Studies on Electrocapillarity with Respect to the Supplementary Reduction in Oscillographic Polarography

By Hideo IMAI

(Received August 8, 1955)

The mechanism of a supplementary reduction has been proposed in a previous report[1], where the supplementary reduction was assigned to the reduction of the inner metal ion (the potential determining ion which establishes the electrical double layer of a colloidal metal hydroxide with the counter ion (anion)). Hence, the difference between the peak potential of the normal reduction (i. e. the reduction of an aquo metal ion) and that of the supplementary reduction may be the measure of Coulombic attraction between the inner ion and the colloidal metal hydroxide. In this paper are presented the estimation of the Coulombic attraction in various supporting electrolytes and some related phenomena.

Experimental

The multi-sweep oscillographic technique of a current potential curve was employed[1]. The rate of potential change, 70 v./s. (20 c. p. s.), was used throughout the measurments. Waves were recorded during the lifetime of a single drop, but for the sake of clarity, only the pattern corresponding to the maximum size of the mercury drop is shown in Figs. 1–4. In general it is observed that the cathodic peak potential is shifted toward more negative values as the drop grows. This shift is caused by an increase in the ohmic drop in the cell and the measuring circuit. Likewise, the anodic peak potential is shifted toward more positive potentials as the drop grows. The shift in the peak potential is indicated in Figs. 1–3 by a straight line. In order to obtain correct peak-potentials it suffices to extrapolate the potential to zero current as is indicated in Figs. 1–3. The possible error in measuring the peak potential amounts to ±0.005 volt.

The test solution contains about 1 mM/l. Cd^{++}, Pb^{++} or Zn^{++} in N KI, KBr, KCl, KNO_3, $NaNO_3$, Na_2SO_4 or sat. K_2SO_4 and about 0.37 mM/l. oxygen equilibrated with atmospheric oxygen at 25°C. In the preparation of these solutions, reagent grade chemicals were recrystallized twice from their aqueous solutions.

The temperature was 25±0.1°C.

Results

The current-potential curves are illustrated in Figs. 1–3, where full curves and dotted curves denote those of the deäerated solutions and of the undeaerated solutions, respectively. The charging current, i_c, in each solution is also appended.

From these polarograms, peak potentials were estimated by the method described in the preceding section, and are illustrated in Tables I–III. It was confirmed that the peak potential of a metal ion in the presence of the dissolved oxygen approximately coincides with that of a metal ion in the deäerated solution within the experimental error.

TABLE I

$1\cdot10^{-3}$ M/l. Cd^{++} IN N KnX

X^{n-}	π_R	π_S	π_0	$(\pi_R+\pi_0)/_2$	$\pi_R-\pi_S$
I^-	-0.75_5	—	-0.73_0	-0.74_3	—
Br^-	-0.68_0	-0.81_0	-0.63_5	-0.65_8	0.13_0
Cl^-	-0.67_0	-0.80_5	-0.61_0	-0.64_0	0.13_5
OS_4^{--}	-0.63_0	-0.79_0	-0.56_5	-0.59_7	0.16_0
NO_3^-	-0.62_0	-0.79_0	-0.56_0	-0.59_0	0.17_0

TABLE II

$1\cdot10^{-3}$ M/l. Pb^{++} IN N KnX. [( ); ILL-DEFINED DATA]

X^{n-}	π_{R1}	π_{R2}	π_{S1}	π_{S2}	π_{01}	π_{02}	$(\pi_{R2}+\pi_{02})/_2$	$\pi_{R2}-\pi_{S1}$
I^-	-0.59_5	-0.67_5	—	—	(-0.80_0)	-0.59_0	-0.63_3	—
Br^-	-0.47_5	-0.52_5	-0.60_8	(-1.00_0)	(-0.66^0)	-0.48_0	-0.50_3	R1 : 0.13_3 R2 : 0.08_3
Cl^-	—	-0.48_0	-0.61_0	(-1.04_0)	(-0.51_0)	-0.40_5	-0.44_3	0.13_0
NO_3^-	—	-0.45_0	-0.62_7	(-1.05_0)	(-0.45_7)	-0.35_0	-0.40_0	0.17_7
OH^-	—	-0.80_0	—	—	—	-0.70_0	-0.75_0	—

---

1) H. Imai, This Bulletin, 29, 276 (1956).

TABLE III

$1\cdot10^{-3}$ M/l. Zn^{++} IN N KnX. [( ); ILL-DEFINED DATA]

X^{n-}	π_{R1}	π_{R2}	π_{S1}	π_{S2}	π_{01}	π_{02}	$(\pi_{R2}+\pi_{02})/_2$	$\pi_{R22}-\pi_{S1}$
I^-	(-1.01_8)	-1.20_0	-1.38_2	(-1.59_0)	(-1.12_5)	-0.93_8	-1.06_9	-0.18_2
Br^-	(-1.00_0)	-1.20_0	-1.39_0	—	(-1.12_0)	-0.90_2	-1.05_1	-0.19_0
Cl^-	(-0.90_0)	-1.20_0	-1.39_5	—	(-1.11_8)	-0.88_0	-1.04_0	-0.19_5
SO_4^{--}	(-1.10_0)	-1.22_0	-1.42_0	(-1.56_0)	(-1.11_0)	-0.88_0	-1.05_0	-0.20_0
NO_3^-	(-1.10_0)	-1.20_2	-1.40_5	(-1.55_0)	$(-1.11'_0)$	-0.87_5	-1.03_8	-0.20_3
OH^-	—	-1.71_0	—	—	-1.50_0	-1.00_5	-1.36_7	—

Fig. 1. Oscillographic polarogram of $1\cdot10^{-3}$ M/l. Cd^{++} in N KnX (X=negative ion).

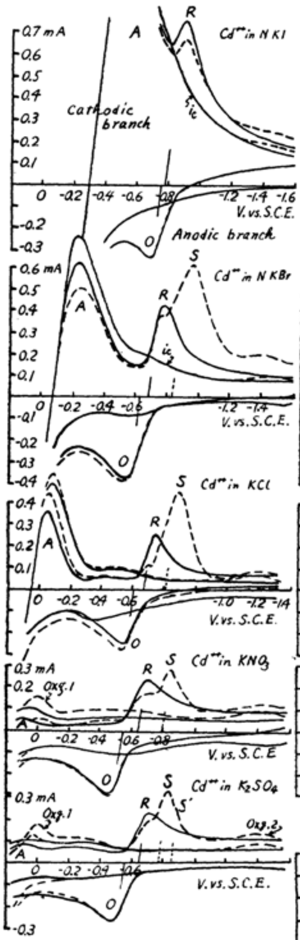


Fig. 2. Oscillographic polarogram of $1\cdot10^{-3}$ M/l. Pb^{++} in N KnX.

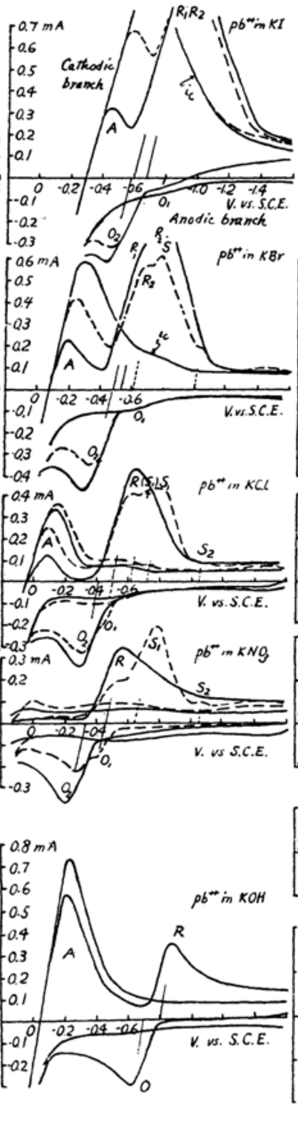


Fig. 3. Oscillographic polarogram of $1\cdot10^{-3}$ M/l. Zn^{++} in N KnX.

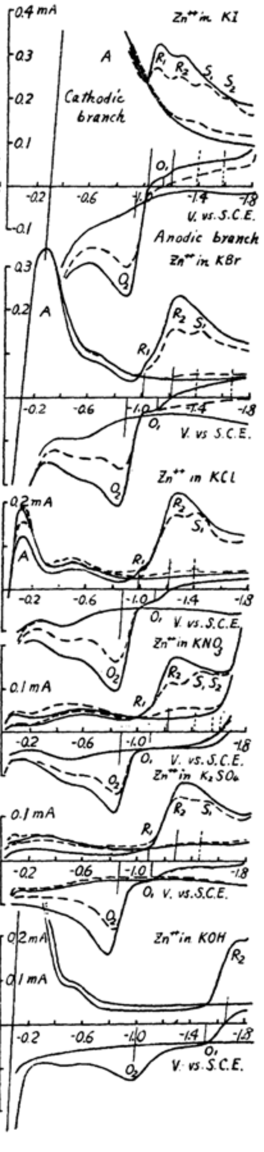
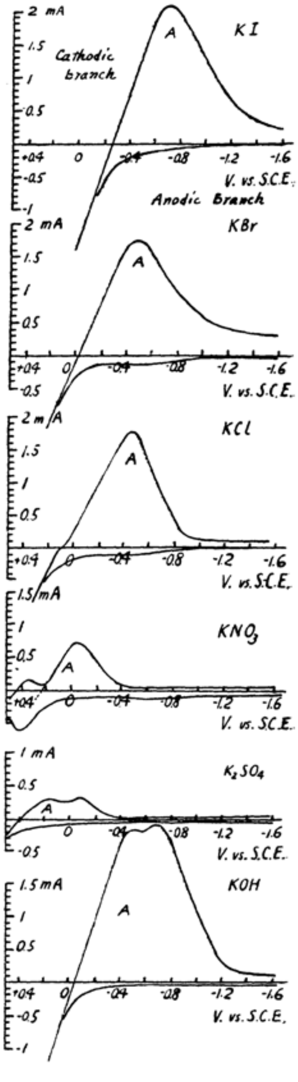


Fig. 4. Oscillographic polarogram of N KnX (X=negative constituent of supporting electrolyte.).



In the current-potential oscillogram of Cd^{++} in N KBr or in N KCl the second supplementary reduction is perceptible by a judicious choice of the initial sweep voltage. Also in the oscillogram of Cd^{++} in K_2SO_4 the supplementary reduction consists of double peaks regardless of any control of the applied sweep. All these auxiliary peaks are ill-defined and are omitted.

In the solutions containing Zn^{++}, the normal reduction waves consist of two peaks in the cathodic branch and in the anodic branch, respectively. This characteristic shape has been discussed by Delahay[2]. However, the remarkable consecutive peaks shown in the case of Zn^{++} in N KBr or KI can not be elucidated by Delahay's concept. The problem remains for the future[3].

The second supplementary reduction, S_2, observed in the case of Pb^{++} or Zn^{++} is that of the hydroxide complex such as $HPbO_2^-$, $HZnO_2^-$. These hydroxide complexes result from their amphoteric nature.

Among these complicated results, the following features hold in common:

(1) Both the peak potential of the normal cathodic process, $\pi_{\rm R}$, and that of the anodic process, π_0, are shifted toward more negative potentials in the solutions of NO_3^-, SO_4^{--}, Cl^-, Br^-, I^- in the order given. The mean potential, $(\pi_{\rm R}+\pi_0)/2$, behaves likewise.

(2) The values of $\pi_{\rm R}-\pi_{\rm S}$ ($\pi_{\rm S}$; the peak potential of the supplementary reduction) increase in the solutions of I^-, Br^-, Cl^-, (SO_4^{--}, NO_3^-) in the order given.

These common features seem to correlate intimately with the electrocapillary behaviors of anions as shown in the following.

The current-potential oscillograms of deäerated supporting electrolytes are shown in Fig. 4.

In every solution an enormously large charging current passes through the cell in the cathodic branch. Every charging current attains a maximum at an appreciably positive or a less negative potential (The potential of the maximum charging current is always positive with respect to the potential referred to the electrocapillary maximum.), then decreases gradually as the applied potential sweeps toward more negative potentials. It is interesting that such a large charging current is not observable in the anodic branch. Moreover, such a current can not be observed by an ordinary polarograph. This irreversible current can be assigned to the variation of a differential capacity as is shown in the following.

The charging current consists of two components, one is the charging current, i_{c_1}, due to the increase in capacity of the electrical double layer and another is the charging current, i_{c_2}, due to the differential capacity. Since the complete current-potential curve is recorded in a small fraction of the drop life, i. e. 1/20 seconds in this experiment, i_{c_1} is very small.

The charging current, i_{c_2}, is equal to the rate of flow of charge due to the variation of the differential opacity, c, i. e.

$$i_{c_2}=\frac{\mathrm{d}Q}{\mathrm{d}t}=c\frac{\mathrm{d}E}{\mathrm{d}t} \tag{1}$$

Under the condition of the experiment where a linearly increasing and decreasing potential sweep is applied to the D. M. E. the rate of potential change with respect to time, t, is equal to a constant, v.[4] Hence,

$$\frac{\mathrm{d}E}{\mathrm{d}t}=v \qquad \therefore \quad i_{c_2}=c\cdot v \tag{2}$$

The linear relation between i_{c_2} and v has been verified experimentally by the present author[5]. Since v is as large as 70 v./s. in this experiment, i_{c_2} is enormously large and i_{c_1} is negligible.

Integration of equation (1) leads to an equation for the charge flowed (Q):

$$Q=\int_{E1}^{E2} c\ \mathrm{d}E+k \tag{3}$$

Substituting Eq. 2 into Eq. 3, one has:

$$Q=\frac{1}{v}\int_{E1}^{E2} i_{c_2}\mathrm{d}E+k \tag{4}$$

where E_1 is the potential of the D. M. E. and E_2 is that of an electrocapillary maximum.

Supposing the surface area of the D. M. E. is kept constant, the area surrounded by the charging current curve means the surface charge density.

The surface area of the D. M. E. is proportional to $m^{2/3}$ $t^{2/3}$ (m; the flow rate of mercury, t; the lifetime of the D. M. E.). In this experiment m is constant and t decreases in the solutions of (NO_3^-, SO_4^{--}), Cl^-, Br^-, I^- in the order given. Hence, the surface area of the D. M. E. under a given applied sweep increases in the solutions of I^-, Br^-, Cl^-, (SO_4^{--}, NO_3^-) in the order given, while from Fig. 4 Q increases vice versa. Hence, the surface charge density at a given applied potential decreases in the solutions of I^-, Br^-, Cl^-, (NO_3^-, SO_4^{--}) in the order given.

---

[2] P. Delahay, *J. Am. Chem. Soc.*, **75**, 1190 (1953).

[3] H. Imai and H. Sunahara, Symposium on presented at the Polarography, Hiroshima (1955).

[4] Strictly speaking, the assumption is not valid, because iR drop affects v. This assumption holds approximately[5].

[5] H. Imai, *J. Electrochem. Soc. Japan*, **23**, 530 (1955)

From the above mentioned results it is reasoned that the surface charge density of is the D. M. E. inversely proportional to the value of $\pi_R-\pi_S$. Here, $\pi_R-\pi_S$ was assumed to be the measure of Coulombic attraction of a metal ion to its colloidal hydroxide. Since a metal ion is attracted both to its hydroxide and to the anion which exists in the electrode surface, it is reasoned that the former attractive force is becoming weaker as the surface charge density of the electrode increases.

In this connection, it was suggested by Heyrovský[6,7] that a halogen ion suffers from a polarization by the negative charge of the electrode. Hence, the electric field exerted on the metal ion results from the polarization of an anion as is illustrated in Fig. 5. Thus, the more polarizable is the anion, the larger is the negative charge represented by $G-G'$. The existence of such a space charge requires an extra applied potential for an electron transfer. (This is best realized by comparing the function of $G-G'$ with that of the grid of a triode vacuum tube.). Thus, the shift of the peak potential listed in Tables I, II and III can be explained. In the same manner, it can be expressed that the more polarizable is the adsorptive anion layer, the less is the attractive force between the inner metal ion and the colloidal metal hydroxide.

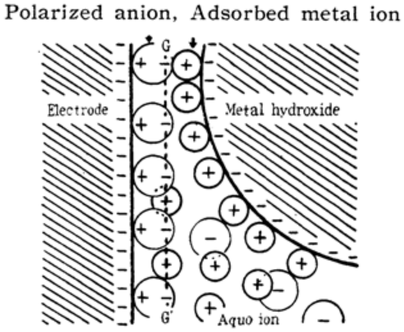


Fig. 5. Schematic representation of the electrode surface.

The author wishes to express his hearty gratitude to Prof. Mutsuaki Shinagawa for his valuable advice and encouragement.

The work is partially supported by a Subsidy for Scientific Research given by the Ministry of Education.

Department of Chemistry, Minami College,
Hiroshima of University,
Hiroshima

---

[6] J. Heyrovsky, *Discs. Faraday Soc.*, **1**, 212 (1947).
[7] J. Heyrovsky, *Wien. Chem. Ztg.*, **48**, 24 (1947).