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DIFFERENCE BETWEEN VOLTAGE AND CURRENT FOLLOWER MODES AS CURRENT MEASURING DEVICE IN ELECTROCHEMICAL OSCILLATORY SYSTEM

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It was found that polarograms of the electrochemical oscillatory systems showed anomalous current increase and oscillation in a narrow region of potentials in the descending branch of the current-voltage curves when the voltage-follower mode was used as a current measuring device, while the usual polarograms were observed by the current-follower mode.

Potentiostatic instrument made of operational amplifiers has been widely used for various electrochemical investigations. The potentiostats1) are classified, with respect to the mode in which current is measured, into those of the voltage-follower mode2) and of the current-follower mode.3) However, no difference between them has been reported in the behavior when they are used to measure a current in electrochemical phenomena.

This paper describes some experimental results obtained using different instrumental configurations of both the modes in the polarographic study of electrochemical oscillatory systems.

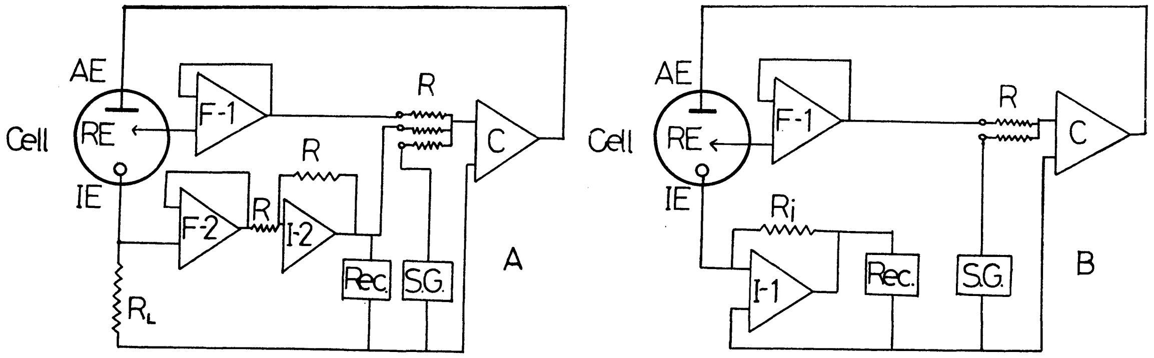

Fig. 1 Potentiostats A: Voltage-follower mode B: Current-follower mode

Amplifier F-1, F-2, I-1 : Philbrick/Nexus QFT-2A
Amplifier I-2 : Philbrick/Nexus SQ-10a
Amplifier C : Philbrick/Nexus SA-3a
Rec. : Recorder S.G. : Signal generator, Integrator circuit composed of operational amplifiers
R : 100 Kohm, 1%
Ri, R_L : 10 ohm to 1 Mohm on multi-step switch, 1%

Solid-state operational amplifiers were employed for making the potentiostats of the two modes as shown in Figs. 1A and 1B. The operational amplifiers of corresponding functions in the two assembly were of the same type, and feedback capacitors across the potential control and current amplifiers for achieving the stable operation were of the same magnitude. Comparison of the potential in these circuits was achieved in a simple bridge network incorporated in the potential control circuit. An X-Y, T recorder (Model D-5SN2, Riken Denshi) was employed to obtain polarograms. The solutions used for the investigation were as follows:

1) 1×10^{-3} M Cd(II) in 0.5M KCl 2) 1×10^{-3} M In(III) in 1M KSCN

3) 1×10^{-3} M Sn(IV) in 0.1M acetate buffer pH 4.58, 1×10^{-2} M α-mercaptopropionic acid and 0.0015% Triton X-100

The solution of Cd(II) in KCl is a reversible diffusion-controlled system. No difference could be detected in the polarograms recorded as shown in Figs. 2A and 2B.

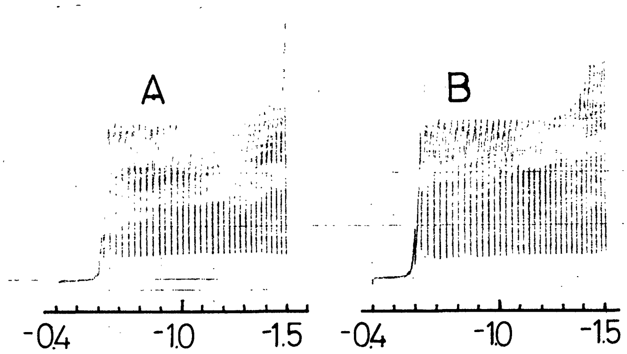

Fig. 2 Polarograms of 1×10^{-3} M Cd(II) in 0.5M KCl
A: Current-follower mode
Ri: 150 Kohm
B: Voltage-follower mode
R_L: 150 Kohm

The solution of In(III) in KSCN is the well-known electrochemical oscillatory system which has been discussed[4][5] in detail. In this system, polarograms obtained by the current-follower mode were the same as those obtained with conventional classical two electrode polarographs. On the other hand, however, those obtained by the voltage-follower mode were entirely different. An abnormal increase and oscillation of current occurred in the very limited region of potential where otherwise the current began to decrease to form a minimum.

A series of polarograms were taken with different values of R_L as shown in Fig. 3B. The larger was the resistance inserted, the wider the potential range of the oscillation and the larger the current in magnitude.

The system of Sn(IV)-α-mercaptopropionate complex in acetate buffer solution is an electrochemical oscillator which has been recently found[6] in my laboratory. Polarograms taken by the two modes were shown in Figs. 4A and 4B. They are clearly distinguishable in their shapes. The polarographic behaviors are the same as the system 2) with a slight difference in the external resistance needed for the current oscillation and in their wave shapes. The difference in the wave shapes is attributed to that of their current-time curves observed on a dropping mercury electrode. Fig. 5 showed several of the current-time curves. For reference, the corresponding d.c. polarograms, showing the potentials at which the current-time curves had been taken were also given in Fig. 5.

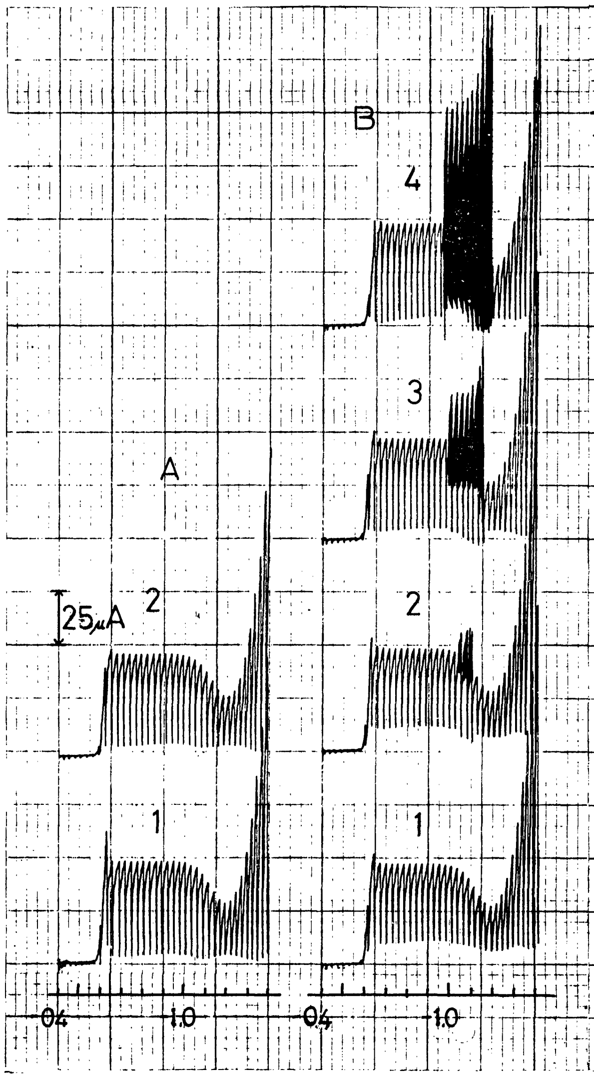

Fig. 3 Polarograms of In(III) in 1M KSCN

A : Current-follower mode
R_i (in Kohm)
1: 50, 2: 150
B : Voltage-follower mode
R_L (in Kohm)
1: 10, 2: 20, 3: 50, 4: 150

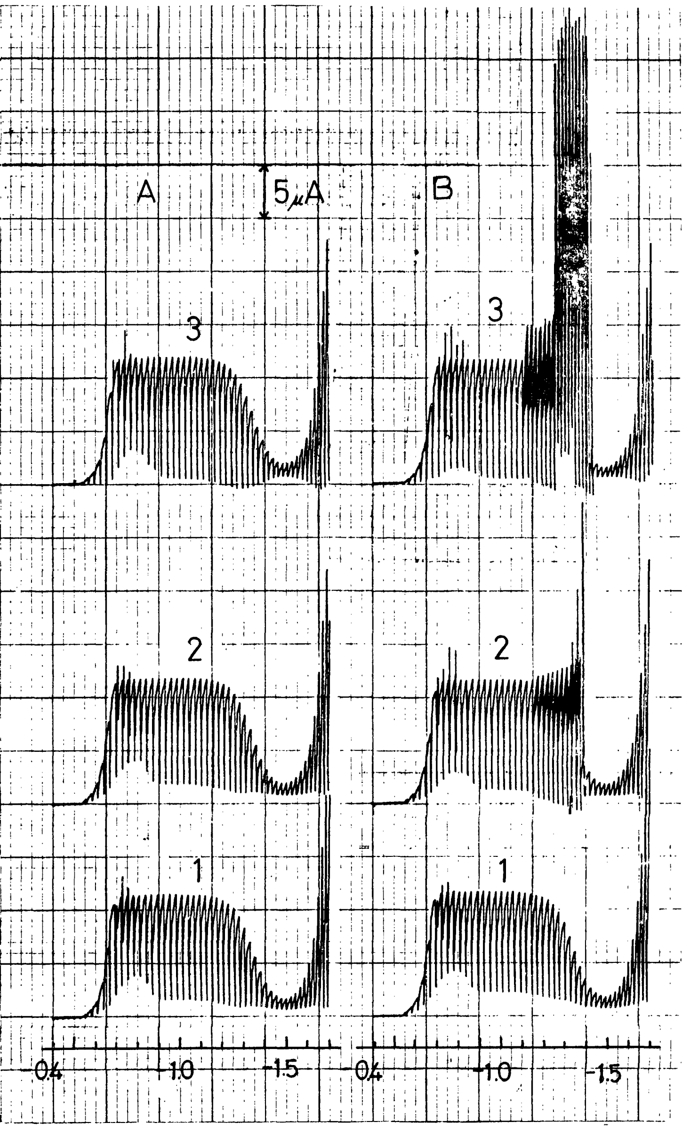

Fig. 4 Polarograms of Sn(IV)-α-mercaptopropionate complex in acetate buffer solution

A: Current-follower mode
R_i (in Kohm)
1: 5, 2: 20, 3: 50
B: Voltage-follower mode
R_L (in Kohm)
1: 5, 2: 20, 3: 50

In the region of potentials where the current is remarkably increased over the diffusion current, spontaneous oscillations of the current were observable in the current-time curves, when the potentiostat in the voltage-follower mode is used. On the other hand, no special abnormality is observed using the potentiostat in the current-follower mode, except for the gradual decrease of the current with increase of the applied voltage.

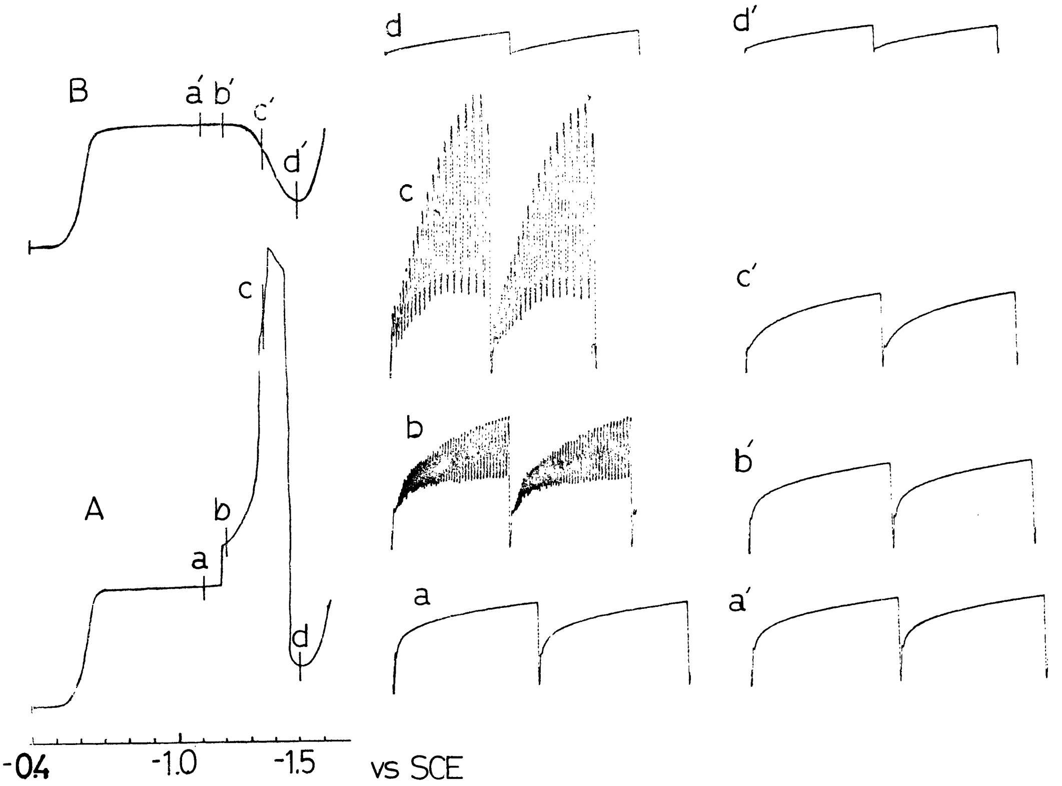

Fig. 5 Current-time curves
A. Voltage-follower mode B. Current-follower mode
a and a' ; -1.100 V b and b' : -1.200 V
c and c' : -1.350 V d and d' : -1.500 V

As De Levie[5] has stated in a qualitative way on the oscillatory behavior of In(III) in KSCN solution, the system becomes unstable effectively due to the interplay between negative charge transfer resistance and iR drop across the externally inserted current measuring resistor. The output of the voltage-follower mode is equal to that of iR drop across the current measuring resistor R_L. In contrast with the voltage-follower mode, the effective input impedance of the current-follower mode is practically zero, that is, a summing point is virtually grounded because of the high gain, so that the potential of the dropping mercury electrode is virtually grounded and the current can be measured without being disturbed by iR drop.

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