Wettability of Sodium Chloride Aqueous Solutions on SUS304 Stainless Steel with Current Flow

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The wettability of NaCl solutions on SUS304 stainless steel was investigated under cathodic and anodic current. It was found that the contact angle became small when a cathodic current of 1.0 mA was applied, with a tendency of higher wettability for higher concentrations (between 0.01% and 0.1%). However, the decrease in the contact angle is irreversible even if the current is stopped or anodic current is applied. This phenomenon can be attributed to changes in the electric charge and the passive film at the interface.

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1. Introduction

The phenomenon of electrowetting, which concerns the change in the wettability of an electrolytic fluid on a thin dielectric film (the film is generally coated on a conductive substrate) in an external electrostatic field, has attracted considerable attention for several decades. The process is generally explained by the alteration of the electricity charge at the fluid/film interface. The Lippmann’s equation provides a satisfactory description of the dependence of the change in the contact angle between the fluid and the surface on the voltage applied between the fluid and the film. The change in the wettability of the fluid has been confirmed to be reversible at low voltages, for example, for a droplet of liquid metal (mercury) or a droplet of 10^{-2} M KNO_{3} electrolyte on various dielectric films. By using this technique, many applications have been recently achieved in micro-actuation, micro-fluidic transport and mixing, switchable devices, liquid lens profile control and self-assembled particle arrays.

However, with the exception of dielectric films, the change in the wettability of fluids on conductive surfaces in external electrostatic fields has not been investigated in detail. In addition, most reports concern only the absolute change in the electricity charge at the fluid/dielectric film interface and ignore the occurrence of electrochemical reactions at the liquid/solid interface. It is known that electrochemical reactions usually occur under the control of an electric double layer (EDL) at the aqueous solution/metal interface, where there usually exists a conductive or semiconductive passive film different from the above mentioned dielectric film. Such wetting behavior of aqueous solutions on metal surfaces has not been investigated sufficiently well until now. The EDL generally forms at the interface even though there is no dielectric film. The intensity of the electrostatic field of the EDL can be controlled externally by altering the electrode potential of the metal surface by applying voltage between the solution and the metal.

It is understandable that the wetting behavior of the solution on the metal surface can influence or be influenced by the electrochemical reaction. Therefore, it is important to know the wettability of the solution on the metal surface not only before and after the electrochemical reaction, but also during the reaction. Y. Tsuru et al. reported the wetting behavior of a sodium sulfate solution on a pure iron electrode by using electronic balance. They found that spreading wetting of the solution occurred during the active dissolution of iron and stopped at the passivation region of iron (tending to form some droplets on the electrode). On the other hand, it is well known that in chloride-containing solutions pitting corrosion usually occurs on stainless steel when the passive film on the surface is destroyed. Therefore, it is also necessary to clarify the changes in the wettability of chloride-containing solutions on stainless steel during the electrochemical reaction.

In this work, aqueous solutions with different concentrations of sodium chloride were used to investigate the changes in wettability when a current flows through the surface of the stainless steel. The current shows the rate of the electrochemical reaction. For comparison, a sodium sulfate aqueous solution was also used. In addition, the pH of several solutions was adjusted. Furthermore, the polarization curves of stainless steel in contact with a small amount of solution were measured to elucidate the relation between corrosion behavior and wettability.

2. Experimental Details

A commercially supplied JIS SUS304 stainless steel plate (solution-treated; thickness: 2 mm) with chemical composition of C: 0.05 mass%, Si: 0.63%, Mn: 0.90%, P: 0.032%, S: 0.002%, Cr: 18.05%, Ni: 8.10%, Fe: balance was cut into 20 mm × 20 mm square specimens. All specimens were polished with #600 emery paper on one side and were ultrasonically cleaned in acetone before use.

The wetting behavior of liquid droplets of (i) pure water, (ii) NaCl-containing aqueous solutions (0.01 mass%, 0.1%, 1.0% and 3.5% NaCl) and (iii) Na_{2}SO_{4}-containing aqueous
solution (1.0% Na₂SO₄) was investigated using the apparatus shown in Fig. 1. The pH of several droplets of 1.0% NaCl solution and 1.0% Na₂SO₄ solution was adjusted to 1.0 and 13.0 with H₂SO₄ and NaOH solutions, respectively. The volume of each droplet was about 80 μL. In this apparatus, the side view and the top view of each droplet were recorded during the flow of current. A platinum (Pt) wire with a diameter of 1.0 mm was used as a counter electrode, with a distance from the specimen surface of about 1.0 mm. Two types of current were applied in this work, one flowing from the power supply unit to the Pt wire with a cathodic reaction on the specimen surface, which is referred to as cathodic current (I_c), and the other flowing from the power supply unit to the specimen with an anodic reaction on the specimen surface, which is referred to as anodic current (I_a).

The polarization curves of the specimens contacted with a small amount (1.2 mL) of solution was investigated using the apparatus shown in Fig. 2. The electrode potential of the specimens was controlled with a potentiostat (HAB-151, Hokuto Co.). A platinum wire was used as a counter electrode and a saturated calomel electrode (S.C.E.) was used as a reference electrode. The polarization started from the cathode side to the anode side, where the potential increased at a constant rate of 20 mV/min. The current on the specimen surface was input to a data recorder for processing.

### 3. Results

#### 3.1 Change in shape of droplets during current flow

Figure 3 shows the diameters and the heights as well as the contact angles of aqueous solution droplets (3.5% NaCl) on polished SUS304 steel. A cathodic current of I_c = 1.0 mA was applied for 10 seconds. Note that all contact angles in this work were measured after stopping the current flow and detaching the Pt electrode from the droplet; the contact line was not changed during the process of stopping the current. The contact angle was obtained from the side view of the droplets. Each value, including the diameter, the height and the contact angle, was averaged from at least six different droplets. As the current flowed, the diameter of the droplets gradually increased from 6.7 mm to 9.0 mm after 10 s. The diameter as obtained from the top view and the side view differed to some extent in all measurements due to discrepancies in the estimation of the contact line between the droplets and the specimen. The height of the droplets decreased from 2.3 to 1.4 mm after 10 s of current flow. The wetting contact angle, obtained from the side view of the droplets, decreased from 70° to 34°, indicating an increase in wettability induced by the application of cathodic current to the surface of the specimen. However, after 10 s of current flow, the shape of the droplets appeared to become relatively stable and did not exhibit any further considerable changes.

Figure 4 shows the changes in the contact angle for NaCl solutions with concentration of 0, 0.01, 0.1, 1.0 and 3.5% on SUS304 steel when a cathodic current of I_c = 1.0 mA was applied. No large differences could be found in the wettability of the solutions before and after the application of current. The shape of the droplets of pure water (0% NaCl) almost did not respond to the current flow, while the height of droplets of NaCl-containing solutions decreased with the
simultaneous increase in the radius with the current flow. There was a tendency of higher wettability for higher concentrations of NaCl (from 0% to 0.1% NaCl); however, no further changes in shape could be found when the concentration of NaCl was higher than 0.1%.

Figure 5 shows the changes in the shape of the droplets and the contact angle of 1.0% Na₂SO₄ solution on SUS304 steel with a cathodic current of \( I_c = 1.0 \) mA. As the flow time of the current increased, the solution displayed tendencies which were similar to those of the 3.5% and 1.0% NaCl solutions. This suggests that the changes in the wettability of solutions should be related to the conductivity of the solutions.

Figure 6 shows the changes in the diameter of droplets with concentration of NaCl of 0, 0.01 and 3.5% on the specimen with anodic current of \( I_a = 1.0 \) mA. No notable changes can be found in the diameter and height of each type of droplet when applying anodic current. This suggests that the wettability of the droplets is immune to anodic current and the changes in wettability are irreversible.

Figure 7 shows the changes in the contact angle of droplets with concentration of 1.0% NaCl and 1.0% Na₂SO₄ with pH = 1.0, 7.0 and 13.0 on SUS304 steel when a cathodic current of \( I_a = 1.0 \) mA flows to specimen surface with the increase in the flowing time.
pH = 1.0, 7.0 and 13.0 on the specimen with cathodic current of $I_c = 1.0 \text{ mA}$. Before the current was applied, the respective contact angles of the droplets with pH = 1.0 and 7.0 were almost the same, while the contact angle for droplets with pH = 13.0 was much smaller. When cathodic current was applied, all contact angles decreased considerably. The decrement for droplets with pH = 1.0 and 13.0 was smaller than that for droplets with pH = 7.0. This indicates that the wetting behavior is strongly related to the pH of the solution.

Figure 8 shows specimen surfaces before and after a current ($I = 1 \text{ mA}$) was applied for 10 s through a droplet of 1.0% NaCl solution.

### 3.2 Polarization curves

Figure 9 shows the polarization curves of polished SUS304 steel for 0.1% NaCl, 1.0% NaCl and 1.0% Na$_2$SO$_4$ aqueous solutions with a volume of 1.2 mL (area of the liquid/solid interface: 175 mm$^2$; height of the contacted solution: 6.8 mm). The amount of solution is about 15 droplets of that used in the wettability observations. The corrosion behavior is expected to change in accordance to the amount of solution.$^{16,17}$ For convenience, the polarization behavior for 1.2 mL of solution can be regarded as the same as that for a single droplet since the height of the contacted solution is close to the initial height of the droplet (2.5 mm). No large differences can be found in the cathodic zone for any of the solutions; however, the pitting corrosion potential for the 1.0% Na$_2$SO$_4$ solution is larger than that for the 1.0% and 0.1% NaCl solutions. The polarization curves for the 0.1% and 1.0% NaCl solutions are almost the same. Since the interface between the droplet and the substrate is about 175 mm$^2$, the current of $I = 1.0 \text{ mA}$ corresponds to current density of $i = 5.7 \text{ A/m}^2$, which is shown in the figure. It is clear that the current flows in the hydrogen reduction zone in the case of cathodic current and in the pitting zone in the case of anodic current. Generally, in the hydrogen evolution zone on the specimen surface, the passive film of stainless steel is uniformly reduced to expose the bare metal surface, while in the case of anodic current pitting corrosion zone pits appear on the surface and most of the passive film remains.
Figure 10 shows the polarization curves of specimen for 1.2 mL 1.0% NaCl and 1.0% Na2SO4 with pH = 1.0 and 13.0. Almost the same curves were obtained for solutions with pH = 1.0, indicating the reduction of hydrogen and the passive film in the cathodic region for a current of \( I_c = 1.0 \) mA. The cathodic current was much larger for the Na2SO4 solution at pH = 13.0 than for the NaCl solution with pH = 13.0. For a current of \( I_c = 1.0 \) mA, a reaction of hydrogen and passive film reduction occurs for NaCl solutions at pH = 13.0, while for the Na2SO4 solution with pH = 13.0 both a reaction of hydrogen/film reduction and oxygen consumption occur.

4. Discussion

It is known that on stainless steel surfaces there is a passive film which is only several nanometers thick and contains mainly chromium oxide and hydroxide, with small amounts of iron oxide and hydroxide.\(^{18,19}\) In general, the conductivity of the thin passive film is as high as that of the bare stainless steel substrate.\(^{20}\) When the steel surface is wetted with an aqueous solution, an electrical double layer (EDL) generally forms at the liquid/solid interface. This EDL model was first proposed by Helmholtz and was subsequently developed by Gouy, Ahapman, Stern and Grahame.\(^{21,22}\) It mainly describes a diffusive distribution of attracted ions near the solid surface enriched with electrical charges, including the differential adsorption of special bare ions directly on the solid surface. In NaCl solutions, Cl\(^{-}\) can be differentially adsorbed on solid defects.\(^{21,22}\) It is known that excessive negative charge usually appears on most solid surfaces in aqueous solutions;\(^{23}\) however, it is still difficult to know whether the steel side is absolutely positive-rich or negative-rich without directly measuring the zeta potential. Considering that the zero charge point of Cr2O3 (including chromium hydride) in water is near pH = 6.5~7.4, it is reasonable to assume that there is no excessive electric charge on the passive film for solutions without the adjustment of pH and the application of external potential (current). It is convenient to discuss the changes in the electric charge of the EDL in this case. Naturally, there is a weak anodic and a weak cathodic reaction occurring simultaneously at the interface even before the application of external current; however, they can be ignored due to the slow reaction rate. The reaction rate can be controlled by changing the electrode potential of the metal (i.e., the intensity of the electrostatic field) by applying reaction current.

In this work, regarding the changes in the contact angle of the droplets, two stages, namely (i) the charge of the EDL within a short time and (ii) the cathodic or anodic reaction at the solid/liquid interface, can be considered as follows.

(i) In the initial stage of the moment when the current flow is applied in the electric circuit, the EDL is charged, however, an electrochemical reaction has not occurred. During this short time period, the wettability of the liquid generally changes in accordance to the following integral version of the Lippmann’s equation:\(^{24}\)

\[
\gamma_{LG} \cos \theta = \gamma_{SG} - \gamma_{SL} + \frac{\kappa_0 (\varepsilon_0 + \varepsilon_s)}{2} (V - V^{ZC})^2
\]

where \( \theta \) is the contact angle of the liquid, \( \gamma_{LG}, \gamma_{SG} \) and \( \gamma_{SL} \) are respectively the tension of the liquid surface, the solid surface and the liquid/solid interface, \( \delta \) is the thickness of the EDL, \( \varepsilon_0 \) and \( \varepsilon_s \) are respectively the permittivity of free space and that of the liquid, \( V \) is the applied potential, and \( V^{ZC} \) is the zeta potential of the solid surface in the liquid, in other words, the potential of zero charge for the solution. This equation is constructed under the assumption that \( \gamma_{LG}, \gamma_{SG} \) and \( \gamma_{SL} \) do not change under applied voltage. This suggests that the chemical composition or the surface structure of the solid surface will not change during the application of voltage. It is known from this equation that the contact angle of the liquid becomes small when \( V \) is verified (\( V > V^{ZC} \); \( V < V^{ZC} \)), where the largest contact angle is at \( V = V^{ZC} \). Accordingly, it is clear that in this work the contact angle of the droplets became smaller when cathodic current started to flow due to the application of negative voltage at the interface. This can also be proven by the smaller contact angle for solutions with higher pH (without current flow; Fig. 7). It is known that the surface of the passive film is negative-rich at high pH and positive-rich at low pH due to the hydration and dehydration of water molecules on the surface.\(^{25}\)

(ii) In the following stage with continuous current flow through the liquid/solid interface, the intensity of the electrostatic field in the EDL is considered stable. This indicates that the last item of the Lippmann’s equation does not change further and the changes in the contact angle are attributed mainly to the continuous current flow. The current flow causes the cathodic or anodic reaction at the interface to alter the surface composition or surface structure of the specimen. This results in changes in the surface tension \( \gamma_{SG} \) of the specimen and the interface tension \( \gamma_{SL} \) in the Lippmann’s equation, which influence the changes in the contact angle.

In the case of cathodic current flow, electrons arrive at the surface of the specimen from the interior of the metal. Few initial electrons participate in the charging of the EDL, while most of them participate in the reduction of hydrogen and the passive film. The former can increase the intensity of the electrostatic field to attract more positive ions to the interface, which directly induces an increase in the wet-
ability of the droplets. Here, we refer to this process as "typical electrowetting". The electrons which arrive later induce an uniform reduction of the passive film (Fig. 8(b)). With the uniform disappearance of the passive film, the solution comes in contact with the hydrophilic surface of the bare metal rather than with the hydrophobic passive film, which increases the wettability of the solution (Fig. 11(a)). This is similar to the wettability of sodium sulfate solutions on iron surfaces.\textsuperscript{15} The differential adsorption of Cl\textsuperscript{-} on the film can further enhance the intensity of the electrostatic field to promote an increase in wettability (the differential adsorption of Cl\textsuperscript{-} is little in this case (Fig. 12(c)), and thus its influence is limited). On the other hand, there is OH\textsuperscript{-} condensation near the interface in the cathodic reaction, which can promote the formation of MO\textsuperscript{-} on the solid surface\textsuperscript{25} (Fig. 12(c)). As hydrogen is combined with water molecules (Fig. 12), this also promotes an increase in the wettability of aqueous solutions. This is another reason why the contact angle of solutions with high pH is small.

Theoretically, from the Lippmann’s equation, in the case of anodic current flow the contact angle of solutions should also decrease. However, in fact no change in the contact angle was found. Several reasons for this result are considered here. (i) In this case, a considerable amount of Cl\textsuperscript{-} is differentially adsorbed on the film,\textsuperscript{21,22} which lowers the intensity of the electrostatic field (Fig. 12(d)). (ii) The occurrence of pitting corrosion on the surface induces the removal of only a little portion of the passive film, and there is no notable change in $\gamma_{SG}$ and $\gamma_{SL}$ (Fig. 11(b)) since small pits cannot induce a considerable increase in surface roughness. (iii) In the anodic reaction, the condensed H\textsuperscript{+} near the interface promote the formation of M\textsuperscript{+} or MOH\textsubscript{2}\textsuperscript{+} and as a result it is difficult for hydrogen to bond to water molecules, which should lower the wettability (Fig. 12(d)). This is also true for larger contact angles for solutions with low pH. The contact angle cannot be recovered when the cathodic current flow is stopped. The reason might be the slow recovery of the passive film or the existence of MO\textsuperscript{+}, where the latter is formed due to the formation of condensed OH\textsuperscript{-} near the interface in the cathode reaction.

It has been known that the contact angles of droplets with pH = 1.0 and 7.0 are much smaller than that of droplets with pH = 13.0. Furthermore, the contact angle at pH = 13.0 is almost the same as that after the application of cathodic current for 10s. This indicates a good correspondence for the wettability between the changes in pH and the current flow, that is, the condensation of OH\textsuperscript{-} at the interface (negative-rich) when cathodic current is applied and the condensation of H\textsuperscript{+} (positive-rich) when anodic current is applied. This indicates that the wetting behavior should be related to both the electric charge of the EDL and the local pH at the interface. The changes in the contact angle for pH = 7.0 are much larger than in the case of pH = 1.0 and pH = 13.0. This should be attributed to the fact that changes in the local pH occur more easily at pH = 7.0 than at pH = 1.0 or 13.0. Naturally, changes in local pH are directly related to changes in the EDL.

On the other hand, the wettability of pure water is immune to both cathodic and anodic current. This is due to the difficulty of forming the EDL at the interface due to the lack of free ions in the liquid. The changes in wettability became saturated when the concentration of NaCl was higher than 0.1%, suggesting a limitation to the concentration of free ions near the interface. In this regard, the wettability was almost the same when Na\textsubscript{2}SO\textsubscript{4} was used. In this work, only predefined cathodic or anodic current was applied for investigating the wetting behavior of NaCl-containing solutions on stainless steel. However, it is also possible that a different behavior might be observed at other values of the currents. This will be investigated and reported in future works.

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**Fig. 11** Change of contact angle and passive film at the interface between solution/SUS304 stainless steel when cathodic (a) or anodic (b) current flows.

**Fig. 12** Change of contact angle and ion arrangement at the interface between solution/SUS304 stainless steel when cathodic (b) (c) or anodic (d) current flows in comparing to that without current flow (a).
5. Conclusions

In this work, the wettability on SUS304 stainless steel of solutions with different concentration of sodium chloride and sodium sulfate was investigated when cathodic or anodic current was applied. The polarization curves of stainless steel in contact with a small amount of solution were measured for the purpose of discussing the relation between corrosion behavior and wettability. The following results were obtained.

(1) The contact angle of a droplet of pure water does not change with the application of either anodic or cathodic current.

(2) The contact angle for 0.01~3.5% NaCl and 1.0% Na$_2$SO$_4$ solutions became small when a cathodic current of 1.0 mA was applied. There was a tendency of higher wettability for higher concentrations (from 0.01% to 0.1% NaCl); however, no further changes were observed when the concentration of NaCl was higher than 0.1%.

(3) The decrease in the contact angle of ionic solutions with the application of a cathodic current of $I_c = 1.0$ mA is irreversible, in other words, the contact angle is not restored when the current is stopped or when anodic current of $I_a = 1.0$ mA is applied.

(4) The changes in wettability were considered to be attributable to the changes in both the electric charge and the passive film at the interface.

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REFERENCES