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Classification of Polarographic Current-Potential Curves of Inorganic Anions as a Function of Reduction Potentials

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DC polarographic behaviors of a variety of inorganic anions are examined systematically. Irrespective of chemical species, the shapes of current-potential curves are classified into three groups as a function of reduction potentials: i) $E_{1/2}>0$ V(SCE); The so-called minima cannot be observed beyond the ecm potentials. ii) 0 V$>E_{1/2}>$ecm; The minima can be observed. iii) $E_{1/2}<$ecm; The distortion at the rising portion of the DC polarograms can always be observed. These results suggest that whether the minima can be observed or not is due to the difference in the relative position of half-wave potentials with respect to the ecm potential. Furthermore, it is likely that the distortion at the rising portion of the DC polarogram of Group iii) is similar in origin to that of the minima of Group ii). The present results are discussed in terms of the electron density and electronic energy level of electrons in the metal electrode. The discussion based on the phenomenological equation of Butler was also given for the sake of comparison to explain the observed phenomena.

The electrochemical method is one of the most important techniques for the study of electron transfer reactions in solution. The characteristic features of the electrode reaction are i) electronic energy level of one of the reactants, *i.e.*, the electrode, is varied artificially by means of applied potentials—"quantum mechanical effect",[1,2] and ii) due to the large charge density of the double layer, electrostatic interaction between the electrode and the charged depolarizer may be much larger than that of the other types of redox reactions—"electrostatic effect".[3]

The purpose of this paper is to demonstrate experimentally the contribution of the above two effects separately in polarography. Polarographic behaviors of a variety of inorganic anions are examined systematically. It is shown that the pattern of the DC polarogram of inorganic anions is classified into three types as a function of reduction potentials. The results are discussed in terms of the quantum mechanical and electrostatic effects as mentioned above. The results of the present study will be useful to clarify the structure of the double layer and to understand the mechanism of the electrode reaction.

Experimental

DC polarograms were taken with a Yanagimoto Model P-8 Polarograph. A Yanagimoto Model MRP was used as the reference electrode (SCE). Capillaries with drop times of 3—4 s in 1 M KCl solution at a mercury height of 70 cm (open circuit) were used. Sample solutions in the cell were deaerated by bubbling purified nitrogen gas before and throughout the measurements. Gelatin was added to the sample solutions as maximum suppressor. All chemicals used were of analytical reagent grade and metal complexes used were prepared according to the usual methods. Half-wave potentials were evaluated directly from the polarograms.

Results

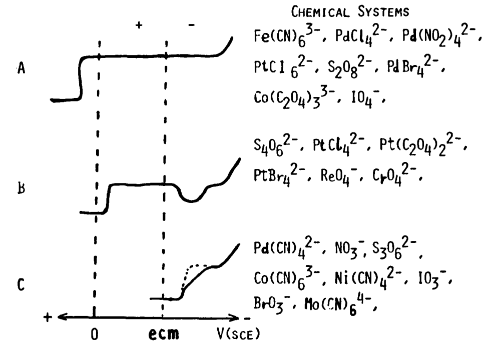

Fig. 1. Typical DC polarographic pattern of inorganic anions as a function of reduction potentials, $E_{1/2}$.
A: $E_{1/2}>0$, B: $0>E_{1/2}>$ecm potential, C: $E_{1/2}<$ecm potential, Supporting electrolyte: 0.1—1 M alkali halide (KCl), Without surface-active substances.

It is found that the shapes of DC polarograms of a variety of anion depolarizers are roughly divided into three groups A, B, C, in the decreasing order of reduction potentials. The results are cited schematically in Fig. 1. Typical DC polarograms which belong to these groups are shown in Figs. 2 and 3. For the systems of Group A, the half-wave potentials, $E_{1/2}$, are relatively more positive than those of Group B. For the system of Group C, $E_{1/2}$ is situated more negative than the electrocapillary maximum (ecm) potential.

Dependence on Chemical Systems. As shown in Fig. 1, the chemical systems are classified into two types

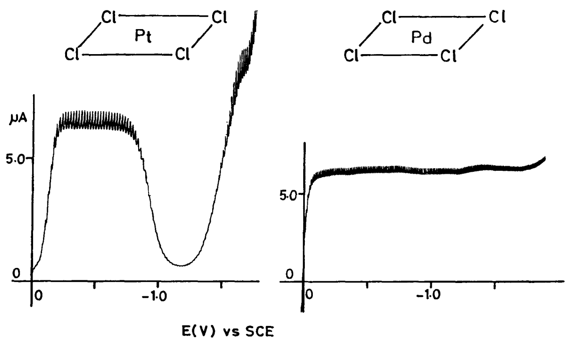

Fig. 2. Typical examples of DC polarograms which belong to Group A and B in Fig. 1.
Right: 1 mM $PdCl_4^{2-}$, 1.0 M KCl, 0.01% gelatin (Group A).
Left: 1 mM $PtCl_4^{2-}$, 1.0 M KCl, 0.01% gelatin (Group B).

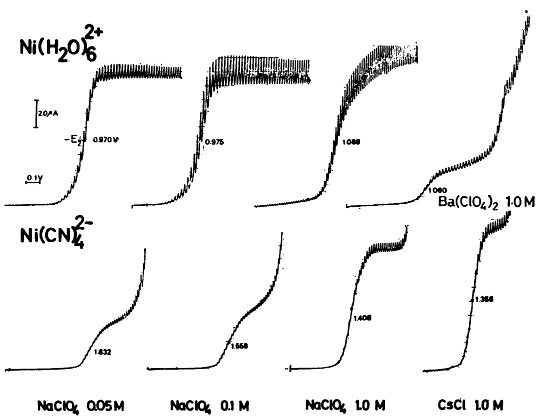

Fig. 3. Typical examples of DC polarograms which belong to Group C in Fig. 1.
Systems: 1 mM $Ni(CN)_4{}^{2-}$ with different kinds of supporting electrolytes, where polarograms of $Ni(H_2O)_6{}^{2+}$ with the same kinds of supporting electrolytes are also cited for comparison.

according to whether they do (B) or do not show (A) the decrease in the limiting diffusion current (the minimum) beyond the ecm. This classification is nonspecific for the type of chemical species such as metal complexes, metal oxides, and oxo acids of halogens, but is only attributed to the difference of the relative position of the half-wave potentials between the two groups.

Effect of Supporting Electrolyte. For the systems of Group A, the decrease in the limiting diffusion current beyond the ecm (the minimum) can be observed in the absence of supporting electrolyte, but it is completely eliminated by suitable amount of supporting electrolyte. The minimum of Group B does not disappear on addition of supporting electrolyte; it merely decreases and becomes narrower in the order of $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ and $CN^- > I^- > Cl^- > ClO_4{}^-$, for the cation and the anion of the supporting electrolyte, respectively. In the case of Group C, the rising portion of the DC polarogram is distorted, which is recovered by added salts in the similar way as the minimum of Group B (Fig. 3).

Effect of Surface-active Substances. The effect of surface-active substances on the shapes of the current-potential curves are also examined systematically. For Group A upon adding suitable amount of gelatin, the decrease in the limiting diffusion current beyond the ecm can be observed even in the presence of supporting electrolyte. This is shown in Fig. 4 taking $Pd(NO_2)_4{}^{2-}$ ion as an example. Similarly, the minimum of Group B and the distortion of the polarogram of Group C are much pronounced by the addition of gelatin. These situations are represented schematically in Fig. 5.

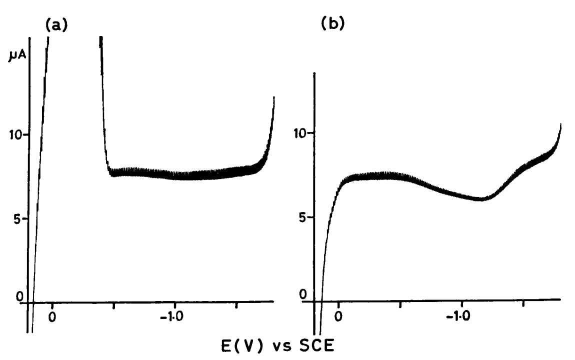

Fig. 4. Effect of surface-active substances on the *i*—*E* curve of Group A in Fig. 1.
System: 1 mM $Pd(NO_2)_4{}^{2-}$ in 0.1 M KNO_2
(a) without gelatin (b) 0.01% gelatin added

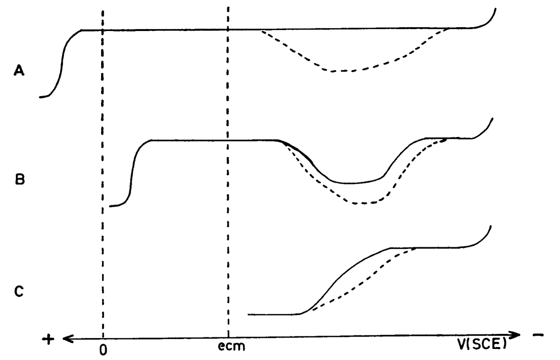

Fig. 5. Effect of surface-active substances on the shapes of *i*—*E* curves of Groups A—C in Fig. 1.
Solid line: without surface-active substances
Dotted line: 0.01% surface-active substances(gelatin) added

Discussion

Electrostatic Effect. It has been well-accepted[3,4] that the electrostatic repulsion of anion depolarizers from negatively charged electrode is the dominant origin of the minimum phenomena. However, quite different behavior between Groups A and B in Fig. 1 cannot be elucidated solely by the simple electrostatic model.[4] The distortion of the DC polarogram of Group C (see Figs. 1 and 3) is generally referred to as the irreversible wave.[3] Results of Fig. 1 imply that the irreversible wave of Group C is similar in origin to that of the minimum of Group B.

At a negative potential E_n beyond the ecm, all the anions are more or less subject to electrostatic repulsion from the negatively charged electrode surface, which

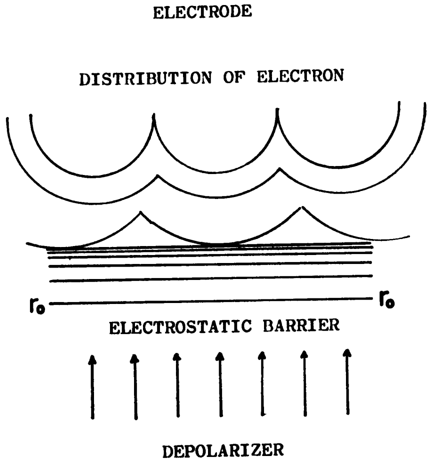

Fig. 6. Distribution of electron cloud of the metal electrode at the interface (See Text)

is non-specific for Group A, B, or C. Because the electron in the metal electrode is represented by a wave function, it will not vanish at the surface of the metal, but will die away exponentially into the remote from the electrode.[1] In Fig. 6 is drawn the distribution of the electron density of the metal electrode at the interface, where r_0 denotes the mean distance of the nearest approach of an anion against the coulombic field at the potential E_n. In the presence of the electrostatic repulsion, the anion cannot go within r_0 resulting in the small probability of electron transfer at r_0 in comparison with that at the surface of the metal. This is probably the important origin of the minimum for the systems of Groups A and B, and the distortion at the rising portion of the polarogram for the systems of Group C.

Electronic Level of the Electrode. The highest occupied electronic energy level of the metal electrode can be represented as:[1,5]

$$\phi = E_F + V \qquad (1)$$

where E_F is the Fermi level of the metal electrode in contact with the electrolyte solution at open circuit, V the applied potential *vs.* the SCE. Because the current density at the dropping mercury cathode is small in polarography, the potential of the anode is made constant by the SCE. Equation (1) indicates that the effect of an electrode potential of 1 V is to raise the highest occupied level at the cathode, ϕ, by 1 eV. This situation is shown in Fig. 7. It is also seen in Fig. 7 that the number of electrons (electron density) in the metal cathode whose energy is higher than any given value is increased with increasing applied negative potentials. Among a great number of electrons in the metal cathode, only the electrons that have any energy higher than the half-wave potential of depolarizers can participate in the electrochemical reduction process. As shown in Fig. 1, the half-wave potential of the system of Group B, $(E_{1/2})_b$, is always more negative than that of Group A, $(E_{1/2})_a$,

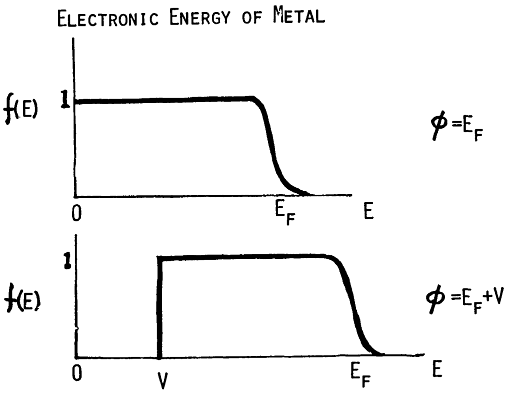

Fig. 7. Electronic energy level of the metal cathode as a function of applied potential, V.
ϕ: Highest occupied level of the metal cathode in contact with the electrolyte solution
E_F: Fermi level of the electrode in contact with the electrolyte solution
$f(E)$: Fermi distribution function

$$(E_{1/2})_a > (E_{1/2})_b > E_n \qquad (2)$$

where E_n is a negative potential beyond the ecm, where the minima appear. From the above considerations, it may be concluded that in the metal cathode at the potential E_n, numbers of electrons which can participate in the electrochemical reduction for Group A is greater than that for Group B. Therefore, it appears that the different behavior of the minimum between Groups A and B is due to the difference in the numbers of electrons as mentioned above, resulting from the difference in the half-wave potential between two Groups.

In the case of the minimum of Group B, the increase of the current at rather negative potentials can be observed (Figs. 1 and 2). Furthermore, in the case of Group C, the distortion of the polarogram at the rising portion is recovered with increasing applied negative potentials until the limiting diffusion current is attained (Figs. 1 and 3). These two phenomena can also be explained in terms of the increase with increasing applied negative potentials in the numbers of electrons which can participate in the electrochemical reduction.

The effect of gelatin in Figs. 4 and 5 can be explained as being due to the enhancement by gelatin of repulsion of anions from the electrode surface (see Fig. 6).

Phenomenological Equation. According to the phenomenological equation of the irreversible electrode reaction, the current much smaller than the limiting diffusion current can be written as:[3]

$$i = nFqk_e{}^0[\mathrm{Me}^{n+}]_s \exp\left\{-\frac{\alpha nF(E-E^0)-W}{RT}\right\} \qquad (3)$$

$$[\mathrm{Me}^{n+}]_s = [\mathrm{Me}^{n+}] \exp(-zFW/RT) \qquad (4)$$

where n, F, q, and R are as usual, k_e^0 the heterogeneous rate constant at the standard potential E^0, α the transfer coefficient, W the mean electrostatic potential at the distance of an ionic radius from the surface of the electrode, $[\mathrm{Me}^{n+}]_s$ the surface concentration of depolarizers. In the above equations, it is assumed that the electrode process involves only ions in direct contact with the electrode and that electron transfer to more distant ion is hardly likely.[3] The increment of applied negative potentials beyond the ecm influences upon the observed current intensity through different two terms in Eq. (3), *i.e.*, i) $[\mathrm{Me}^{n+}]_s$ and ii) the exponential term. Of these two, $[\mathrm{Me}^{n+}]_s$ decreases in a similar way both in Groups A and B, which is due to the electrostatic repulsion of anions from the negatively charged electrode surface. As shown in Fig. 1 the half-wave potential of Groups A is always more positive than that of Group B. Therefore, it appears that in the case of Group A appreciable increase beyond the ecm potential in the exponential term of Eq. (3) prevents the appearance of the minima. This conclusion is to be compared with the discussion given in the previous section (*Electronic Level of the Electrode*).

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