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Electrolytic Reduction of Carbon Dioxide at Mercury Electrode in Aqueous Solution

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Cathodic reduction of carbon dioxide at a mercury pool electrode was investigated in aqueous solutions of $NaHCO_3$, NaH_2PO_4–Na_2HPO_4, NaCl, $NaClO_4$, Na_2SO_4, $LiHCO_3$, and $KHCO_3$ as well as their combinations. The reaction product was confirmed to be $HCOO^-$ by a qualitative spot test. $HCOO^-$ was quantitatively analyzed by a permanganate titration. The partial current densities of $HCOO^-$ formation (i_C) and H_2 evolution (i_H) were calculated. In the present paper, relationships between electrode behavior and solution properties, some of which have been qualitatively described in previous papers, are quantitatively clarified as follows. The electrode potential E_C for constant i_C (0.5 mA/cm^2) remains constant irrespective of pH and anions in the pH region of 2.4 to 7.8, whereas the potential E_H for constant i_H (0.5 mA/cm^2) varies linearly with a slope of 125 mV/pH. The present experimental results verify Eyring *et al.*'s presumption that in a relatively high overvoltage region (region 2) the cathodic reduction of CO_2 at Hg proceeds with the charge transfer to CO_2 as the rate determining step. CO_2 reduction and H_2 evolution are concluded to proceed independently at the Hg electrode. The dependence of E_C on electrolyte concentration is interpreted in terms of the diffuse double layer theory. The effect of cation species on E_C also is discussed.

Carbon dioxide has been suggested to be feasible as an energy storage medium by Russell *et al.*[1] and Williams *et al.*[2] Carbon dioxide is electrolytically reduced to methanol or formic acid, which in turn can be fed to a fuel cell or a decomposer to generate hydrogen. This process is superior to the hydrogen energy system, since the transport and storage of these liquid fuels are more convenient and less expensive than hydrogen. In addition to the advantage of energy storage, this process will contribute to fixation of carbon dioxide and prevent the recent increase of atmospheric concentration of carbon dioxide.

The electrolytic reduction of carbon dioxide in aqueous solution has been reported by many authors.[1–11] The principal difficulty of this process appear to be high overvoltage and low current efficiency. Excellent electrocatalysts are consequently requisite for the development of this process. However, the overvoltage and current efficiency depend upon properties of electrolytic solutions as well as electrodes.

Udupa *et al.*[6] studied cathodic reduction of CO_2 at a rotating amalgamated copper electrode in aqueous solutions. They reported that the current efficiency increased in the presence of sodium hydrogencarbonate in the solution as compared with the reaction in the solution containing sodium sulfate alone. Paik *et al.*[5] and Ryu *et al.*[7] studied pH effect on the reaction at Hg. They reported that the current efficiency tends to decrease with increasing acidity of the solution because of the competition with hydrogen evolution. Ito *et al.*[10] studied the reaction at various metal cathodes in several aqueous solutions. According to Ito *et al.*, the current efficiency at In electrode increased in alkali metal carbonate solutions with the sequence of Rb^+, K^+, Na^+, and Li^+, whereas the current efficiency increased with the sequence of PO_4^{2-}, SO_4^{2-}, and CO_3^{2-} in lithium salt solutions.

In these previous papers, effects of pH and species of electrolytes on the electrode reactions of CO_2 reduction and H_2 evolution were only qualitatively reported. In the present paper, they are quantitatively investigated at a mercury electrode which has a smooth and reproducible surface. The results obtained will contribute to the investigation of the electrocatalysis and reaction mechanism.

Experimental

Apparatus and Procedures. The experiments were carried out in a Pyrex H-type cell immersed in a thermostat maintained at 25 °C. The cathode and anode compartments were separated by a sheet of cation exchange membrane (Selemion) donated by Asahi Glass Co., Ltd. The cathode consisted of a pool of purified mercury (4.9 cm^2) which was electrically connected by a Pt wire lead. The anode was a Pt sheet. The potential of the cathode was measured with respect to an Ag/AgCl electrode at room temperature (20±1 °C), which was connected to the cathode by a Pyrex Luggin tube.

The galvanostatic electrolysis measurements were carried out for 15 to 100 min (depending on the current density), by a potentiogalvanostat (Model 2020) manufactured by Toho Giken Co., Ltd. The electrode potential was measured and recorded by a Yokokawa digital voltmeter (Model 2502) and recorder (Model 3066).

The product resulting from the reduction of CO_2 was qualitatively tested by the chromotropic acid test.[12] The solutions in the cell were quantitatively analysed for their $HCOO^-$ content by the permanganate titration technique. pH of the solution was measured before and after electrolysis; the difference between the two pH values was within 0.2.

Materials and Solutions. Commercial reagent grade mercury was washed with 2 M HNO_3,† distilled and again washed with 2 M HNO_3. The mercury thus purified was used as the cathode.

The electrolytes used were aqueous solutions of $NaHCO_3$, Na_2HPO_4–NaH_2PO_4, NaCl, Na_2SO_4, $NaClO_4$, H_3PO_4, and their combinations. The reagents except $NaClO_4$ and H_3PO_4 were triply recrystallized from reagent grade chemicals. The solutions were prepared from distilled water treated with active charcoal and ion exchange resin. The solutions used are tabulated in Table 1.

Commercial nitrogen and CO_2 were purified by passing them through columns of activated copper and wash bottles

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† 1 M=1 mol dm^{-3}.

containing aqueous solution of $KHCO_3$. The gases were then introduced to the electrolytic cell and bubbled through the solution under the atmospheric pressure.

Results

Reaction Products and Current Efficiency. The pH-potential diagram was constructed for the system CO_2–water at 25 °C on the basis of the thermochemical data.[13] (Fig. 1) The substances considered in Fig. 1 are CO_2, HCO_3^-, CO_3^{2-}, HCOOH, and $HCOO^-$, the activities of which are taken to be unity.

The product resulting from the electrolytic reduction of CO_2 was confirmed to be formic acid in all the solutions by the chromotropic acid test, which agrees with the previous reports.[1,3,5,7,8] CO_2 stably exists in aqueous media of pH less than 8 (Fig. 1). The equilibrium potential of CO_2 reduction is more cathodic in the lower pH range than that of the competitive reaction of H_2 evolution. Therefore, the reduction of CO_2 would effectively proceed between 7 and 8 of pH.[††] Figure 1 shows also $HCOO^-$ to be formed predominantly instead of HCOOH in the solution of pH above 3.7.

The activity of hydrogencarbonate ion $[HCO_3^-]$ is related to the pH value in equilibrium with CO_2 at 1 atm:[†††]

$$pH = pK_a + \log[HCO_3^-], \qquad (1)$$

$$pK_a = 7.82 \ (25\ °C).$$

The pH of phosphoric buffer solution will alter from the value originally prepared with formation of HCO_3^-, according to Eq. 2, if CO_2 is in contact with the solution:

$$HPO_4^{2-} + CO_2 + H_2O = H_2PO_4^- + HCO_3^-. \qquad (2)$$

The pH is determined by the following reactions

$$H_2PO_4^- = HPO_4^{2-} + H^+, \qquad (3)$$

$$CO_2 + H_2O = HCO_3^- + H^+. \qquad (4)$$

The equilibrium concentrations of respective ions are readily calculated in accordance with Eqs. 3 and 4 and corresponding pK_a values; the equilibrium concentrations thus obtained are given in Table 1.

The results of the permanganate titration are to give the values of the current efficiency and the partial current i_C of $HCOO^-$ formation. The experimental current efficiencies are presented as a function of pH in Fig. 2. The trend in Fig. 2 qualitatively agrees with the thermodynamic considerations.

Partial Current of CO_2 Reduction. The limiting current of CO_2 reduction would be approximately 7—10 mA/cm²,[15] and the present experiments were made under the condition where the partial current density of CO_2 reduction did not exceed 1.5 mA/cm².

The electrode potential of cathode remained constant within 2 to 3 mV in every run during the steady state galvanostatic electrolysis of carbon dioxide. The measured potential did not vary by more than 10 mV on different runs in solutions of identical compositions. Each partial current i_C of $HCOO^-$ formation may include an error of up to 2% due to the inaccuracy of the titration technique. The partial current i_H of H_2 evolution was estimated as the difference between the total electrolytic current i and i_C. i, i_C, and i_H are plotted against the electrode potential E (referred to SHE) for the phosphate buffer solution of pH=5.7 (Fig. 3), the composition of which is shown in Table 1. Figure 3 contains also the data obtained in ternary electrolytes consisting of NaCl, $NaClO_4$, or Na_2SO_4 solution mixed with phosphate buffer (NaH_2PO_4–Na_2HPO_4) (pH=5.5). These data for ternary electrolytes were corrected for pH values and zeta potential as described later.

The results for all the solutions showed that the Tafel relationship holds as exemplified in Fig. 3. The values of transfer coefficient α are 0.26—0.28 for CO_2 reduction and 0.41—0.45 for H_2 evolution in the solutions of pH below 6. Thus, the potentials E_C and E_H can be determined at a constant partial current

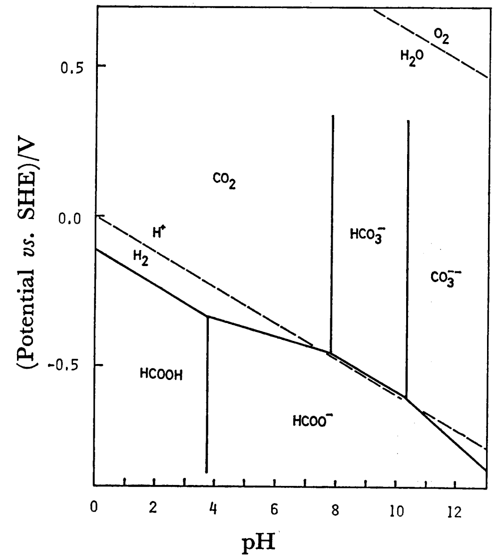

Fig. 1. pH-potential diagram of CO_2 and its related compounds.
pH-potential relations for water are shown in broken lines.

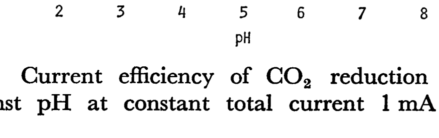

Fig. 2. Current efficiency of CO_2 reduction plotted against pH at constant total current 1 mA cm⁻².

[††] Iwahara *et al.*[14] recently reported that HCO_3^- was electrolytically reduced on Hg without bubbling CO_2. Their observation contradicts with van Rysselberghe *et al.*'s;[3] the details of this reaction still remain unclarified.

[†††] 1 atm=1.013×10⁵ Pa.

TABLE 1. EQUILIBRIUM COMPOSITION OF AQUEOUS ELECTROLYTE SOLUTIONS

Electrolyte	pH	Total cation concentration/M	Equilibrium composition of electrolyte solution/M							Correction ζ/mV
			H_3PO_4	NaH_2PO_4	Na_2HPO_4	$NaHCO_3$	NaCl	$NaClO_4$	Na_2SO_4	
Phosphate buffer	2.48	0.50	0.16	0.34						15
	2.78	0.50	0.095	0.41						15
	4.86	0.50		0.49	0.0023	0.0011				15
	5.00	0.29		0.28	0.0035	0.0013				1
	5.74	0.26		0.21	0.022	0.010				−1
	6.72	0.29		0.076	0.060	0.076				0
Phosphate-Cl^-	5.48	0.63		0.10	0.0089	0.0084	0.50			21
Phosphate-ClO_4^-	5.47	0.64		0.11	0.012	0.0098		0.50		22
Phosphate-SO_4^{2-}	5.54	0.63		0.11	0.010	0.0091			0.246	21
HCO_3^-	6.57 —7.89	0.056 —1.20				0.056 —1.20				
$HCO_3^-+Cl^-$	6.50 —7.80	1.20				0.050 —1.00	1.15 —0.20			
$HCO_3^-+ClO_4^-$	7.04 —7.86	1.20				0.22 —0.43		0.98 —0.77		
$HCO_3^-+SO_4^{2-}$	6.62 —7.31	1.20				0.10 —0·38			0.55 —0.41	

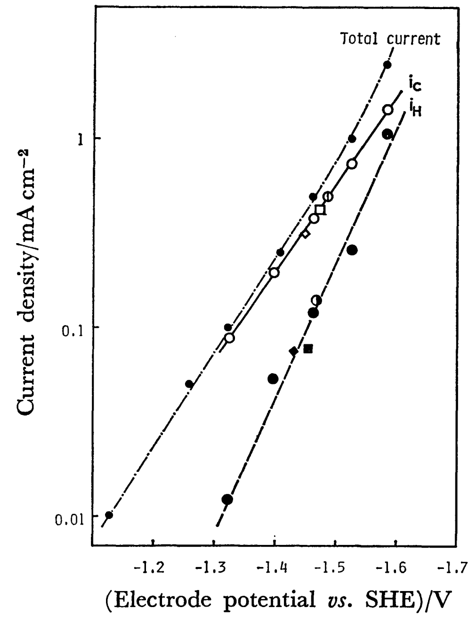

Fig. 3. Current density *vs.* electrode potential (SHE) for cathodic reduction of CO_2 at Hg in aqueous solutions (pH=5.7).
i_C: Partial current of CO_2 reduction, i_H: partial current of H_2 evolution.
Symbols: phosphate buffer; i_C ○, i_H ●, phosphate-Cl^-; i_C ⦶, i_H ◑, phosphate-ClO_4^-; i_C ◇, i_H ◆, phosphate-SO_4^{2-}; i_C □, i_H ■.
ζ is corrected with reference to 0.274 M solution of 1-1 electrolyte.

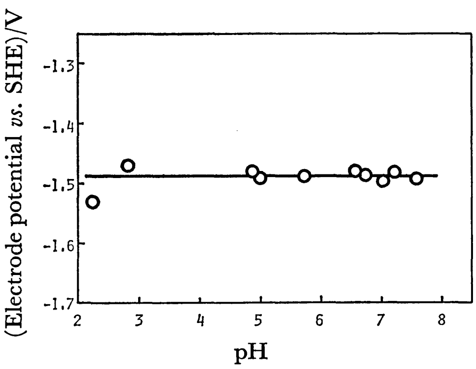

Fig. 4. Electrode potential E_C for CO_2 reduction at i_C=0.5 mA/cm^2 plotted against pH.

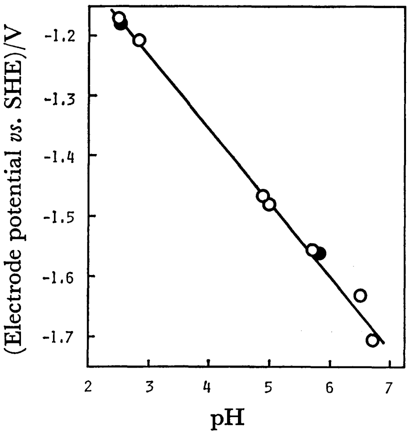

Fig. 5. Electrode potential E_H for H_2 evolution at i_H= 0.5 mA/cm^2 plotted against pH.
○: E_H observed during CO_2 cathodic reduction, ●: E_H observed under N_2 flow.

i_C and i_H from the Tafel relationship like Fig. 3.

pH Dependence of Electrode Potentials E_C and E_H. The values of E_C thus obtained at the partial current 0.5 mA/cm^2 are plotted against pH in Fig. 4. The variation of ζ potential was corrected as mentioned later. E_C values obviously stay constant irrespective of pH. Figure 5 presents the relationship between E_H and pH. The current-potential measurements for hydrogen evolution at Hg under a N_2 flow give the electrode potentials at 0.5 mA/cm^2, which also are shown in Fig. 5, falling on the line. The slope is approximately 125 mV/pH. Therefore, the hydrogen evolution reaction, taking place simultaneously with CO_2 reduction, appears to proceed in the same way as in a N_2 flow.

Electrolytes and their Concentrations. The current efficiencies of $HCOO^-$ formation were 100% within the experimental error in the solutions containing $NaHCO_3$ and at pH above 6.6. The potentials E_C at a constant cathodic current density 0.5 mA/cm^2 are shown in Fig. 6 for various concentrations of $NaHCO_3$. E_C varies linearly with $NaHCO_3$ concentration, the slope being approximately 60 mV/decade. However, E_C at 0.5 mA/cm^2 is independent of $NaHCO_3$ concentration, where the total equivalent concentrations of electrolytes are kept constant at 1.2 equiv·dm^{-3} by adding NaCl, $NaClO_4$, or Na_2SO_4. pH in aqueous solution increases from 6.6 to 7.8 with increasing $NaHCO_3$ concentration from 0.05 to 1.2 M while the CO_2 pressure is kept 1 atm. E_C consequently depends upon the total concentration of electrolytes but not upon pH values.

Figure 7 shows the variation of E_C at 0.5 mA/cm^2 of CO_2 reduction with respect to the concentration of electrolytes $LiHCO_3$ and $KHCO_3$. The slopes are about 75 mV/decade and 66 mV/decade for $LiHCO_3$ and $KHCO_3$, respectively. They are close to the value for $NaHCO_3$. E_C for a constant concentration of the electrolyte appears to become remarkably nobler with the sequence of Li^+, Na^+, and K^+.

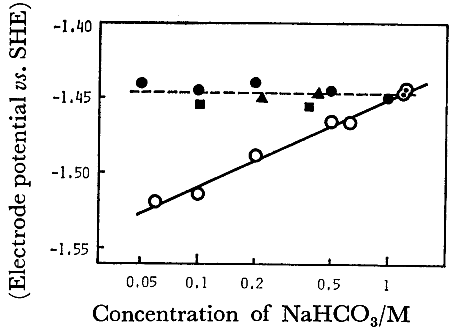

Fig. 6. Electrode potential E_C for CO_2 cathodic reduction in various concentrations of HCO_3^-.
○: Aqueous solution of $NaHCO_3$ alone, ●: mixed electrolyte $NaHCO_3$+NaCl, total equivalent concentration 1.2 mol dm^{-3}, ▲: mixed electrolyte $NaHCO_3$+$NaClO_4$, total equivalent concentration 1.2 mol dm^{-3}, ■: mixed electrolyte $NaHCO_3$+Na_2SO_4, total equivalent concentration 1.2 mol dm^{-3}.

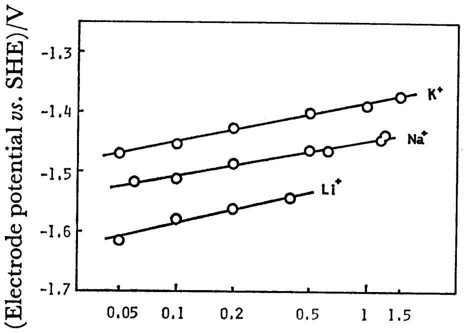

Fig. 7. Electrode potential E_C for CO_2 reduction in various concentrations of $LiHCO_3$, $NaHCO_3$, and $KHCO_3$.

Discussion

Reaction Mechanism and Electrode Potential. Paik *et al.*[5] and Ryu *et al.*[7] studied CO_2 reduction on mercury in neutral aqueous solution. They revealed that the feature of this reaction is the occurrence of two Tafel regions: one at low current densities (region 1) and the other at high current densities (region 2). The present measurements were made in the region 2. They presumed that the following reaction determines the rate of the reaction in region 2:

$$CO_2 + e^- \longrightarrow CO_2^- \text{ (ads)}$$

or

$$CO_2 + H_2O + e^- \longrightarrow HCO_2\cdot\text{(ads)} + OH^-. \qquad (5)$$

If one of them is the rate determining step, the electrode potential will be written as follows:

$$E_C = -\frac{RT}{\alpha_C F}\cdot\ln|i| + \zeta + \text{const}, \qquad (6)$$

where α_C is the transfer coefficient. This expression suggests that the electrode potential at a constant current will not depend upon pH, if ζ is kept constant. Since E_C obtained experimentally remains constant irrespective of pH (Figs. 4 and 6), the present results confirm Paik *et al.*'s and Ryu *et al.*'s presumptions in the pH region of 2.4 to 7.8.

The point of zero charge (pzc) for the mercury electrode without specific adsorption in aqueous media is about 0.4 to 0.5 V (referred to the normal calomel electrode),[16] and the potential region discussed in this paper is far below pzc. The bulk concentration of Na^+ is much higher than H^+. Na^+ will naturally predominate in the neighborhood of the electrode surface in the present experimental conditions. The surface of the mercury electrode will not significantly be covered with H or H_2, because the discharge of H^+ is considered to be the rate determining step of H_2 evolution. Thus the pH change will not practically affect the ionic distribution near the electrode surface. Accordingly, the CO_2 reduction process will proceed irrespective of pH.

The hydrogen evolution reaction proceeds at mercury in acidic to neutral aqueous media with the discharge of proton as the rate determining process:

$$H^+ + e^- \longrightarrow H. \qquad (7)$$

The electrode potential will be expressed as[17]

$$\begin{aligned} E &= -\frac{RT}{\alpha_H F}\cdot\ln|i| + \frac{RT}{\alpha_H F}\cdot\ln[H^+] - \frac{1-\alpha_H}{\alpha_H}\zeta + \text{const} \\ &= -\frac{0.05916}{\alpha_H}\cdot\ln|i| - \frac{0.05916}{\alpha_H}\text{pH} - \frac{1-\alpha_H}{\alpha_H}\zeta \\ &\quad + \text{const (25 °C)}. \qquad (8) \end{aligned}$$

The values of α_H are between 0.41 and 0.45 as determined from the Tafel plots in the present study. The dependence of E_H on pH with constant current and ζ is thus seen to be *ca.* 137 mV/pH at 25 °C from Eq. 8, which agrees approximately with a value of

125 mV/pH as estimated from the slope in Fig. 5, where CO_2 is simultaneously reduced. The hydrogen evolution process is apparently independent of the competitive CO_2 reduction. Aylmer-Kelly *et al.*[18] studied the intermediate species in the CO_2 cathodic reduction at mercury in aqueous media by means of reflectance spectroscopy. They reported that the coverage of the intermediate CO_2^- on mercury is approximately 0.02. Such a small value of coverage would not affect the hydrogen evolution reaction.

Thus, the two reactions, CO_2 reduction and H_2 evolution, proceed independently at the Hg electrode. The current efficiency of CO_2 reduction varies with pH (Fig. 2) as derived from the pH dependence of H_2 evolution.

Effects of Electrolyte. The zeta potential ζ at the outer Helmholtz plane for mercury and 1-1 electrolyte without specific adsorption varies approximately according to

$$\zeta = \text{const} \pm \frac{RT}{n_iF}\cdot\ln C, \tag{9}$$

where n_i and C are the charge number of ion and the bulk concentration of the electrolyte, respectively, and the ±sign holds for $\zeta \gtrless 0$.[16] The above relationship was verified by Delahay for electrode potentials sufficiently positive or negative with respect to the pzc. The pzc for mercury in aqueous media without specific adsorption is about 0.4 to 0.5 V (referred to the normal calomel electrode),[16] and E_C at i_C 0.5 mA/cm^2 is about -1.5 V (referred to SHE) as shown in Fig. 4; Eq. 9 would be applicable to the present experimental situations.

With Eq. 9 inserted into Eq. 6, the electrode potential E_C at constant current is expected to vary with the logarithm of electrolyte concentration with a slope of 0.05916 V/decade at 25 °C. This value is in good agreement with the experimentally observed one as described for $NaHCO_3$ (Fig. 6).

All the electrolysis experiments were not carried out at the same electrolyte concentration; the corrections of ζ were made for different concentrations as mentioned in the previous sections. The correction was made for 1-1 electrolyte according to Eq. 9 with the reference concentration of 0.274 M arbitrarily chosen. The corrections for electrolytes other than 1-1 ones were calculated according to the manner as described in Appendix. Tafel relationship illustrated in Fig. 3 (pH 5.7) contains experimental values for phosphate buffer solutions mixed with NaCl, $NaClO_4$, or Na_2SO_4 after appropriate corrections. The partial current i_H is corrected not only for ζ potential according to Eqs. 9 and 13 but for pH difference, because the electrolyses in phosphate buffer solution mixed with NaCl, $NaClO_4$, or Na_2SO_4 were carried out at pH≈5.5. These data for i_C and i_H fall on the respective lines representing experimental values in phosphate buffer solution without other electrolytes.

Since the electrode potential is far below pzc, anions will hardly affect the structure of the Helmholtz layer of the electrode, if these anions are not specifically adsorbed. The present study confirms this expectation, since any anions employed make no difference in either CO_2 reduction or H_2 evolution (Figs. 3—6).

As pointed out previously, the electrode potential E_C varies to noble values with the sequence Li^+ to Na^+ to K^+. It will qualitatively result from the increasingly specific adsorption of the larger cations, and ζ will become more positive.

The authors would like to thank Mr. Nobuyuki Nakajima for his assistance in part of experiments.

Appendix

The correction of ζ for electrolytes other than 1-1 followed the derivation of Eq. 9 for 1-1 electrolytes given by Delahay.[16] According to the Gouy-Chapman theory of the diffuse double layer, the charge q on the electrode per unit area is deduced as

$$q = \pm\left[\frac{RT\varepsilon}{2\pi}\cdot\Sigma C_i^s\left\{\exp\left(-\frac{n_iF}{RT}\cdot\zeta\right)-1\right\}\right]^{1/2}, \tag{10}$$

where ε is dielectric constant, and C_i^s and n_i are the bulk concentration of solution and the ionic valence (with sign) of ion i, respectively.

The correction of ζ is exemplified below for an aqueous solution consisting of xM NaH_2PO_4, yM Na_2HPO_4, and zM $NaHCO_3$. The concentrations of each ionic species are tabulated in Table 2. Insertion of these values into Eq. 10 will give

$$\begin{aligned}\frac{2\pi}{RT}\cdot\frac{q^2}{\varepsilon} &= (x+2y+z)\cdot\exp\left(-\frac{F}{RT}\cdot\zeta\right)\\ &+ (x+z)\cdot\exp\left(\frac{F}{RT}\cdot\zeta\right)\\ &+ y\cdot\exp\left(\frac{2F}{RT}\cdot\zeta\right) - (2x+3y+2z).\end{aligned} \tag{11}$$

Then, for $\zeta < -0.1$ V which is applicable to the present case, the terms $\exp\left(\frac{F}{RT}\cdot\zeta\right)$ and $\exp\left(\frac{2F}{RT}\cdot\zeta\right)$ can be dropped. If q is considered to be independent of electrode potential E in the present narrow range of E, the following equation is obtained by differentiation:

$$\frac{F}{RT}\cdot\mathrm{d}\zeta = \frac{\mathrm{d}(x+2y+z)}{x+2y+z} - \frac{\mathrm{d}(2x+3y+2z)}{x+2y+z}\cdot\exp\left(\frac{F}{RT}\cdot\zeta\right). \tag{12}$$

When the variations $\Delta(x+2y+z)$ and $\Delta(2x+3y+2z)$ are small, Eq. 12 is written as

$$\frac{F}{RT}\cdot\Delta\zeta = \frac{\Delta(x+2y+z)}{x+2y+z} - \frac{\Delta(2x+3y+2z)}{x+2y+z}\cdot\exp\left(\frac{F}{RT}\cdot\zeta\right). \tag{13}$$

TABLE 2. CONCENTRATION OF EACH IONIC SPECIES IN AN AQUEOUS SOLUTION CONSISTING OF xM NaH_2PO_4, yM Na_2HPO_4, AND zM $NaHCO_3$

Electrolyte	Concentration/M	Na^+	HCO_3^-	$H_2PO_4^-$	HPO_4^{2-}
NaH_2PO_4	x	x		x	
Na_2HPO_4	y	$2y$			y
$NaHCO_3$	z	z	z		
n_i		1	-1	-1	-2
C_i^s		$x+2y+z$	z	x	y

If ions are not specifically adsorbed on the electrode, the value of ζ will be close to the one estimated for NaF solutions.[16] $\Delta\zeta$ is thus calculated as the deviation from the reference solution 0.274 M of 1-1 electrolyte, *i.e.*, $x+2y+z=0.274$ and $2x+3y+2z=0.548$, with ζ -0.11 V. The values of $\Delta\zeta$ are tabulated in the last row of Table 1.

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