Effect of Liquid Junction Potential on Galvanic Current

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The galvanic current between copper electrodes immersed in solutions of different salt concentration is investigated for the aqueous systems of $\text{CuSO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$. The effect of the liquid junction potential caused by the concentration difference in Na_2SO_4 or H_2SO_4 on galvanic currents were measured quantitatively and elucidated by modified Evans' diagrams. As an extreme case of liquid junction potential effect apparently abnormal phenomena in which the position of higher electrode potential becomes anode against the position of lower electrode potential is demonstrated in galvanic cell. Furthermore the change in polarization resistance due to the difference in salt concentration brings remarkable effect on the amount of galvanic currents.

1. Introduction

In the situation that different position of a metallic body respectively face to solutions of different salt concentration in a continuous environment, it is not surprising that a corrosion cell with separate anode and cathode takes place, but it is difficult to predict which position will act as a localized anode. There are two well known cases in this type of "salt concentration cell".

When "the normal metals", according to the classification of Piontelli, which includes for example copper, tin, and lead face to different concentration of its own cation, electrode potential difference due to the Nernst equation drives corrosion cells in which areas of low ionic concentration becomes anode. This effect is not expected for "inert metals" including ferrous materials.

When oxygen solubility difference occurs due to salt concentration difference, it drives corrosion cell according to the differential aeration mechanism.

In this report, the third case of "salt concentration cell" in which liquid junction potential plays essential role in corrosion cell, is newly demonstrated. Apparently abnormal phenomena in which the position of a higher electrode potential becomes anode against the position of a lower electrode potential are provided as extreme cases of this mechanism.

The new mechanism of "liquid junction potential

effect" is established by the studies made on galvanic behavior of copper electrodes in aqueous solutions of copper sulfate and either sodium sulfate or sulfuric acid.

The amount of galvanic current is greatly affected by a change in polarization resistance due to difference in salt concentration irrespective of the open circuit potential of a galvanic cell. This effect is demonstrated experimentally as well.

2. Experimental

The arrangement of apparatus is shown in Figure 1. The rectangular box of plexiglas ($150\text{ mm} \times 150\text{ mm} \times 250\text{ mm}$) was used in a closed type. A square diaphragm of filter paper (No. 2, $100\text{ mm} \times 100\text{ mm}$) was set to separate the cell in compartment I and II symmetrically and to prevent a solution of electrolytes in compartment I from mixing with another solution in compartment II. The electrode was of a rectangular copper plate ($50\text{ mm} \times 20\text{ mm}$), the rear of which was coated with epoxy resin.

Copper sulfate, sodium sulfate and sulfuric acid were used as electrolytes. The concentration of these electrolytes was chosen as the only one variable in experimental conditions.

The fronts of the copper electrodes were physically polished, and pretreated in a mixed solution of $0.1\text{ mol/dm}^3\text{ CuSO}_4$ and $0.1\text{ mol/dm}^3\text{ Na}_2\text{SO}_4$ at room temperature for one hour. In the study of the effect of concentration difference, two copper electrodes with same rest potential in the pretreat-

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Fig. 1 Experimental assembly.

ment solution were chosen for minimizing galvanic current caused by difference in electrochemical nature of the electrodes. These copper electrodes were set in each compartment with polished surfaces facing each other.

A solution of 1.5 liter in volume, bubbled with nitrogen gas to remove dissolved oxygen gas, was carefully and gradually introduced onto the bottom of each compartment filled with nitrogen gas.

Two saturated calomel electrodes (S.C.E.) with same and stable potential were respectively connected to the solution in each compartment by an agar salt bridge of saturated potassium chloride for measurements of liquid junction potentials and electrode potentials.

Electrode potentials in compartment I, E_I , and those in compartment II, E_{II} , were measured against S.C.E.. A liquid junction potential ΔE_j (difference in potential between a solution in compartment I and another solution in compartment II) was measured by an electrometer as the potential of S.C.E. in compartment I, ϕ_I^N , against that of S.C.E. in compartment II, ϕ_{II}^N (i.e. $\phi_I^N - \phi_{II}^N$).

In this paper, the electrode potential E and the potential ϕ are defined in separate meaning. The potential ϕ means absolute electric potential, the single value of which can never be measured. Only the difference between ϕ 's of electronic conductive phases is measurable. The electrode potential is

determined with the measurement of the difference between ϕ^M and ϕ^N , where ϕ^M is the potential of the working electrode and ϕ^N is the potential of the reference electrode.

The measurements of short-circuit I_s flowing through the two copper electrodes connected each other were made by a zero-shunt-ammeter.

The estimated galvanic current I_G^* was measured by the procedure that the electrode set in the compartment I was polarized by a potentiostat until the difference in the electrode potentials, $E_{II} - E_I$, reached the value of the liquid junction potential for the solution used. Measurements of the galvanic current without junction I_G was obtained by the polarization which made the potential of both electrodes the same value. The positive sign of galvanic currents represents that the direct current flows from the electrode II to the electrode I through a lead wire.

In measurements of potential, a great care of eliminating the electric interference and the instability of electric sources was paid to the choice of polarity of an electrometer and of a recorder and to the method of electric screening and grounding. The solutions were bubbled with nitrogen gas during measurements of the galvanic current and the potential of copper electrodes. The measurements were made at room temperature.

Table 1 The aqueous system, $\text{CuSO}_4\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$.

case		1	2	3	4	5	6	7	8	9	10
compartment I	CuSO_4 (mol/l)	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.001	0.005	0.050
	Na_2SO_4 (mol/l)	0	0.010	0.050	0.100	0	0.120	0	0.067	0.067	0.067
	E_I^0 (mV, SCE)	32.0	25.3	18.8	16.8	31.5	15.6	31.5	-7.7	9.5	38.0
compartment II	CuSO_4 (mol/l)	0.050	0.010	0.010	0.010	0.100	0.100	0.100	0.100	0.100	0.100
	Na_2SO_4 (mol/l)	0.200	0.005	0.005	0.005	0	0	0.100	0	0	0
	E_{II}^0 (mV, SCE)	36.5	27.7	26.7	28.5	55.0	54.0	47.5	54.0	54.0	53.0
$E_{II}^0 - E_I^0$ (mV)		4.5	2.4	7.9	11.7	23.5	38.4	16.0	61.7	42.5	15.0
$\phi_{II}^M - \phi_I^M$ (mV)		-8.5	3.1	14.4	21.7	23.2	46.2	6.0	66.2	48.5	18.7
ΔE_j $= \phi_I^S - \phi_{II}^S$	measured (mV)	13.0	-0.7	-6.5	-10.0	0.3	-7.8	10.0	-4.5	-4.0	-3.7
	calculated (mV)	8.2	-0.7	-3.2	-4.6	-4.5	-3.6	0.8	-3.9	-3.7	-2.1
I_G^* (μA)		-390	150	595	705	440	2200	480	2750	2120	820
I_G (μA)		630	120	470	480	450	1780	800	2600	1930	660
I_S (μA)		-130	20	90	190	160	690	95	720	580	250

Fig. 2 Relation between rest potential of copper electrodes and molarity of copper sulfate.

3. Result

3.1 The aqueous system, $\text{CuSO}_4\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$

The potentials of copper electrodes, the liquid junction potentials and the galvanic currents were measured in aqueous solutions of copper sulfate and sodium sulfate. Some of typical examples in the effects of the liquid junction potential and of solution composition on the polarization behaviours of the copper electrodes are shown in Table 1.

The copper electrode in compartment II had a rest potential higher than the copper electrode in compartment I. Table 1 suggests that the rest potential of copper electrodes increases with the increases of concentration of copper sulfate but decreases with the increase of concentration of sodium sulfate.

It is shown in Table 1 that difference between the rest potential of a copper electrode in one compartment and that of another copper electrode in

Fig. 3 Relation between rest potential of copper electrodes and molarity of sodium sulfate.

the other compartment, and the liquid junction potential had the order of a few tens millivolts in every case. Thus, this study probably requires the rest potential to be measured within error of few tenths of one millivolt in each solution.

The rest potentials of copper electrodes were measured in aqueous solutions of copper sulfate and sodium sulfate of varying concentrations. The relation between the rest potential of copper electrodes and the molarity of copper sulfate, and the relation between the rest potential and the molarity of sodium sulfate are shown in Figures 2 and 3, respectively. Figure 2 shows that the rest potential E^0 of copper electrodes is approximated for the concentration of copper sulfate (C mol/dm³) by

$$E^0(\text{mv, S.C.E.}) = 28.9 \log C + 77.2 \quad (1)$$

This equation (1) is rewritten in the Nernst form:

$$E^0(\text{mV, S.C.E.}) = E^\phi + (RT/2.04 F) \ln 0.29 C \quad (2)$$

where E^ϕ shows the standard electrode potential of copper, $-92.6(\text{mV, S.C.E.})$, and R , T and F show

Fig. 4 Relation between short-circuit current and time (case 1).

the gas constant, absolute temperature, and the Faraday constant, respectively.

Figure 3 shows that the rest potential E^0 lowers with the increase of Na_2SO_4 concentration. The measured liquid junction potential decreased with the increase of the concentration of sodium sulfate in compartment I for a fixed concentration of the salt in compartment II (cases 2, 3 and 4). For a fixed concentration of the salt in compartment I, the liquid junction potential increased with the increase of the concentration of sodium sulfate in compartment II (cases 5 and 7). However, the liquid junction potential was hardly affected by the difference in the concentration of copper sulfate in both compartments and remained almost unchanged (cases 8, 9 and 10).

The measured cell voltage, potential $\phi_{\text{II}}^{\text{M}}$ of a copper electrode in compartment II against potential $\phi_{\text{I}}^{\text{M}}$ of another copper electrode in compartment I, i.e. $\phi_{\text{II}}^{\text{M}} - \phi_{\text{I}}^{\text{M}}$, agreed in the accuracy of few tenths of one millivolt with the value of potential consisting of the rest potential and the liquid junction potential, $E_{\text{II}}^0 - E_{\text{I}}^0 - \Delta E_j$. Here E_{II}^0 , E_{I}^0 and ΔE_j show the rest potential of copper electrode in compartment II, the rest potential of copper electrode in compartment I and the liquid junction potential, respectively. This agreement in cell voltage shows that the potentials measured in this study have a reliability of the order of few tenths of one millivolt.

The cell voltage showed a negative value ($\phi_{\text{II}}^{\text{M}} < \phi_{\text{I}}^{\text{M}}$) in case I and the short-circuit current I_s in order of few hundred microamperes flowed from compartment II through the diaphragm to compartment I when the two copper electrodes were short-circuited. The short-circuit current slightly decreased with time, as shown in Fig. 4. It should be noted that the liquid junction potential in this case had a value much higher than difference in the rest potentials of two copper electrodes.

Fig. 5 Polarization of copper electrode in aqueous solution of varying concentration.

The cell voltage, the rest potentials of the two copper electrodes and the liquid junction potential, measured after continuous measurements of the short-circuit current for thirty minutes, agreed within error of one millivolt with those observed at the beginning of measurements respectively in every case. This agreement and the constancy in the short-circuit current suggest that the time variation in the composition of the aqueous solutions did not give a noticeable effect on it.

The values of I_G^* and I_s are of the same sign: at the case 1 in the Table 1, they are negative, and in the other cases they are positive. The absolute of I_G^* is always larger than that of I_s . The value of I_G is always positive, which means that except for the liquid junction potential the electrode with lower rest potential always becomes anode in galvanic systems.

In the cases of negative liquid junction potential ($\Delta E_j < 0$), the value of I_G^* is larger than that of I_G (cases 2, 3, 4, 6, 8, 9). The negative value of ΔE_j increases the driving force of the galvanic cell, and makes the anodic position more anodic. The positive value of ΔE_j makes the value of I_G^* smaller than that of I_G , which indicates that the galvanic current is depressed due to liquid junction potential effect. If ΔE_j overcomes the difference in the electrode potentials ($E_{\text{II}}^0 - E_{\text{I}}^0$), the cell voltage ($\phi_{\text{II}}^{\text{M}} - \phi_{\text{I}}^{\text{M}}$) becomes negative and I_G^* as well as I_s show negative values. The observed negative value of I_G^* corresponds to the abnormality that the electrode with higher rest potential becomes anode in an galvanic system.

In the cases 5 and 7 in Table 1, composition of copper sulfate in both compartment are of the

Table 2 The aqueous system, $\text{CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$.

compartment I	dilution			2	4	8	16
	CuSO_4 (mol/l)	H_2SO_4 (mol/l)	E_I^0 (mV, SCE)	0.354	0.177	0.089	0.044
				0.969	0.485	0.242	0.121
				62.5	61.0	57.0	55.0
compartment II							
	CuSO_4 (mol/l)	H_2SO_4 (mol/l)	E_{II}^0 (mV, SCE)	0.708	0.708	0.708	0.708
				1.939	1.939	1.939	1.939
				72.0	73.0	73.0	73.0
$E_{II}^0 - E_I^0$ (mV)				9.5	12.0	16.0	18.0
$\phi_{II}^M - \phi_I^M$ (mV)				-3.7	-6.9	-9.0	-13.3
ΔE_j $= \phi_I^S - \phi_{II}^S$	measured	(mV)		13.2	18.9	25.0	31.3
	calculated	(mV)		4.4	10.2	17.3	25.6
I_G^* (μA)				-350	-580	-820	-1150
I_G (μA)				1050	1450	1810	2030
I_S (μA)				-280	-510	-760	-980

Fig. 6 Relation between dilution of standard solution and liquid junction potential and difference in rest potentials (Broken line: calculated liquid junction potential).

same value, i.e. 0.010 [mol/dm³] in compartment I and 0.100 [mol/dm³] in compartment II respectively. Only the difference in Na_2SO_4 concentration in compartment II, makes clear difference in the values of E_{II}^0 , ΔE_j and $\phi_{II}^M - \phi_I^M$. The cell voltage is larger in the case 5 than in the case 7, however, the value of I_G^* and I_S are smaller in the case 5 than in the case 7. This abnormality suggests that the polarization resistance of the copper electrode was greatly affected by the presence of sodium sulfate in the aqueous solution.

The polarization of copper electrodes was measured in aqueous solutions with sodium sulfate of varying concentration. Figure 5 shows that the polarization resistance of copper electrodes decreased with the increase of concentration of sodium sulfate.

Experimental results provide the two kinds of abnormality caused by the addition of an indiffer-

ent salt of Na_2SO_4 , the abnormality in the direction and the amount of the galvanic current.

3.2 The aqueous system, $\text{CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$

For the solution of copper sulfate and sulfuric acid of varying concentrations (with a given concentration ratio for copper sulfate and sulfuric acid) in compartment I, the rest potentials of copper electrodes, the liquid junction potentials, and three kinds of galvanic currents were measured as in the proceeding section (Table 2).

An aqueous solution of 0.71 mol/dm³ CuSO_4 and 1.94 mol/dm³ H_2SO_4 , which is an electrolytic solution commonly used in industrial electro-refining of copper and which we call the standard solution hereafter, was put in compartment II in every case. The standard solution was diluted with distilled water and the resultant diluted solution was put in compartment I.

The rest potential of a copper electrode in compartment I, E_I^0 , decreased with the decrease of the concentration of aqueous solution in compartment I, that is, with the increase of the dilution D of the standard solution as shown in Fig. 6. The dilution D is defined by a ratio of the molarity of copper sulfate in the solution in compartment II to that in the solution in compartment I. The rest potential of a copper electrode immersed in the standard solution freshly prepared in compartment II, E_{II}^0 , showed 73.0 ± 0.5 (mV, S.C.E.) in every case. Thus, difference in the rest potentials of the copper electrodes, $E_{II}^0 - E_I^0$, increased with dilution of the standard solution.

The measured liquid junction potential ΔE_j was always positive and of the order of a few tens

Fig. 7 Relation between short-circuit current and time for $D=8$.

Fig. 8 Relation between galvanic currents I_G^* , I_G and dilution of standard solution.

millivolts (the potential of S.C.E. in compartment I, ϕ_I^N , gave a few tens millivolts higher than that in compartment II, ($\phi_I^N > \phi_{II}^N$)) and exceeded difference in the rest potentials, $E_{II}^0 - E_I^0$, in every case. The measured liquid junction potential ΔE_j increased with the dilution of the standard solution, D , as shown in Figure 6. The plots of ΔE_j versus $\log D$ in the range from 0.3 to 1.5 gave an approximately straight line with a slope of about 20 (mV/unit of $\log D$). The measured cell voltage, $\phi_{II}^M - \phi_I^M$, agreed with the value, $E_{II}^0 - E_I^0 - \Delta E_j$, in the accuracy of a few tenths of one millivolt, and showed a negative value ($\phi_{II}^M < \phi_I^M$) in every case.

The observed values of $\phi_{II}^M - \phi_I^M$ suggest a possible generation of the abnormal galvanic current mentioned in the proceeding section that makes the electrode of a higher rest potential more anodic to the electrode of a lower rest potential. The measured short circuited current I_s , actually flowed from the electrode in the diluted solution through a lead wire to the electrode in the standard solu-

Fig. 9 Polarization of copper electrode in aqueous solution of varying dilution.

Fig. 10 Evans' polarization diagram for a copper electrode polarized in dilute solution and a copper electrode polarized in standard solution.

tion in every case. The relation between I_s and time for the $D=8$, as an example, is shown in Figure 7. Contrary to the direction of flow for I_s and I_G^* , the galvanic current without junction I_G of the order of a few milliamperes flowed from the electrode in the standard solution to the electrode in the diluted solution. The absolute value of I_G^* and I_G both increased with the increase of the dilution of the solution as shown in Figure 8.

The polarization of copper electrode was measured in aqueous solutions of varying dilution. It is given from Figure 9 that at a fixed overpotential, the observed current density decreased with

the increase of the dilution of the standard solution.

For convenience for latter discussion of the effect of liquid junction potentials on the galvanic currents, Evan's polarization diagrams were made with the measured polarization curves and liquid junction potentials for copper electrodes in aqueous solution of copper sulfate acidified with sulfuric acid.

Figure 10 shows as Evans' polarization diagram for a copper electrode polarized in a solution of 0.09 mol/dm³ CuSO₄ and 0.24 mol/dm³ H₂SO₄ (line B; $D=8$), and a copper electrode polarized in the standard solution (line A). The galvanic state for no liquid junction potential and no ohmic loss of the aqueous solutions can be determined by the point of intersection (c) of the lines A and B. The galvanic current without junction I_G is given by the value of current at the point of intersection (c).

The galvanic current with liquid junction potential effect is given with the broken line B', drawn in parallel to and above the line B by +25.9 (mV), the value of the measured liquid junction potential. This broken line B' corresponds to the modified polarization curve of the copper electrode of polarization line B against the reference electrode II on the assumption that the liquid junction potential is not affected by the corrosion current and remains unchanged.

The galvanic state with liquid junction potential effect for no ohmic loss of the aqueous solution, thus, can be determined by the point of intersection (c_A^*) of the line A and the broken line B'. The value of the estimated galvanic current I_G^* is given by the value of current at the point of intersection (c_A^*). The point of intersection (c_A^*) lying on the lefthand side of the ordinate shows that the galvanic current flows from the copper electrode for the line A though the solutions to the copper electrode for the line B. It should be noted that this galvanic current flows in the opposite way to the direction of flow of the former galvanic current for the case of no liquid junction potential. The former and the latter galvanic currents obtained by the modified Evan's method agreed approximately with the values of measured galvanic currents, I_G and I_G^* , for $D=8$ in Table 2, respectively. This agreement in galvanic currents suggests that the assumption of the liquid junction potential little affected by the flow of corrosion current under present experimental conditions hold well, that potentials and currents were measured

in a reliable way, and that in the presence of liquid junction potential, Evans' polarization diagram can be given with the modified polarization curve.

4. Discussion

4.1 The liquid junction potential and the cell voltage in open circuited cells

The liquid junction potential, ΔE_j , is measured as the difference in potential of two reference electrodes. The liquid junction potential can also be written with potentials of test solutions (ϕ^s), of agars (ϕ^A) of saturated KCl in salt bridges, and of reference electrodes (ϕ^N):

$$\begin{aligned}\Delta E_j &= \phi_I^N - \phi_{II}^N \\ &= (\phi_I^N - \phi_I^A) - (\phi_I^S - \phi_I^A) + (\phi_I^S - \phi_{II}^S) \\ &\quad + (\phi_{II}^S - \phi_{II}^A) + (\phi_{II}^A - \phi_{II}^N)\end{aligned}\quad (3)$$

The difference in potential between the reference electrode and the agar, $\phi^N - \phi^A$, is not affected by the composition of test solutions at fixed temperature and atmospheric pressure. Thus,

$$\phi_I^N - \phi_I^A = \phi_{II}^N - \phi_{II}^A \quad (4)$$

The first and fifth terms on the right-hand side of equation (3) are cancelled out. The third term on the right-hand side of equation (3), $\phi_I^S - \phi_{II}^S$, gives the liquid junction potential (Δe_j) generating between two test solutions. The second and fourth terms, $\phi_I^S - \phi_I^A$ and $\phi_{II}^S - \phi_{II}^A$, give respectively the liquid junction potential (Δe_I) generating between test solution I and an agar in salt bridge I and the potential (Δe_{II}) between test solution II and another agar in salt bridge II:

$$\Delta E_j = \Delta e_j - \Delta e_I + \Delta e_{II} \quad (5)$$

The simplest estimation for the liquid junction potential can be made by Henderson's equation. The comparison of the measured potential and the calculated potential gives some informations on liquid junction potentials in this system.

For Δe_j , Henderson's equation gives

$$\begin{aligned}\Delta e_j = \phi_I^S - \phi_{II}^S &= \frac{RT \sum_i u_i |z_i| (c_i^{II} - c_i^I) / z_i}{F \sum_i u_i |z_i| (c_i^{II} - c_i^I)} \\ &\quad \cdot \ln \frac{\sum_i u_i |z_i| c_i^{II}}{\sum_i u_i |z_i| c_i^I}\end{aligned}\quad (6)$$

where, R , T and F show the gas constant, absolute temperature and the Faraday constant, respectively, and u_i , z_i and c_i show the ionic mobility of, the charge of and the concentration of an ion species i , respectively.

The liquid junction potentials, thus, calculated with the equations, (6) and (7), are shown with the

measured ones in Table 1 and 2. The calculated ΔE_j agreed with the measured ΔE_j within error of the order of ten millivolts. This agreement suggests that the measured liquid junction potentials have reliabilities in present hydrodynamic situation and that Henderson's equation can be employed for the estimation of the actual liquid junction potential.

The study of the role of cell voltage on corrosion current gives some significant insight on the driving force of corrosion current. The cell voltage is measured as the difference in potential of two test electrodes, $\phi_{II}^M - \phi_I^M$. The cell voltage can be written with potentials of test electrodes (ϕ^M) and of reference electrodes (ϕ^N):

$$\phi_{II}^M - \phi_I^M = (\phi_{II}^M - \phi_{II}^N) - (\phi_I^N - \phi_{II}^N) - (\phi_I^M - \phi_I^N) \quad (7)$$

Thus, the first and third terms on the right-hand side of equation (7), $\phi_{II}^M - \phi_{II}^N$ and $\phi_I^M - \phi_I^N$, give the rest potentials of test electrodes, E_{II}^0 and E_I^0 , respectively, and the second term, $\phi_I^N - \phi_{II}^N$, gives the liquid junction potential, ΔE_j :

$$\phi_{II}^M - \phi_I^M = E_{II}^0 - E_I^0 - \Delta E_j \quad (8)$$

The measured rest potential E^0 is related to the theoretical rest potential e^0 by

$$E^0 = e^0 + \Delta e \quad (9)$$

where Δe represents the liquid junction potential generating in salt bridge. With equations (5), (8) and (9), the cell voltage, the theoretical rest potentials and the liquid junction potential generating between two test solutions are related by

$$\phi_{II}^M - \phi_I^M = E_{II}^0 - E_I^0 - \Delta E_j = e_{II}^0 - e_I^0 - \Delta e_j \quad (10)$$

This equation (10) shows that the measured values, $E_{II}^0 - E_I^0 - \Delta E_j$, are not affected by the liquid junction potentials generating in salt bridges. Even for polarized electrodes in closed circuit, equation (10) can also be employed. Rearrangement of equation (10) gives:

$$e_{II} - e_I - \Delta e_j = E_{II} - E_I - \Delta E_j \quad (11)$$

This equation (11) shows that the corrosion current to be generated by the theoretical driving force in voltage, $e_{II} - e_I - \Delta e_j$, can be estimated even from the measured values, E_{II} , E_I and ΔE_j . The discussion made in the following section will focus on the effect of liquid junction potential on galvanic current flowing in closed circuit with the measured values, E_{II} , E_I and ΔE_j .

* The discussions are made only for uniform current distribution over electrode surfaces.

Fig. 11 Evans' polarization diagram.

4.2 The galvanic current and polarized potential in closed circuited cells*

The theoretical considerations of the effect of liquid junction potential on the galvanic current and polarized potential in closed circuit will give some invaluable insight into the understanding of the unusual corrosion behaviours such as unexpected direction in flow and unexpected amount of galvanic current mentioned in the previous section of results.

The short-circuited current I_s is related to the polarized potentials, E_{II} and E_I , by

$$0 = E_{II} - E_I - \Delta E_j - I(R_M + R_S) \quad (12)$$

where R_M and R_S show the ohmic resistances of test electrodes and of test solutions, respectively.

For simplification in discussion, the assumption that R_M and R_S are negligibly small is made:

$$R_M = R_S = 0 \quad (13)$$

Under this assumption, the coupled state is given by the galvanic current and polarized potential satisfying the following relation:

$$E_{II} - E_I - \Delta E_j = 0 \quad (14)$$

The galvanic current satisfying this equation (14) is not affected by the dimension of test cells used. This requires that the two test electrodes in the cells have given surface areas and that the corrosion current has uniform current distribution over the entire electrode surfaces exposed to the electrolyte.

The effect of the liquid junction potential on this galvanic current can now be estimated with Evans' polarization diagram (Fig. 11).

Without liquid junction potential ($\Delta E_j = 0$), the

coupled state can be given by the point of intersection (c in Fig. 11) of two polarization lines, as normally done. Thus, one of the two lines shows an anodic polarization of the electrode in compartment I (line B), and the other shows a cathodic polarization of the electrode in compartment II (line A). The electrode potentials of the coupled electrodes in the normal shortcircuited state, as given by one of the principle lying in Evans' polarization diagram and also by equation (14), have the same value:

$$E_{II} - E_I = 0 \quad (15)$$

Liquid junction potential makes the difference in potential of an anode and a cathode at a coupled state. This follows that reference electrode I has a higher potential ϕ_I^N than reference electrode II (ϕ_{II}^N) by the value of the liquid junction potential ΔE_j for positive liquid junction potential, and vice versa for negative liquid junction potential, as given by equation (3):

$$\phi_I^N = \phi_{II}^N + \Delta E_j \quad (16)$$

The principle in Evans' polarization diagram requires electrode potentials on the same reference electrode potential, in practice, the potential of the electrode I against the potential of reference electrode II, $\phi_I^N - \phi_{II}^N$, called the modified electrode potential (E_I') of the electrode I throughout this paper. Thus, the test electrode I has the modified electrode potential (E_I') higher than the measured electrode potential (E_I) by the liquid junction potential:

$$E_I' = \phi_I^N - \phi_{II}^N = (\phi_I^M - \phi_I^N) + (\phi_I^N - \phi_{II}^N) = E_I + \Delta E_j \quad (17)$$

The corrected polarization lines of test electrode I against reference electrode II, the modified polarization lines thus made, lie in parallel to and above the measured polarization line B against reference

electrode I by the liquid junction potential, as shown by the broken lines in Fig. 11.

The effect of the liquid junction potential on the direction and amount of electricity in corrosion is given by the modified Evans' diagram. This diagram gives, for $0 < \Delta E_j < E_{II}^0 - E_I^0$ as an example, that the corrosion potentials of an anode and a cathode at the corrosion state are given by the potential at point $c_B^*(E_I^*)$ and by the potential at point $c_A^*(E_{II}^*)$ in Fig. 11, respectively and that the corrosion current is given by the current at the point of intersection (c_A^* in Fig. 11).

For liquid junction potential with negative values ($\Delta E_j < 0$), the broken line B' is drawn below the line B and the point of intersection (c_A^* in Fig. 11) lies on the line A and on the right-hand side of the point c . Thus, the corrosion current, I_g^* , has a larger value than that for no liquid junction potential, I_g .

For $0 < \Delta E_j < E_{II}^0 - E_I^0$, the broken line B' is drawn above the line B and the point of intersection (c_A^* in Fig. 11) lies on the left-hand side of the point C. Thus, the current, I_g^* , has a smaller value than I_g .

For $E_{II}^0 - E_I^0 < \Delta E_j$, the point of intersection (c_A^* in Fig. 11) lies on the left-hand side of the ordinate and the corrosion current, I_g^* , flows from the test electrode II of the polarization line B through the solution to the test electrode I of the polarization line A, that is, in the opposite way to the direction of flow of the corrosion current I_g .

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