Studies on A.C. Polarography. IV. Reversible Behaviour of Anions

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Introduction

A comprehensive polarographic investigation of various anions was carried out by Revenda,(1) and Kolthoff and Miller,(2) who introduced the polarographic equations of those anions depolarizing the dropping mercury anode. Recently, Breyer et al.(3) have communicated many investigations on a. c. polarography of anions, using an a. c. polarographic equipment, and have shown that the summit-potential of an a. c. polarogram does not agree with the half-wave potential of the ordinary polarogram and also that the shape of Breyer's polarogram is unsymmetrical, which is different from the fact found in the case of cations.

In the previous paper, the theoretical equation representing the a. c. electrolytic current in a. c. polarography was introduced by Tachi and others(4) and it has been confirmed that Breyer's polarogram is a derivative curve of the ordinary polarogram, provided that the depolarizing process is reversible. And now, the authors will show the results of the experiments in which they attempted to discover whether Breyer's polarogram of anions would agree with the derivative curve led from the equation of the polarographic diagram introduced by Kolthoff and Miller. And also, the experimental results of the behaviour of d. c. component in a. c. polarography, i. e. Fournier's current, and the relationship between the concentration of the depolarizer and the polarographic current intensity of Breyer's polarograms will be reported.

Experimental

The anions used here as the depolarizer were Cl^-, Br^-, I^-, $S_2O_3^=$ and CN^-, which are in the form of KCl, KBr, KI, $Na_2S_2O_3$ and KCN respectively. They were polarographed in the concentration range from 10^{-4} N to 10^{-3} N for the ease of comparing Breyer's polarogram with the ordinary polarogram, since the ordinary polarograms of anions, especially halogen ions, in the concentration higher than 10^{-3} N are not well-defined in general.

The concentration of KNO_3 aq. solution as the supporting electrolyte was made 0.2 N to keep the low impedance of the solution in the polarographic cell. But in the case of polarographic electrolysis of CN^-, 0.2 N NaOH aq. solution was used instead of 0.2 N KNO_3 aq. solution.

The circuit of a. c. polarography used was the same one as described in the previous papers. A pool condenser (50μF electrolytic condenser) was always connected between the bottom mercury and reference electrode in order to decrease the impedance of the liquid junction. In the case of polarographing Breyer's polarogram, the amplitude of a. c. voltage superimposed upon d. c. voltage was kept always 50 mv (60 c/s), and in registering Fournier's polarogram, it was changed from 0 to 100 or 120 mv (60 c/s).

The drop time of mercury electrode was 4.6 sec. and the rate of mercury flow was 2.2 mg/sec. (at O v *vs.* N.C.E.). The normal calomel electrode was employed as the reference electrode. All measurements were carried out at room temperature (about 17°C). The sensibility of the galvanometer was 2.87×10^{-9} amp./mm/m.

Experimental Results and Discussion

(1) The Shape of Breyer's Polarogram

(i) Cl^-, Br^-, I^-.—Kolthoff and Miller gave the following equation for the polarographic wave of the depolarizers which form slightly soluble mercurous compounds at the dropping mercury electrode

$$i=\left\{\begin{matrix} i_d-\exp\dfrac{-F(E-E_o')}{RT} & \text{for } E\geqq E_{st} \\ O & \text{for } E\leqq E_{st} \end{matrix}\right\} \quad (1)$$

where E_{st} represents the starting potential of the ordinary polarogram, and E_o' is determined by the solubility product of the mercurous compound formed at the anode, and i_d is the limiting current of the polarographic wave and the positive sign of i means the anodic current. Thus the derivative curve of the ordinary polarogram is given by

$$\frac{di}{dE}=\left\{\begin{matrix} \dfrac{F}{RT}\exp\dfrac{-F(E-E_o')}{RT} & \text{for } E\geqq E_{st}, \\ O & \text{for } E\leqq E_{st}. \end{matrix}\right\} \quad (1a)$$

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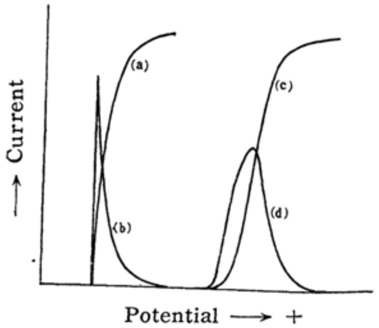
1) J. Revenda, *Collection Czech. Chem. Communs.*, 6, 453 (1934).

2) I. M. Kolthoff and C. S. Miller, *J. Am. Chem. Soc.*, 63, 1405 (1941).

3) B. Breyer, F. Gutman and S. Hacobian, *Aust. J. Sci. Res.* **A3**, 558, 567, 595 (1950), **A4**, 611 (1951).

4) I. Tachi, et al., This Bulletin 28, 25, 31, 37, (1955).

The curves represented by the equations (1) and (1a) are illustrated in Fig. 1 (a) and (b).



(a) and (c); i—E curve
(b) and (d); di/dE—E curve.

Fig. 1. The model curves of the ordinary polarographic wave and the derivative polarographic wave.
(a) i—E curve in the case of Cl^-, Br^- and I^-.
(b) di/dE—E curve of the upper.
(c) i—E curve in the case of $S_2O_3^=$ and CN^-.
(d) di/dE—E curve of the upper.

Now, assuming that Breyer's polarogram would be given by the derivative curve of the ordinary polarogram as stated in the introduction, Breyer's polarographic wave is supposed to be the curve whose peak potential agrees with the starting potential of the ordinary polarographic wave.

The experimental results are shown in Table I and Fig. 2 (a), (b) and (c), and it is recognized that the summit potentials of Breyer's polarograms (E_s) generally coincide with the starting potentials of the ordinary polarograms (E_{st}) except in the case of Br^-, whose E_s always agrees with the potential at which a kink appears on the ordinary polarogram. Further, this kink suggests that the ordinary polarogram of Br^- consists of two steps, of which the first step may be due to the adsorption of Br^- at the electrode. The reasons are as follows.

The fact that the shape of Breyer's polarogram of Br^- is different from those of Cl^- and I^- in the point of having a prewave adjoining the main wave (Fig. 3), shows that another increase of the admittance at the dropping mercury electrode occurs at more negative potentials than E_s of Breyer's

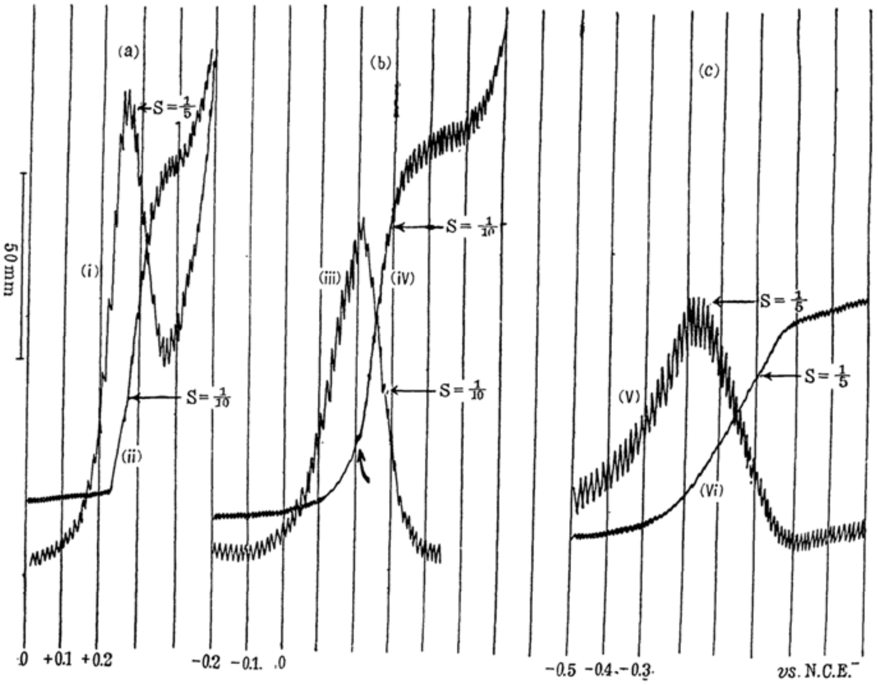


Fig. 2. Breyer's and the ordinary polarogram of Cl^-, Br^- and I^-.
(i) Breyer's polarogram of 6×10^{-4}N Cl^-.
(ii) Ordinary polarogram of (i).
(iii) Breyer's polarogram of 8×10^{-4}N Br^-.
(iv) Ordinary polarogram of (iii).
The arrow points the kink on the ordinary polarogram of Br^-.
(v) Breyer's polarogram of 1×10^{-3}N I^-.
(vi) Ordinary polarogram of (v).

TABLE I

Depolarizer	Potential *vs.* N. C. E.	Conc. $\times 10^4$ N 2 (V)	4 (V)	6 (V)	8 (V)	10 (V)
	E_s	0.270	0.260	0.240	0.230	0.230
Cl^-	$E_{1/2}$	0.275	0.275	0.275	0.280	0.280
	E_{st}	0.250	0.240	0.230	0.220	0.210
	E_s	0.160	0.140	0.120	0.110	0.100
Br^-	$E_{1/2}$	0.150	0.140	0.160	0.150	0.150
	E_{st}	0.100	0.090	0.050	0.090	
	E_s	−0.170	−0.170	−0.160	−0.170	−0.180
I^-	$E_{1/2}$			−0.025	−0.030	−0.060
	E_{st}			−0.210	−0.210	−0.200
	E_s	−0.140	−0.165	−0.180	−0.200	−0.220
$S_2O_3^=$	$E_{1/2}$	−0.100	−0.110	−0.120	−0.120	−0.120
	$E_{(\sqrt{2}-1)id}$	−0.130	−0.135	−0.145	−0.150	−0.150
	E_s	−0.320	−0.330	−0.330	−0.335	−0.335
CN^-	$E_{1/2}$	−0.335	−0.340	−0.340	−0.340	−0.350
	$E_{(\sqrt{2}-1)id}$	−0.340	−0.350	−0.355	−0.355	−0.355

E_s: Peak potential of Breyer's polarogram.
$E_{1/2}$: Half-wave potential of the ordinary polarogram.
E_{st}: Starting potential of the ordinary polarogram.
$E_{(\sqrt{2}-1)id}$: Potential of the inflection point of the ordinary polarogram, namely the potential at which $i=(\sqrt{2}-1)i_d$.

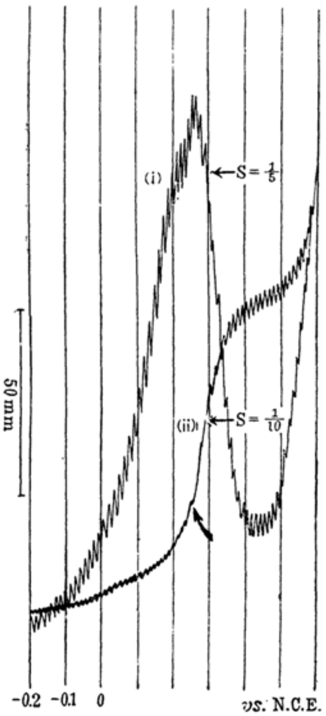


Fig. 3. Breyer's and the ordinary polarogram of Br^- with gelatine.

(i) Breyer's polarogram of 5×10^{-4}N Br^- with gelatine.

(ii) Ordinary polarogram of (i). The arrow points the kink on the ordinary polarogram of Br^-.

polarographic wave of Br^-, owing to the adsorption of the surface-active bromide ion. And the fact that the height of the prewave in the ordinary polarogram does not vary with the change of the concentration of the depolarizer suggests that the prewave may be due to the electro-oxidation of bromide ions oriented at the surface of the dropping mercury electrode.

(ii) $S_2O_3^=$ *and* CN^-.—Kolthoff and Miller introduced the following equation for the polarographic wave of depolarizers, which form slightly dissociated mercuric compounds or stable complex ions with mercuric ion; it can be written in the form

$$i=i_d+\frac{1}{2}\exp\frac{-2F(E-E_o')}{RT}-\frac{1}{2}\sqrt{4i_d\exp\frac{-2F(E-E_o')}{RT}+\exp\frac{-4F(E-E_o')}{RT}} \qquad (2)$$

It follows therefore that

$$\frac{di}{dE}=-\frac{F}{RT}\left\{\frac{2i_d+\exp\dfrac{-2F(E-E_o')}{RT}}{\sqrt{4i_d\exp\dfrac{2F(E-E_o')}{RT}+1}}-\exp\frac{-2F(E-E_o')}{RT}\right\} \qquad (2a)$$

From these equations, it will be shown that the potential (E_s), where di/dE becomes maximum, namely the inflection point of the equation (2), is to be the potential ($E_{(\sqrt{2}-1)id}$) given by $i=(\sqrt{2}-1)i_d$. Therefore, it is seen that the model curve of Breyer's polarogram of these anions is to be the curve which is unsymmetrical and have the peak potential (E_s) at the potential ($E_{(\sqrt{2}-1)id}$) of the ordinary polarogram as shown in Fig. 1 (d).

The experimental results obtained with $S_2O_3^{=}$, CN^- are shown in Tabe I and Fig. 4 (a) and (b). It was found that E_s was near to $E(\sqrt{2}-1)id$, though the sharp agreements of these two potentials were not obtained, in the case of CN^-. But E_s of $S_2O_3^{=}$ shifts remarkably to more negative potential than $E(\sqrt{2}-1)id$ of the ordinary polarogram, for which the reason is not clear and a further study is necessary.

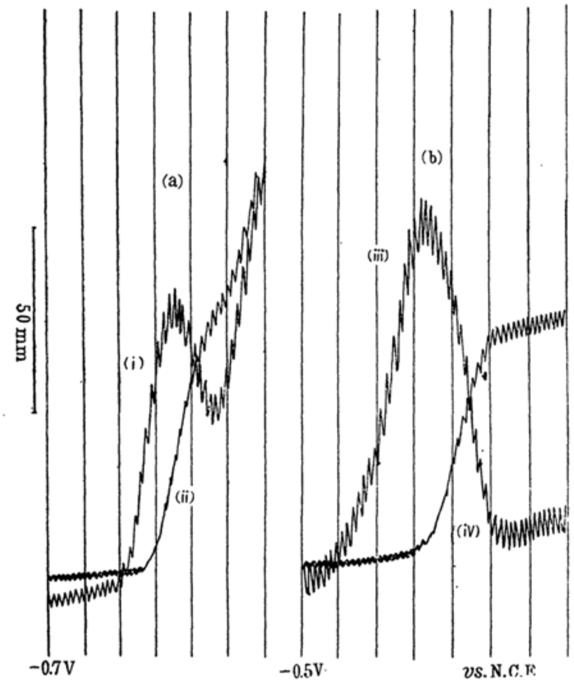


Fig. 4. Breyer's and the ordinary polarogram of $S_2O_3^{=}$ and CN^-.
- (i) Breyer's polarogram of 6×10^{-4}N CN^-.
- (ii) Ordinary polarogram of (i).
- (iii) Breyer's polarogram of 6×10^{-4}N $S_2O_3^{=}$.
- (iv) Ordinary polarogram of (iii).

(2) Fournier's Polarogram.—In this section, it will be reported that the experimental results as to the d.c. component in the a.c. polarography, i.e. Fournier's current, i_{Four}, generally agree with the theoretical consideration that Fournier's current observed by a galvanometer would be the mean value of the ordinary polarographic currents at both extreme potentials given by the superposition of small a.c. voltage (ΔE) on the d.c. potential, namely; $i_{Four}=\frac{1}{2}(i_{E-\Delta E}+i_{E+\Delta E})$.

Then the curves of Fournier's polarograms of Cl^-, Br^- and I^- are given by

$$i_{Four}=i_d-\exp\frac{-F(E-E_o')}{RT}\cdot\cosh\frac{E}{RT}\Delta E \qquad (3)$$

Thus from equations (1) and (3), it follows that

$$i-i_{Four}=\exp\frac{-F(E-E_o')}{RT}\cdot\left(\cosh\frac{F}{RT}\Delta E.\right.$$
$$\left.-1\right)\geqq 0. \qquad (4)$$

Whence it follows that

$$i\geqq i_{Four}. \qquad (5)$$

Namely, Fournier's current increases more slowly than the ordinary polarographic current with increasing positive potential.

Next, in the case of $S_2O_3^{=}$ and CN^-, the equation representing Fournier's theoretical polarogram is comparatively complicated so that we merely assume that Fournier's polarogram would be less steep than the ordinary polarogram and the former would cross the latter at the inflection point of the ordinary polarogram.

The experimental results shown in Fig. 5 agree with the theoretical consideration. The fact that Fournier's polarogram of $S_2O_3^{=}$ crosses the ordinary polarogram at a more negative potential than that of the inflection point is not theoretically clear as well as the above mentioned discrepancy between E_s and $E_{(\sqrt{2}-1)id}$, and a further investigation will be necessary for the complete explanation of it.

(3) The Dependency of Breyer's Polarographic Current and the Ordinary Polarographic Current on the Concentration of Depolarizers.—The relationship between Breyer's polarographic current and the concentration of depolarizer is shown in Fig. 6. The relationship between the ordinary polarographic current and the concentration of the depolarizer is shown in Fig. 7.

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5) M. Fournier, *Comp. Rend.*, 237, 1673 (1951).

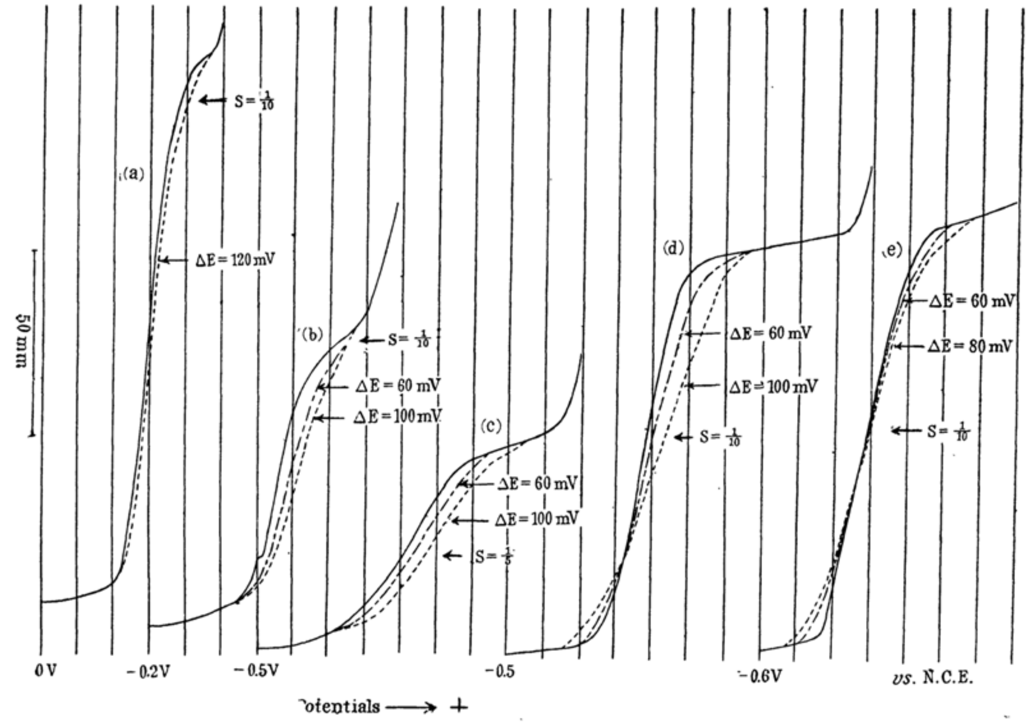

Fig. 5. Fournier's polarogram indicating the reversible electrode reactions of the named anions.
(a) 1×10^{-3}N Cl^-. (b) 6×10^{-4}N Br^-. (c) 1×10^{-3}N I^-. (d) 1×10^{-3}N $S_2O_3^{=}$. (e) 1×10^{-3}N CN^-.
The ordinary poralogram is demonstrated by full lines, and Fournier's polarograms are indicated by dotted lines.

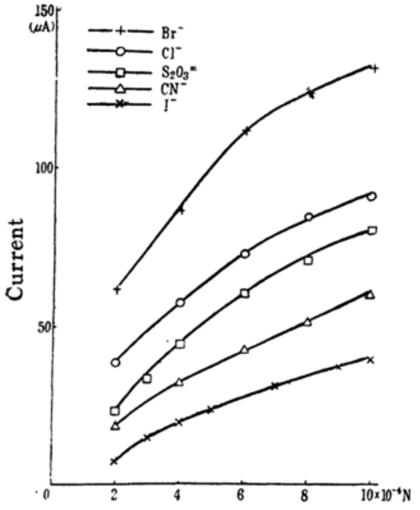

Fig. 6. The relationship between Breyer's polarographic current intensity and the concentration of depolarizer.

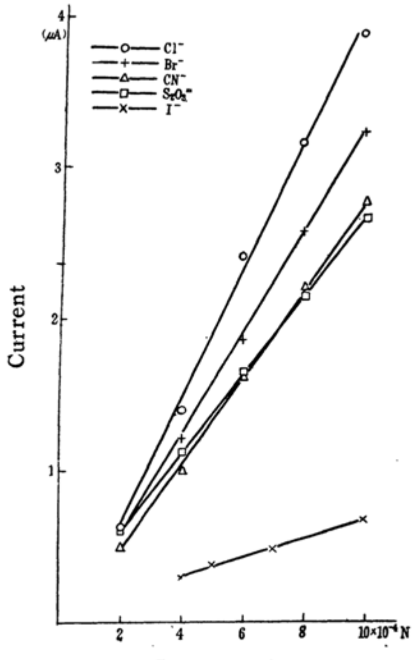

Fig. 7. The relationship between the ordinary polarographic current intensity and the concentration of the depolarizer.

The experimental results show that the linearity of the former holds generally over the concentration range from 2×10^{-4} N to 8×10^{-4} N, while the latter is linear over a tenfold concentration range. The non-linearity in a. c. polarography is probably due to the external impedance caused in the circuit. And the application of a. c. polarographic method to the quantitative determination of the anions is considered to be available, and for that purpose it must be cautioned that the external impedance in the circuit should be kept negligibly small.

Summary

A train of a. c. polarographic investigations on several anions, which depolarize the dropping mercury anode, was carried out. The experimental results of a. c. polarography of Cl^-, Br^-, I^- and CN^- generally agreed with the theoretical consideration based on the reversible electrode process. Namely, it can be concluded that Breyer's polarogram shows the derivative curve of the ordinary polarogram and Fournier's current of these anions is regarded as the mean of two current intensities at both the extreme potentials of the pulsing potential produced by the superposition of a small a. c. voltage on the ordinary d. c. potential. Thus the electrode processes of these anions are found to be reversible. And the possibility of the application to the quantitative determination of these anions was found in the proper concentration range.

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