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Alternating Current Polarography of Peroxodisulfate and Ferricyanide Ions in the Absence of Supporting Electrolytes

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The admittance and its phase angle of the polarographic reduction of peroxodisulfate and ferricyanide ions in solutions containing no supporting electrolytes were measured at very low frequencies. The series resistance components, measured at 30 cps, of these systems gave anomalously small values at the electrode potentials where the falling-off of the cathodic current was observed on the direct current polarograms. This anomaly in the alternating current polarization behavior was attributed to the negative charge-transfer resistance due to the double layer effect on the charge-transfer process.

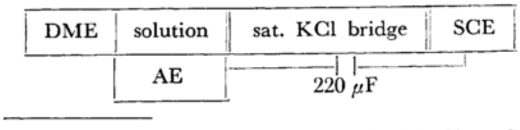
The electrochemical reduction behavior of peroxodisulfate and ferricyanide ions has been studied extensively by Frumkin and his coworkers.[1,2] They reported that the cathodic current of these ions in solutions of very low ionic strength shows a remarkable decrease at the electrode potentials more negative than the point of zero-charge; they attributed this anomaly to the double layer effect.

A similar decrease in the cathodic current was observed by the polarographic reduction of In(III)-SCN^-, Ni(II)-SCN^-, and In(III)-Br^- systems in solutions of moderate ionic strength, but in these cases the falling-off of the cathodic current appears at the potentials where the adsorption of the anions on the electrode surface begins to decrease.[3,4] On alternating current (a. c.) polargorams of these systems an anomalous admittance is observed in the potential region where the cathodic current decreases with the increase in the negative polarization.[5] From the measurement of faradaic impedance, the anomalous behavior of the a. c. polarograms was confirmed to be due to the negative charge-transfer resistance.[3,4]

In the absence of supporting electrolytes, the reduction process of peroxodisulfate and ferricyanide ions at a dropping mercury electrode is expected to give a negative charge-transfer resistance because of the large double layer effect. This study deals with the a. c. polarization behavior of peroxodisulfate and ferricyanide ions at very low frequencies; the results are discussed in terms of the double layer effect.

Experimental

The electrolytic cell used is represented by the scheme,



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[1] A. Frumkin, *Z. Elektrochem.*, **59**, 807 (1955).

[2] A. N. Frumkin, *Trans. Faraday Soc.*, **55**, 156 (1959).

[3] N. Tanaka and R. Tamamushi, "Proceedings 1st Australian Conference on Electrochemistry 1963," Pergamon Press, Oxford (1965), p. 248; N. Tanaka, T. Takeuchi and R. Tamamushi, This Bulletin, **37**, 1435 (1964).

[4] R. Tamamushi and K. Matsuda, *J. Electroanal. Chem.*, **12**, 436 (1966).

[5] H. Shirai, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **81**, 1248 (1960).

where DME is a dropping mercury electrode, and AE, an auxiliary electrode of a platinum spiral surrounding the tip of the DME; the terminals of AE and SCE were connected by a 220 μF tantalum condenser in order to reduce the impedance between the DME and SCE. The drop time and the flow rate of mercury of the DME used were 8.1 sec and 0.88 mg/sec, respectively, in a 1 M potassium chloride solution at open circuit.

The direct current (d. c.) polarograms were recorded by a potentiostatic polarograph similar to that of Durst, Ross and Hume.⁶⁾ The d. c. polarograms of peroxodisulfate and ferricyanide ions have large maxima of the first kind, the appearance of which is affected by the scanning direction of the electrode potential. In this study, the electrode potential of the DME was scanned from the negative to the positive side; by this scanning direction a more well-defined limiting current plateau was obtained at the potentials less negative than the point of zero-charge.

The admittance and its phase angle of the system were measured by a potentiostatic a. c. polarograph as shown in Fig. 1. The electrode potential of the DME, both the d. c. and a. c. components, was controlled against the SCE by means of a stabilized operational amplifier, C, and the alternating current flowing through the cell was amplified by a current amplifier, CA (stabilized operational amplifier), and a tuned amplifier, TA (Model 4403A, Yokogawa-Hewlett-Packard), the output of which was then introduced to a rectifier circuit or to a phase meter, PM (Model PHM-8, Ando Electric Co., Ltd.). The d. c. component of the electrode potential was applied to the DME by a mechanical voltage scanner, POT, with the scanning rate of about 45 mV/min. The superimposed sinusoidal voltage, whose amplitude was approximately 10 mV and kept constant during each measurement, was supplied by an audio-frequency oscillator, OSC (Model VP-702B, Matsushita Communication Industrial Co., Ltd.). The admittance and phase angle readings were calibrated by using known resistors and capacitors as a dummy cell, and the values measured at the maximum size of a mercury drop of the DME were reported in this paper.

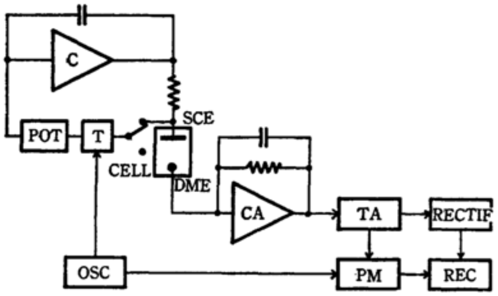

Fig. 1. Potentiostatic a. c. polarograph: C, controller (stabilized operational amplifier); CA, current amplifier (stabilized operational amplifier); TA, tuned amplifier; RECTIF, rectifier; PM, phase meter; REC, recorder; OSC, audio-frequency oscillator; T, transformer; POT, potentiometer (mechanical voltage scanner).

The square-wave polarization behavior was measured by essentially the same circuit as shown in Fig. 1. The square-wave voltage of 50 cps, whose amplitude was about 15 mV, was superimposed to the d. c. electrode potential, and the corresponding current flowing through the cell was observed by a cathode-ray oscilloscope (Tektronix Type 564) at the output of the current amplifier, CA.

The solutions were prepared from the analytical reagent grade chemicals and redistilled water, and vacuum-distilled mercury was used for the DME. The dissolved oxygen in the solution was expelled by bubbling nitrogen through the solution. Peroxodisulfate and ferricyanide ions are subjected to some redox reaction in aqueous solutions; an appreciable change in the solution was observed in a relatively short period of time, especially when the solution was kept in contact with mercury. Therefore, each measurement was carried out with fresh solutions, and the DME and the tip of SCE were introduced into the solution after the deaeration. All measurements were made in a water-thermostat of 25.0±0.1°C.

Results

The d. c. polarograms of 1 mM potassium peroxodisulfate and 1 mN potassium ferricyanide in aqueous solutions containing no supporting electrolytes are shown in Fig. 2, and their a. c. polarograms with the phase angle change at 30 cps in Figs. 3 and 4. In the ferricyanide system, the current decrease on d. c. polarograms was very much sensitive to the concentration of ferricyanide ions; a large decrease appeared in a 1 mN solution, while only a very small one was observed in a 1 mM solution.

From the measured values of admittance and phase angle, the series resistance and capacitance components, R_s and C_s, of the equivalent cell impedance were determined as given in Figs. 5 and 6.

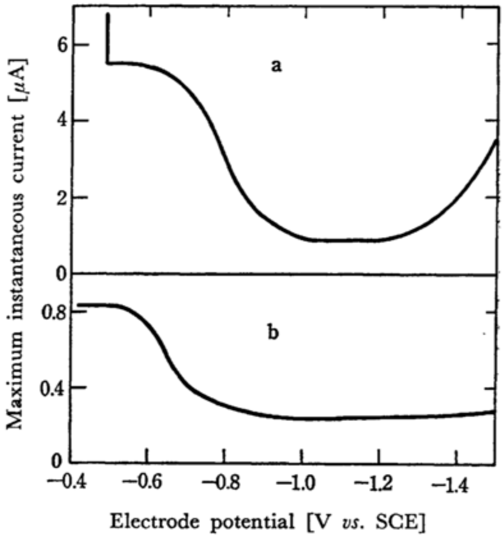

Fig. 2. D. c. polarograms of (a) 1 mM $K_2S_2O_8$ and (b) 1 mN $K_3[Fe(CN)_6]$ in aqueous solutions containing no supporting electrolytes.

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6) R. A. Durst, J. W. Ross and D. N. Hume, *J. Electroanal. Chem.*, **7**, 245 (1964).

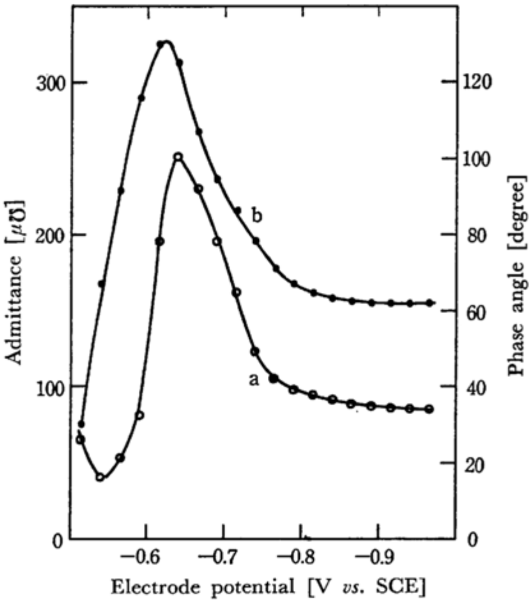


Fig. 3. A. c. polarogram and phase angle change of 1 mM $K_2S_2O_8$ at 30 cps: (a) admittance, and (b) phase angle.

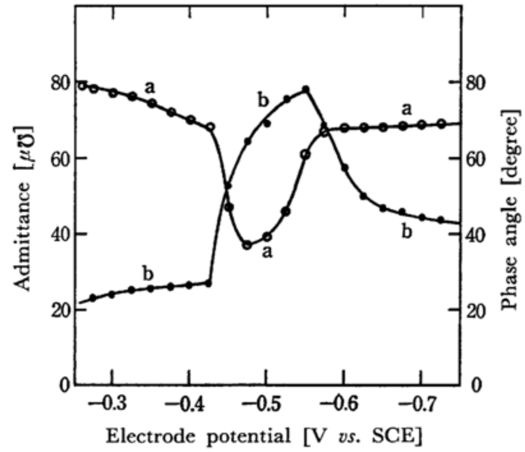
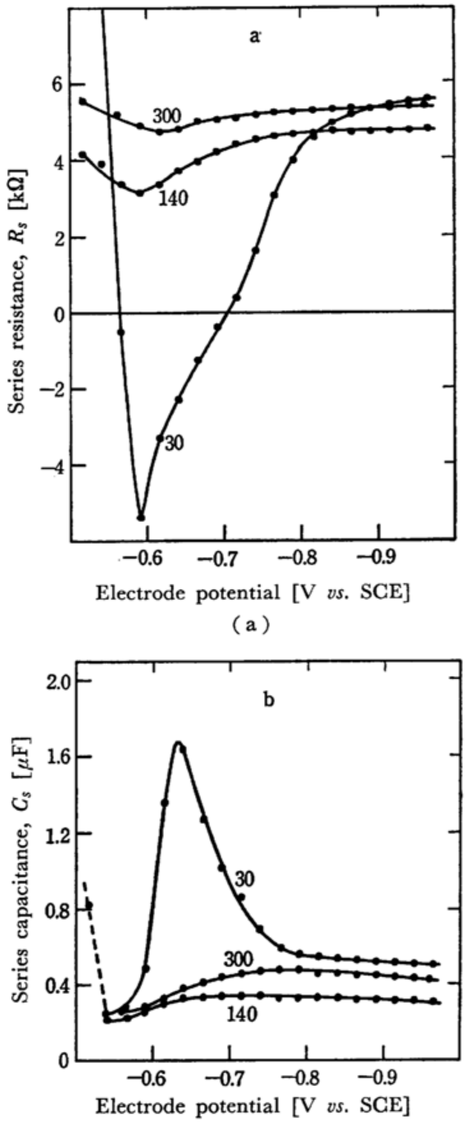


Fig. 4. A. c. polarogram and phase angle change of 1 mN $K_3[Fe(CN)_6]$ at 30 cps: (a) admittance, and (b) phase angle.



(a)

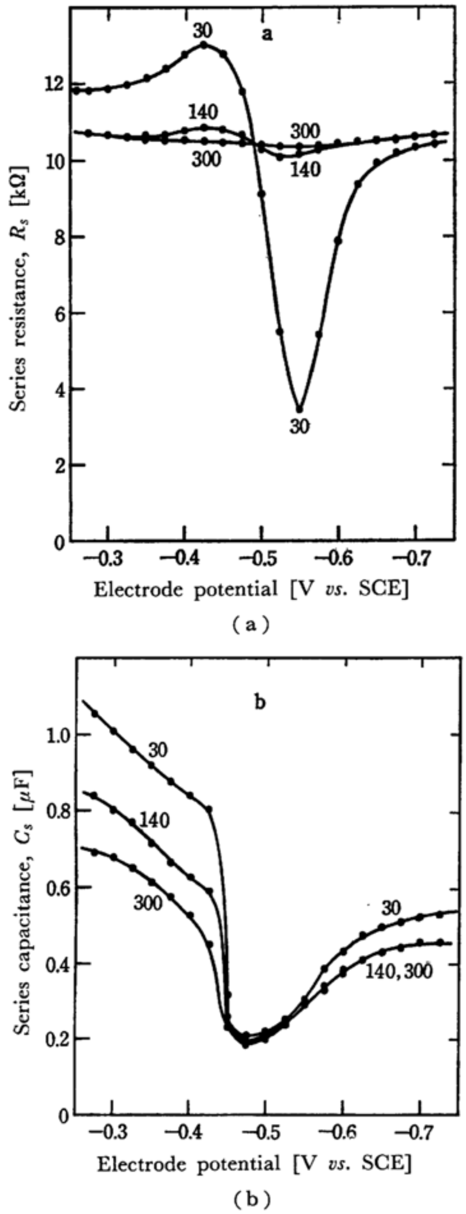
(b)

Fig. 5. Series resistance and capacitance components, R_s and C_s, of the DME/1 mM $K_2S_2O_8$ system: (a) resistance, and (b) capacitance. Figures on each curve represent the frequency of the superimposed sinusoidal voltage.

An example of the square-wave polarization behavior of peroxodisulfate ions is reproduced in Fig. 7; curve (a) represents the output current observed at the electrode potential on the limiting current plateau, and curve (b), the output current at the electrode potential where the cathodic current begins to decrease with increasing negative polarization. Similar results were obtained with the reduction process of ferricyanide ions.

Discussion

The a. c. polarographic behavior of peroxodisulfate and ferricyanide ions at 30 cps shows an anomalously large phase angle at the electrode potentials in the vicinity of the zero-charge point of mercury (Figs. 3 and 4). This anomaly in the phase angle results in a remarkable decrease in the series resistance component, R_s, as shown in Figs. 5 and 6. The R_s-values at 300 cps are assumed to be approximately equal to the resistance of the solution, but the values at 30 cps are very much smaller than the resistance of the solution, even negative in the case of peroxodisulfate ions, at the electrode potentials where the cathodic currents fall off.



(a)

(b)

Fig. 6. Series resistance and capacitance components, R_s and C_s, of the DME/1 mN $K_3[Fe(CN)_6]$ system: (a) resistance, and (b) capacitance. Figures on each curve represent the frequency of the superimposed sinusoidal voltage.

The series capacitances, C_s, of the ferricyanide system at the potentials more negative than −0.5 V *vs.* SCE were not very much affected by the frequency, and they may be assumed to be nearly equal to the double layer capacity. On the other hand, the C_s-values of the peroxodisulfate system at 30 cps gave a peak at about −0.63 V *vs.* SCE, which suggests some complication in the electrode process. The details of the capacitance behavior, however, will not be discussed in this paper.

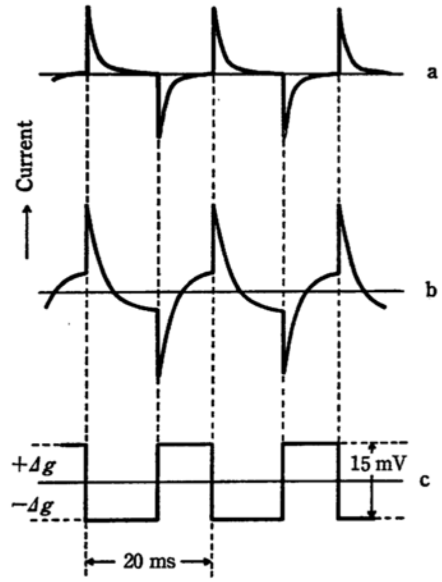


Fig. 7. Square-wave polarization behavior of the DME/1 mM $K_2S_2O_8$ system: (a) $g=-0.50$ V *vs.* SCE; (b) $g=-0.60$ V *vs.* SCE; (c) superimposed square-wave signal. The photographs were taken at the moment just prior to the detachment of a mercury drop from the tip of the DME.

The square-wave polarization behavior of the peroxodisulfate system at −0.60 V *vs.* SCE (Fig. 7, curve (b)) shows that the cathodic faradaic current in the period when the DME is more negatively polarized is smaller than that in the period when the DME is less negatively polarized. This result clearly indicates the decrease in the rate of overall reduction process with increasing negative polarization.

In analogy to the impedance behavior of the polarographic reduction of indium(III) ions in thiocyanate solutions,[3,4] the anomalous decrease in the series resistance component may be attributed to the negative charge-transfer resistance. The negative charge-transfer resistance of the peroxodisulfate and ferricyanide systems can be explained in terms of the double layer effect.

The charge-transfer resistance, Θ, of the electrode reaction,

$$\mathrm{O} + ne \rightleftharpoons \mathrm{R}$$

is given by the equation,

$$\frac{1}{\theta} = \frac{n^2\boldsymbol{F}^2}{\boldsymbol{RT}} k^\circ \left\{\alpha_+ c_\mathrm{R} \exp\left[\frac{\alpha_+ n\boldsymbol{F}}{\boldsymbol{RT}}(g-g^\circ)\right] + \alpha_- c_0 \exp\left[\frac{-\alpha_- n\boldsymbol{F}}{\boldsymbol{RT}}(g-g^\circ)\right]\right\} \quad (1)$$

where k° is the standard rate constant, g, the d. c. component of the electrode potential, g°, the standard electrode potential, c, the d. c. component of the concentration at the plane just outside the diffuse double layer, and α_+ and α_- are the apparent transfer coefficients for the anodic and cathodic directions, respectively.[7]

At the electrode potentials where the dip in cathodic currents appears, the condition $g<g^\circ$ can be satisfied, and Eq. (1) is simplified as

$$\frac{1}{\theta}=\frac{n^2\boldsymbol{F}^2}{\boldsymbol{RT}}k^\circ\alpha_-c_0\exp\left[\frac{-\alpha_-n\boldsymbol{F}}{\boldsymbol{RT}}(g-g^\circ)\right] \tag{2}$$

This relation indicates that the sign of θ is determined by that of the apparent transfer coefficient, α_-, for the cathodic direction; θ should be positive when $\alpha_->0$, and should be negative when $\alpha_-<0$.

By assuming the simple Boltzmann-type distribution of reacting species in the diffuse double layer and that the charge-transfer process proceeds at the outer Helmholtz plane, the apparent transfer coefficient, α_-, is represented by Eq. (3) as a function of the electrode potential,

$$\alpha_- = (1-\beta) + \frac{1}{ng}[z_0 - n(1-\beta)](\phi_2-\phi^{\mathrm{S}}) \tag{3}$$

where β $(1>\beta>0)$ is a symmetry factor, z_{O}, the charge of O with sign, and ϕ_2 and ϕ^{S} are the inner potentials of the outer Helmholtz plane and the bulk of solution, respectively.[7]

Equation (3) suggests that by the reduction of polyvalent anions in solutions of low ionic strength the apparent transfer coefficient, α_-, may assume negative values especially at the electrode potentials. in the vicinity of the point of zero-charge. No data is available for the double layer behavior of the mercury electrode in peroxodisulfate and ferricyanide solutions, and thus the quantitative estimation of $(\phi_2-\phi^{\mathrm{S}})$ is not feasible. The double layer effect, however, can reasonably be assumed to be large enough to give negative α_--values for the polarographic reduction of peroxodisulfate and ferricyanide ions in aqueous solutions of very low ionic strength. Peroxodisulfate and ferricyanide ions are supposed to be subjected to a specific adsorption at the DME, the effect of which was ignored in the present discussion. The specific adsorption of these species, if any, will increase the double layer effect.

Frumkin suggested the possibility that the rate determining step of the reduction of ferricyanide ions may be the penetration of the anion through the electric field of the diffuse double layer and not the charge-transfer process.[2] According to Matsuda[8] and Senda and Delahay,[9] the repulsion of the discharged species due to the electric field of the diffuse double layer results in an additional resistance in series with the Warburg impedance in the equivalent circuit of the faradaic impedance. This additional resistance is then expected to increase the resistance component, R_s, and therefore, the remarkable decrease in R_s of the ferricyanide system as shown in Fig. 6 (a) could not be explained without considering the effect of the double layer on the apparent transfer coefficient of the charge-transfer process.

In conclusion, the qualitative behavior of the a. c. polarization of the peroxodisulfate and ferricyanide systems can be explained satisfactorily by assuming the double layer effect on the charge-transfer process. The a. c. polarography with the phase angle measurement, particularly at very low frequencies, was proved to be a useful method of analyzing the mechanism of electrode reactions.

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[7] R. Tamamushi, "Denki Kagaku (Electrochemistry)," Tokyo Kagaku Dōzin, Tokyo (1967), Chap. 5.

[8] H. Matsuda, *J. Phys. Chem.*, **64**, 339 (1960).

[9] M. Senda and P. Delahay, *ibid.*, **65**, 1580 (1961).