A METHOD OF LOW-FREQUENCY POLAROSCOPY AND A UNIVERSAL SCHEME FOR RECORDING POLARIZATION CURVES

A. V. Gorodyskii, Yu. K. Delimarskii, É. V. Panov, and É. A. Balezin

The Institute of General and Inorganic Chemistry, Academy of Sciences, UkrSSR
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A method of low-frequency polaroscopy is proposed, with which it is possible to obtain polarograms undistorted by the charging current. The method is applicable to the analysis of fused electrolytes. A universal apparatus has been constructed for recording current, potential, and their derivatives, as functions of each other and of time, which is suitable for various polaroscopic investigations.

The main method of investigating polarization in electrochemical cells is to study current–potential and current–voltage curves [1]. This method was greatly improved by the invention of the polarograph [2]. However, this did not solve the problem of obtaining reproducible data with unrenewable electrodes. The latter, unlike the dropping mercury electrode, may undergo irreversible changes under the influence of electrolysis products. In addition, the values of the current and potential alter with time owing to lack of constancy of the diffusion layer [3]. Various means of stabilizing the diffusion layer [4-8], and mechanical [9-11] or electrochemical [12-14] means of renewing the electrode, either only partially solve the problem [4-8], or disturb the process under investigation [10-11, 13-14].

In normal polarographic investigations the plotting is carried out within a few hundred seconds. Slow recording of polarization curves with unrenewable electrodes is always accompanied by more or less significant nonperiodic and often irregular changes in the system (passivation of the electrode, polarization, changes in crystal structure and active surface).

The only effective means of obtaining reproducible curves is to use such rapid recording that there is not time for the size or state of the electrode surface to change. If the recording time is reduced by a factor of a hundred, i.e., to a few seconds, there is a corresponding decrease in the quantity of electricity passed through the cell. All the changes occurring in the system during recording are easily eliminated by a subsequent brief depolarization of the electrodes by short circuiting.

A short recording time, of the order of hundredths of a second, is also used in oscillographic polarography [15, 16]. However, a large charging current passes through the cell and distorts the curve. Oscillographic polarography is therefore a special field, subject to special laws. Also, the high value of the charging current requires the use of electrodes with a smooth surface, mercury or amalgam [16, 17].

In the method proposed, which we have called low-frequency polaroscopy [18], the charging current is less by two orders of magnitude than in oscillographic polarography. This means that the charging current can be neglected [19] and the polarograms have the normal "classical" form. As regards recording time (one second), low-frequency polaroscopy occupies an intermediate position between normal polarography (10^2 sec) and oscillographic polarography (10^{-2} sec).

Recording in a few seconds was used by Weidmann [20] and Randles [21]. These authors polarized a dropping mercury electrode. However, they were not interested in the reproducibility problem but in reducing the charging current at a dropping mercury electrode. The idea of using rapid recording to obtain reproducible data with nonrenewing electrodes was first suggested and solved technically by Vagramyan [19]. The change in electrode potential with linear change in current was recorded with a loop oscillograph.

In developing the method of low-frequency polaroscopy our object was to improve the technique, so as to make it applicable to fused electrolytes, and to construct a universal apparatus for recording current i, potential φ, and their derivatives, as functions of each other or of time t, i.e., to recording of the functions: i, φ; $di/d\varphi$, φ; $d\varphi/di$, φ; $d\varphi/di$, i; i, t; φ, t; di/dt, t; $d\varphi/dt$, t.

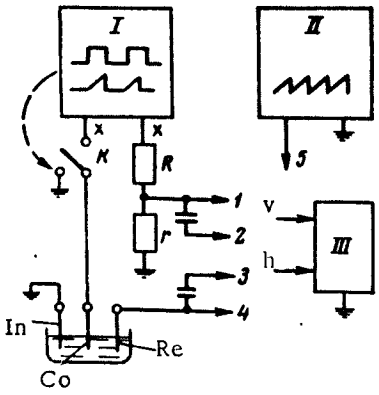

Fig. 1. Block diagram of universal apparatus for recording polarization curves.

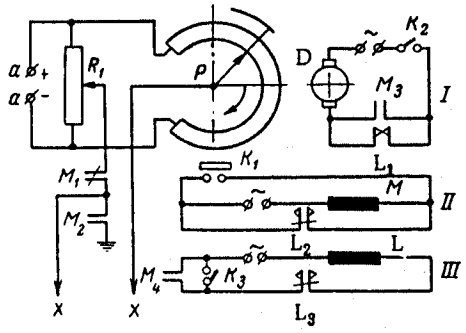

Fig. 2. Source of sawtooth and square-wave pulses.

Fig. 1 shows a block diagram of the apparatus. The source I fed sawtoothed or square-wave pulses to the indicator electrode In and the counter electrode Co. Depending on the value of the quenching resistance R, the system operated with a given current (R = 10-100 kΩ) or with a given voltage (R = 0). The potential drop across the standard resistance r, proportional to the current i, was measured at point 1. The potential φ of the indicator electrode In, relative to the unpolarized reference electrode Re was measured at the point 4. The values of di/dt and $d\varphi/dt$ were measured at the points 2 and 3, after the differentiating condensers.

Block II represents the scanning generator, and the point 5 is an electric parameter of time, t. The recording of any pair of these values could be achieved with any instrument which provided for the recording of electrical parameters as two coordinates (a cathode-ray tube or a quick-acting coordinatograph [22]). The instrument, block III, should have a high ohmic input. The values to be measured, from the points 1-5, were fed to the vertical v and horizontal h inputs. Between pulses (interval) the contact K, controlled from block I, short circuited the electrodes In and Co to depolarize them. A more detailed description of the apparatus and the recording of curves is given below.

Pulse Source (See Fig. 1, block I)

The 500 ohm potentiometer P (Fig. 2) fed sawtooth pulses to the source output (X, X). The potentiometer arm was rotated by a motor D and depressed the button K_1 after each rotation, thus activating the coil of relay M. The latter short circuited the electrodes by means of contact M_3, and switched in the time relay L by means of contact M_4. After time τ_1 (interval) the contact L_1 switched on the motor, the potentiometer arm released the switch K_1, and the system rotated to its original position.

To obtain square-wave pulses the motor D was switched off (switch K_2), the arm of the potentiometer P was placed in a given position, and the contact M_4 was short circuited (switch K_3). When the system was switched on, the relay M short circuited the electrodes (interval period) by means of the contacts M_1 and M_2, and the time relay L switched on the contact L_2 which, after a time τ_2, switched off the relay M and thus closed the polarization circuit. After a time τ_3 ($\tau_3 > \tau_2$), the contact L_3 switched off the relay L and restored the whole system to its original state. As a result the cell received square-wave pulses of duration $\tau_3 - \tau_2$ with intervals of τ_2 in between. Should the relay L be of low inertia, then, when the contact L_3 is switched on, it may activate the coil of L before the system has achieved its original state. It is recommended that an intermediate relay should be used to avoid this. The contact L_3 should be included in the circuit of the intermediate relay, and the normal interrupting contact of the intermediate relay should be included in the circuit of the relay L.

For the measurements we used an RPT-100 relay (M), an E-58 motor time relay (L), and an E-58 intermediate relay. The 1000 ohm resistance R_1 was included to shift the zero line of the pulse. The feed to the source (a, a) was either from a battery of storage cells (50-100 V), or from a rectifier, connected as a normal bridge circuit to four shunted diodes DG-Ts24 with a single unit filter.

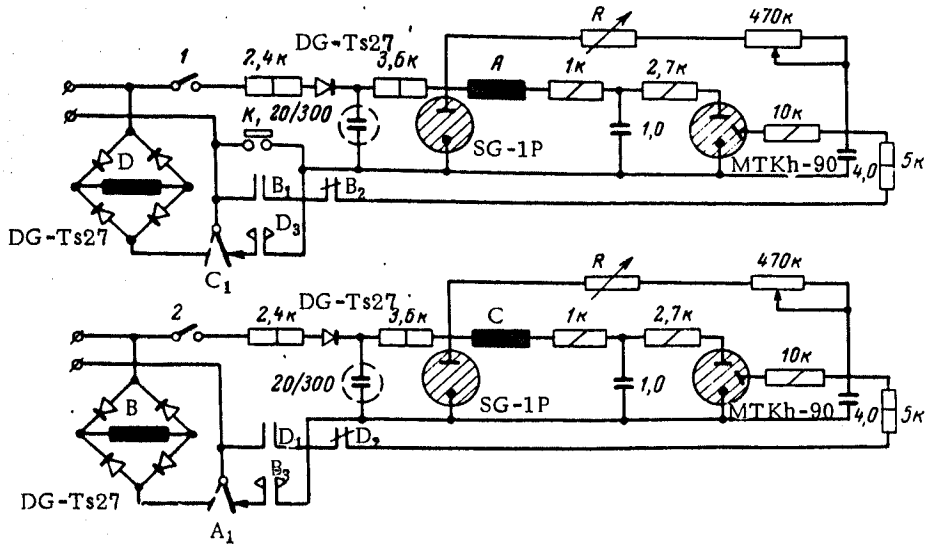

Fig. 3. Electronic time relay.

Besides the circuit shown in Fig. 2, we also used an electronic circuit which considerably reduced the size of the apparatus. This circuit (Fig. 3) operated with two RP-4 polarized relays (A and C) and two direct current telephone relays (b and D). Only half the circuit (relays A and B) was used to control the motor with the switch 2 closed. When the button K_1 was pressed the 1 μF condenser was charged up to the striking voltage of the stabilitron SG-1P. At the moment of striking a current pulse passed through the coil of relay A, and the contact A_1 engaged the left hand position and switched on the relay B. The contact B_1 then blocked the button K_1. The whole process took about 20 μsec.

When the contact B_1 operated, the 4.0 μF condenser began to charge up through the resistance R to the striking potential of the thyratron MTKh-90. The moment the thyratron struck a current pulse passed through the coil of relay A in the opposite direction. The contact A_1 switched over to the right hand position, the relay B was deenergized, and the instrument was ready for another cycle.

All four relays were used to obtain square-wave pulses. The operation was started by pushing the button K_1, as in the previous case, but, after the first cycle, the relay C was switched on by throwing over the contact A_1 to the right hand position. For this the contacts B_3 and D_3 had time delays on the opening side, achieved by a tighten-

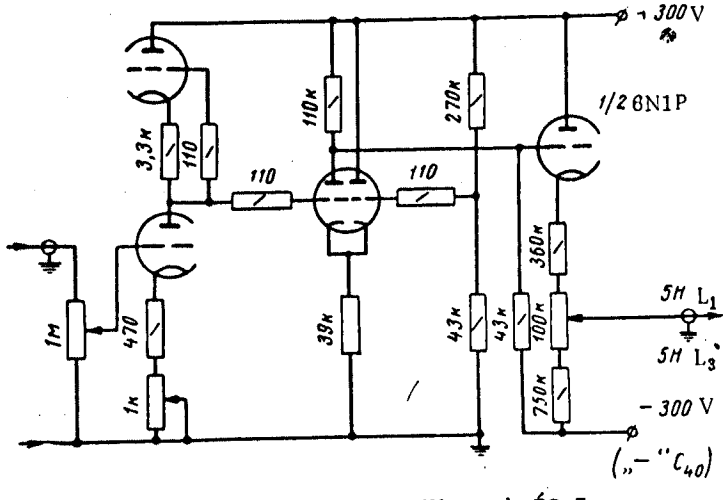

Fig. 4. Attachment to oscillograph ÉO-7.

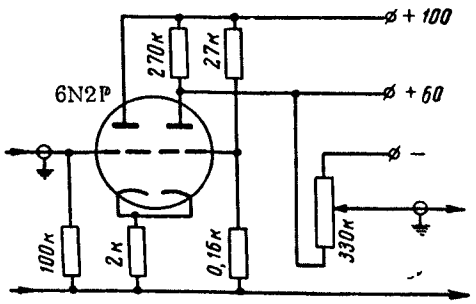

Fig. 5. Preamplifier.

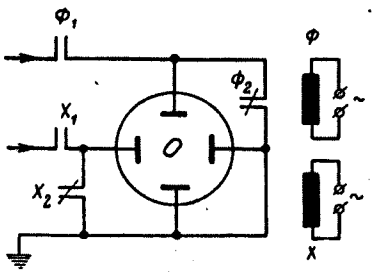

Fig. 6. Switching arrangement for input signals.

ing of the adjustment (slackening of the armature) of relays B and D at the expense of the currents closing through two successive arms of the feed bridge (DG-Ts24).

Both relays (A and C) could give a delay fo from 1 to 60 sec with switching after 0.5 sec (resistance R).

Registering Instrument (See Fig. 1, block III)

The most convenient registering instrument was an electron oscillograph, having a long persistence screen and direct current amplifiers to both inputs. Of normal instruments the oscillographs [23] L'vPI, ÉO-7, and ÉNO-1 can be recommended.

The L'vPI oscillograph, with direct current amplifiers to a sensitivity of 1 mV/mm in both inputs, could be used without any alterations. It was more convenient to replace the 13LO37 tube by the persistent tube 13LO36. This replacement was carried out without any other alterations.

The ÉO-7 oscillograph required two identical attachments, consisting of direct durrent amplifiers (Fig. 4) with transmission bands from 0 to 100 kc [24]. The amplification coefficient was about 300.

Optimum conditions for adjustment were achieved with a variable resistance of 1 kΩ in the cathode circuit of the first tube. The output tube of the amplifier was sealed on to the control grid of the 6P6 tube of the final stage of the ÉO-7 oscillograph amplifier. In the instruction booklet, and on the chassis of the ÉO-7 oscillograph (see Fig. 4), this tube is denoted as L_3 for the vertical amplifier and L_7 for the horizontal amplifier. The feeds to the attachments were provided from the oscillograph; inoperative connections were disconnected. The 13LO37 tube was replaced by a 13LO36.

For most of the measurements we used an ÉNO-1 oscillograph with a vertical amplifier of sensitivity 3 mv/mm and a band pass of 0-1 Mc. An exactly similar amplifier was fitted to the horizontal input so that two variables could be recorded. This was built on a separate chassis, housed in the same casing. The supply to the filament and anode circuits was at the expense of the feed to the sweep generator and internal amplifier of the horizontal movement, which was switched off when the extemal amplifier was switched on. This kept down the current in the windings of the power transformer and the temperature inside the oscillograph casing.

When working with the small differential signals, a direct current preamplifier (Fig. 5) was connected to the oscillograph input. This amplifier was fed from a BAS-G-80-U-2,1 (100-AMTsG-2-2,0) battery and the filament from a 6 V (5NKN-10) storage battery. The amplification coefficient was about 15. The signal to the oscillograph input was picked up after an auxiliary battery (point "60" of the same BAS battery), which compensated for the anode voltage on the stage output.

Sweep Generator (See Fig. 1, block II)

The appropriate section of the oscillograph was used as a sweep generator.

Coordinate Axes

For the measurements it was convenient to carry out simultaneous recording of the functions investigated and of the coordinate axes i, φ, or t. For this purpose (Fig. 6) the oscillograph inputs were switched to the signals investigated at a frequency of 100 cps and short circuited, by means of the contacts Φ_1, Φ_2, X_1, X_2, and the relays Φ and X. In this way three traces appeared on the screen, the relation to be investigated and the two coordinate axes. RSM-2

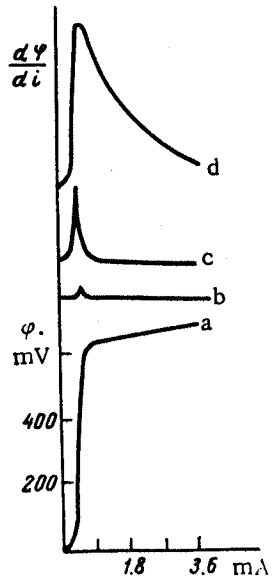

Fig. 7. a) Normal and b),c), d) differential polarograms of pure $PbCl_2$ at platinum electrodes (the cathode was a wire 10 mm long and 0.5 mm in diameter), at 600°C, with differentiating capacities of b) 0.1 μF, c) 2μF, and d) 25 μF.

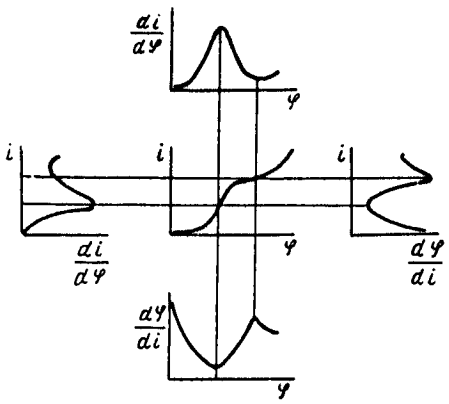

Fig. 8. Typical polarograms.

direct current relays, fed from a 24 V alternating supply, were used for the switching. In order that all three traces should be clearly seen on the screen, the current in the relay coils should be subjected to a phase shift, by including a condenser in one of the coil circuits, or should be of different frequency. For recording differential signals, the differentiating circuit should be inserted before the contacts Φ_1, Φ_2, X_1, X_2.

Recording of Curves

The curves could be recorded with any mirror camera, with a normal objective and adaptor lenses or connecting rings. A film of normal sensitivity was used; the exposure time was the time for recording the curve. It was desirable to reverse the film during development [25]. Use of a 13LO36 tube also made it possible to trace curves directly from the screen.

Differentiation of Curves

Differentiation of the values of i and φ was carried out by the differentiating circuit of the ÉNO-1 oscillograph, consisting of a 0.1 μF condenser and a 0.5 Mohm input resistance. This circuit was included by switching the operating conditions at the input (direct and alternating current). The shape of the curve obtained depended very much on the parameters of the differentiating circuit. Fig. 7 shows normal (φ, i) and differential (dφ/di, i) polarograms of fused lead chloride, using platinum electrodes, recorded with various differentiating capacities. Thus, the parameters of the differentiating circuit should be selected or calculated to suit the recording speed and the sensitivity and resistance of the input.

The pulse source operated continuously with a period of 10-30 sec. The persistence time of the screen was 1-2 min, and the curve investigated remained stationary on the screen for the whole of this time. The short polarization time of the electrodes ensured that the results were highly reproducible. The curves obtained, for various melts with solid electrodes, remained unchanged with continuous periodic recording over a period of several hours.

The low-frequency polaroscopic apparatus was shown to be suitable for various measurements.

Polarographic Investigations (Curves Recorded for i, φ; di/dφ, φ; di/dφ, i; dφ/di, φ; dφ/di, i).

Sawtoothed pulses were fed to the cell. Curves relating i and φ could be obtained at a given current or at a given voltage. The value of di/dφ was obtained at a given voltage (di/dφ ≈ di/dt), and the value of dφ/di at a given current (dφ/di ≈ dφ/dt). Fig. 8 shows some typical polarograms.

All our measurements were carried out at a given current. To carry out measurements at a given voltage it would have been necessary to use a potentiometer P (Fig. 2) of lower resistance (10-20 ohms).

In this way we used platinum electrodes to study the ions of Zn, Ni, Ag, Tl, Pb, Co, and Cd, with a fused mixture of KCl and NaCl as supporting electrolyte at 720°C. In all cases the wave height was found to be proportional to the concentration of depolarizer. The discharge potentials of the metals investigated agreed well with re-

sults obtained by normal polarography [27]. When the same material was investigated, the polaroscopic method was as sensitive [26] as the polarographic method [28], and also made it possible to observe more waves simultaneously.

By using a reference electrode of the metal investigated it was possible to estimate the reversibility of a process directly [29] by the wave shift from the potential of the quiescent metal.

Chronopotentiometric Measurements (Curves for φ, t; and $d\varphi/dt$, t)

Square-wave current pulses were fed to the cell. In this way the electrode was charged up from zero to the discharge potential of the depolarizer. Calculations based on the charging curves made it possible to calculate the capacity of the electrical double layer [30]. Depletion of the layer of electrolyte in the vicinity of the electrode produced a further charge on the electrode up to the potential of the supporting electrolyte. The depletion time of the layer of electrolyte round the electrode was determined by the diffusion coefficient of the depoloarizer [15] which could be deduced conveniently from the $d\varphi/dt$, t curve. In this way we determined diffusion coefficients for the ions of Pb, Zn, Ag, Ni, and Cd in fused KCl-NaCl [31].

Chronopotentiometric measurements can also be used for determining the rates of chemical reactions and the dissociation constants of complexes in melts.

Chronoamperometric Measurements (Curves for i, t)

Square-wave voltage pulses were applied to the cell. The current dropped from the pulse value to a steady value [32]. We used the curves for checking the applicability of the nonstationary diffusion equation [32] to melts [33]; they can also be used for studying reaction kinetics [34].

Use of the polaroscopic method is not restricted to the above [35]. Our investigations showed that low-frequency polaroscopy has the following advantages over normal polarography: high reporducibility without electrode renewal; high sensitivity; rapidity and ease of observation of polarization curves; the possibility of carrying out measurements relative to a nonpolarized reference electrode; a great variety in applications; the possibility of working with a given voltage; the simple way of obtaining differential curves (low capacity in the differentiating circuit); the possibility of observing phenomena not detectable by normal polarography.

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