Concentration of external CaCl_2 solution (N)	0.2	0.5	2.0
Specific conductivity measured ($\Omega^{-1} \text{ cm}^{-1}$)	0.00140	0.00142	0.00135
Specific conductivity calculated ($\Omega^{-1} \text{ cm}^{-1}$)	0.00054	0.00091	0.00130

The values measured are larger than those calculated. As pointed out by Spiegler²⁾ and Despic³⁾, these disagreements were due to the fact that the convection current in the membrane was neglected in the calculation of the specific conductance. The result of the above comparison shows that the disagreement is larger in diluted solutions than in concentrated ones, and this is considered to prove the theory that the convection current takes a fairly large part of the electric current in the membrane, especially in diluted solutions.

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Study on Corrosion Inhibitors by Impedance Measurement (I)

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Effectiveness of corrosion inhibitors has been measured by (1) weight loss of metals in corrosive solutions containing inhibitors, (2) decrease of galvanic current¹⁾, (3) polarization characteristics²⁾, (4) suppression of polarographic maxima³⁾, and (5) the Pearson bridge method^{4),5)}. Measurement of alternating current impedance of metal surface in electrolytic solution is a useful experimental method especially for the study of the structure of oxide film or passivity. The authors have tried to apply the method to investigate the adsorption mechanism of corrosion inhibitors on metals.

When two sheets of steel are immersed in acid containing inhibitors, the change of their surface impedance is due to two different phenomena, that is, surface state change by corrosion and adsorption of organic substances. In order to identify them and to make their characteristics clear, impedance changes both on platinum surface (as noncorrosive metal) in sulfuric acid containing inhibitors and on the steel surface being corroded in sulfuric acid with and without inhibitors were measured and compared.

Since R- and C-values measured in the device of Fig. 1 contain solution resistance between two electrodes, the calculation must be done to eliminate it and then to represent R and C in series or parallel equivalent

Cell: Measuring cell, OSC: Oscillator, AMP: Amplifier, Cx, Cy: Arm-ratio condensers, Cp, R: Variable condenser and variable resistance, CRO: Cathod-ray oscillograph as detector

Fig. 1 Device and circuit for the measurement of electrode impedance

(a) Series equivalent circuit, (b) Parallel equivalent circuit, Rp, Cp, R'p, C'p: Polarization resistance and polarization capacity, Rs: Resistance of solution

Fig. 2 Equivalent circuits of metal surface and solution

circuit as shown in Fig. 2 (a) or (b). Surface impedance of platinum plate in 12% sulfuric acid showed rather remarkable changes when thiourea of 0.1% concentration was added (Fig. 3 and 4). Polarization capacity decreased and polarization resistance increased and the tendency of change was the same whether the values were shown in a parallel combination of R_p and C_p or a series combination of them. These changes of resistance and capacity can be explained from the assumption that the surface of metal was covered by inhibitor and its real surface area decreased.

Impedance change of steel surface, when it is being corroded in 12% sulfuric acid without any inhibitors, is shown in Fig. 6. Decrease of R_p and increase of C_p are caused by the porous surface of the steel dissolved in acid.

The result obtained by the measurement of impedance change of steel surface in 12% sulfuric acid, when inhibitor consisting of several amines was added during corrosion, is shown in Fig. 7. Addition of inhibitor stops or retards the change of C_p from increasing and R_p from decreasing, and if the inhibitor is effective enough to protect the surface, polarization capacity and polarization resistance are caused to reverse their tendency of changes and reach constant values (Fig. 8). Desorption phenomena of inhibitors were also studied. Fig. 5 shows the adsorption and desorption of inhibitors when some treatments were done on the surface of platinum. The experiment shows that inhibitors cannot be desorbed very easily if

Fig. 3 Adsorption of thiourea on smooth platinum

Fig. 4. Impedance changes of platinum surface immersed in 12% sulfuric acid when 0.1% thiourea was added

- (1) Clear platinum surface immersed in sulfuric acid.
- (2) Thiourea was added.
- (3) Platinum was washed with distilled water and then was immersed in sulfuric acid without any inhibitors.
- (4) Thiourea was added again.
- (5) The platinum plate was ignited in oxidizing flame.

Fig. 5 Adsorption and desorption of inhibitor

Fig. 6 Impedance change of steel surface being corroded in 12% H_2SO_4

Fig. 7 Polarization capacity and resistance changes of steel surface in 12% H_2SO_4 , when inhibitor (mixture of amines) was added

Fig. 8 Change of C_p vs. concentration of inhibitor

Fig. 9 Relation between natural electrode potential and polarization capacity

the surface of metal is washed only with water. To remove inhibitors completely from platinum surface, it must be ignited in the oxidizing flame of gas burner.

The authors have come to the conclusion that degree of adsorption and desorption of corrosion inhibitors can be measured by alternating current impedance of metal surfaces as well as natural electrode potential (Fig. 9), and effectiveness of inhibitors can be evaluated by polarization capacity and polarization resistance. This method may be applied to the investigation of the effectiveness of inhibitors under various working conditions.

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