the additives affected the inhibition and the potentials were in order of (noble) *m*-aminophenol>toluidine>*o*-aminophenol>*p*-aminophenol>no additive (base), but the difference among the sorts of additives was not appreciable.

In case of pH 11.8, aminophenols showed inhibitive effect, and the potentials were in order of (noble) *m*-aminophenol>*p*-aminophenol>*o*-aminophenol (base), but the difference among the sorts of additives was small. The addition of toluidine showed no effect.

In case of pH 13.2, the addition of additives showed inhibitive effect, and the potential by addition of toluidine was more noble than those by that of aminophenols. The potentials

Fig. 1 Corrosion potential (pH 11.8)

by addition of aminophenols were the similar values.

2) **Polarization characteristics** An example of polarization curves obtained is shown in Fig. 2 and the corrosion current densities obtained from the polarization curves are listed in Table 2. In case of pH 8.7, corrosion current density decreased with additives and the order was *o*-aminophenol<*m*-aminophenol<toluidine<no additive. The difference among the sorts of additives was small.

In case of pH 10.5, similar tendency was seen, and the order was *p*-aminophenol<*o*-aminophenol<toluidine<*m*-aminophenol<no additive.

In case of pH 11.8, corrosion current density decreased linearly with increasing amount of additives and the inhibitive effect was observed. The order was *o*-aminophenol<*m*-aminophenol<*p*-aminophenol <toluidine<no additive. The difference among the sorts of additives was small.

In case of pH 13.2, similar effect was seen and the order was *o*-aminophenol<*p*-aminophenol<*m*-aminophenol<toluidine. However the additives diminished current density, large current and corrosion were seen in this case.

3) Relation between the amount of additive and corrosion current density The relation

Table 2 Corrosion Current Density of Aluminum

pH	Addition	Amount (%)	Corrosion current density (μA/cm ²)
NaOH pH 8.7	no addition	—	1.7
	<i>o</i> -aminophenol	0.1	0.5
	<i>m</i> -aminophenol	0.1	0.7
	toluidine	0.1	0.8
NaOH pH 10.5	no addition	—	3.7
	<i>o</i> -aminophenol	0.1	2.6
	<i>m</i> -aminophenol	0.1	3.2
	<i>p</i> -aminophenol	0.1	2.1
	toluidine	0.1	3.1
NaOH pH 11.8	no addition	—	120
	<i>o</i> -aminophenol	0.025	116
	"	0.05	101
	"	0.1	80.5
	"	0.2	50
	<i>m</i> -aminophenol	0.05	119
	"	0.1	118
	"	0.2	52
	<i>p</i> -aminophenol	0.05	100
	"	0.1	82
	"	0.2	56
	toluidine	0.1	80
	"	0.2	90
NaOH pH 13.2	"	0.25	395
	"	0.5	300
	no addition	—	3,000
	<i>o</i> -aminophenol	0.05	2,160
	"	0.1	1,590
	"	0.2	2,750
	"	0.25	1,140
	<i>m</i> -aminophenol	0.05	2,500
	"	0.1	1,770
	"	0.2	2,400
	<i>p</i> -aminophenol	0.05	2,450
	"	0.1	1,710
	"	0.2	1,930
	toluidine	0.1	2,740
	"	0.2	2,250
	"	0.5	1,600
	"	1.0	1,800

1: No addition 3: Toluidine, 0.5%
2: *o*-aminophenol, 0.25%
Fig. 2 Polarization characteristics (pH 11.8)

A : pH 11.8 B : pH 13.5
Fig. 3 Relation between the amount of *o*-aminophenol and the corrosion current density

derived from the data in Table 2 is shown in Fig. 3. The corrosion current density was decreased with the additive in the range of less than 0.1% but not affected by the additive in case of the range of more than 0.1%.

4) Surface of aluminum Observing the surface of aluminum immersed into the alkaline medium, yellowish green film was formed just in case of pH 11.8 solution added *o*-aminophenol, while no films were seen in any other case,—in other pH range or in other additives.

Discussion and Conclusion

From the results obtained by the experiments, the following conclusions were induced: Not only in case of *o*-aminophenol, but in cases of *m*- and *p*-aminophenols, inhibitive action were seen in alkaline medium. Considering also the surface film formation, a film of aluminum chelate of *o*-aminophenol was supposed to form on aluminum surface in case of pH 11.8, but the inhibitive action due to the film formation was not so strong as supposed. In case of the addition of additives which cannot form chelate, inhibitive action is probably due to the adsorption of amine group. The inhibitive action of *o*-aminophenol was found to be most poor among the inhibitors used in this experiment.

In the lower pH range, chelate compound of *o*-aminophenol with aluminum was supposed not to form due to its small stability, so the inhibitive action due to the adsorption of amine group was only seen. However very small current density was observed in pH 13.2, corrosion was promoted even in case of addition of *o*-aminophenol and any film of chelate did not seem to be due to its remarkable dissolution of aluminum in such strong alkaline medium.

From these results obtained from the experiment, it is concluded that the inhibitive action of aluminum in alkaline medium caused by addition of *o*-aminophenol was not due to the formation of chelate film.

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