

DETERMINATION OF RATE CONSTANT OF ELECTROCHEMICAL REACTION BY LINEAR POTENTIOSTATIC PULSE METHOD IN LOW CONDUCTIVITY MEDIA

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An analogue apparatus was proposed for polarization of an electrode with a linear potentiostatic pulse enabling to compensate the ohmic potential drop between the indicator and reference electrodes. The apparatus was used to determine the rate constant of the reaction $\text{Li}^+ + e + x \text{Hg} = \text{LiHg}_x$ in the medium of propylene carbonate.

In the usual method of measurement of the rate constant of an electrochemical reaction by the linear potentiostatic pulse method after Matsuda and Ayabe¹, a potential difference, E' , is applied between the indicator and reference electrodes changing linearly with time, and the dependence of current, I , on E' is recorded. However, the theory assumes that the potential drop in the double layer of the indicator electrode changes linearly with time and that the dependence of the current on voltage, E , is measured, where the latter is equal to the difference of potential drops in the double layers of both electrodes. The polarization of the reference electrode should remain constant. The rates of change of E and E' are interdependent:

$$|dE/dt| = |dE'/dt| (1 - R|dI/dE'|). \quad (1)$$

Here R denotes effective resistance of the electrolyte between both electrodes and t time.

As follows from Eq. (1), the time derivatives of E and E' can differ appreciably from each other even if the absolute value of the difference, $E - E'$, due to the ohmic potential drop in the electrolyte, is relatively small. Eq. (1) enables to decide whether the measured dependence of I on E' can be used in calculating the rate constant or the concentration of the electroactive substance. The proposed analogue circuit (Fig. 1) makes it possible to change the potential E linearly with time and to record the dependence of current on E . (The voltage measured against earth is denoted as U .)

EXPERIMENTAL

Analogue Apparatus

The source of linear pulses is an integrator (part A) fed with a constant voltage from a voltage divider R_1 which enables to change the integrated voltage and so the slope of the pulse in steps,

always doubling the preceding value. A ten- or hundred-fold change of the slope of the pulse is effected by changing the feedback capacity C_x .

The integrator is controlled by a couple of electronic relays Re_1 and Re_2 of own construction based on MOS integrated circuits of the type MP 19 A (A. S. Popov State Research Institute, Prague; channel p, threshold voltage -4 V, characteristic 2.5 mA/V). The relays can be used universally in summing junctions of analogue networks and can be controlled by Czechoslovak logic circuits of the type MH which is identical with the type SN manufactured by Texas Instruments (logic 1 higher than 2.4 V, logic 0 lower than 0.4 V). The relay (Fig. 2) is in the conductive

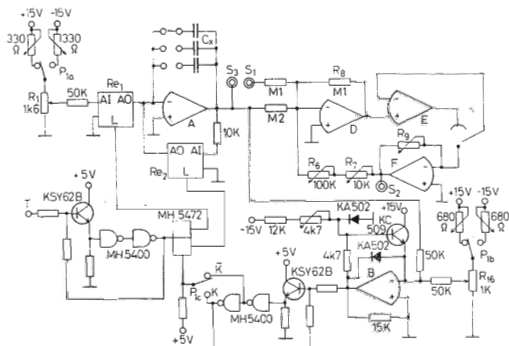


FIG. 1

Circuit for Polarizing the Electrode with a Linear Potentiostatic Pulse

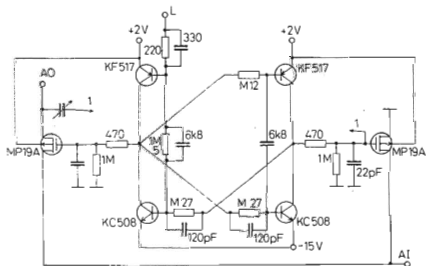


FIG. 2

Electronic Relay for Integrator Control

state (resistance smaller than $200\ \Omega$) if the voltage of logic 1 is fed to the logical input L. In the opposite case, it is in the nonconductive state and the analogue input AI is connected to the earth. Its switching time is smaller than $1\ \mu\text{s}$ and the charge passed during switching over to the analogue output AO is smaller than $100\ \text{pC}$.

The pulse amplitude can be changed continuously by a comparator (Fig. 1, part B). The reference voltage for the latter is taken from a helicoidal potentiometer R_{16} ("Aripot", Aritma, Prague) connected to a positive or negative voltage source by means of a change-over switch P_{1b} coupled with a change-over switch $P_{1a,c}$ serving to control the pulse polarity. If the sum of the reference and compared voltages is negative, the output of the comparator gives a voltage of logic 1 ($+5\ \text{V}$); if it is positive, the output gives a voltage of logic 0 (zero V). The output of the comparator is connected with a Schmitt circuit composed of a switching transistor and a couple of gates NAND (a part of a type MH 5400 logical circuit) which cancels noise in the region of switching of the comparator output and has two outputs. The voltage on the output K has the same logical value as that on the output of the comparator, the voltage on \bar{K} is its negation.

Integration is started by the falling edge of the clock pulse from an electronic stop watch. The pulse is shaped by the Schmitt circuit and fed to the clock input of a flip-flop circuit "master-slave" (type MH 5472) whose outputs control electronic relays. After a chosen amplitude is reached the integration is stopped by feeding the signal logic 0 to the reset input of the flip-flop circuit from the output K or \bar{K} according to the pulse polarity.

A linear pulse from the output of the integrator is fed to a summing circuit (part D), where it is summed with a constant voltage from a polarograph (fed to the socket S_1) and with the product of $(R_8/R_6 + R_7)$ times the output voltage of the current detector (part F) which is the product of R_9 times the current passing through the indicator electrode. The inverted signal from the summator is fed to the input of a potentiostat (part E) formed by an operating amplifier with MOS transistors on its inputs. The vertical input of an oscilloscope is connected to the socket S_2 , the horizontal one to S_3 .

The basic circuit used in measuring the effective resistance of the electrolyte between the indicator and reference electrodes is shown in Fig. 3. The method is based on measurement of the stepwise change of voltage between these electrodes due to the passage of a rectangular galvanostatic pulse. Relay Re_3 with an activation time smaller than $0.5\ \mu\text{s}$ serves as a source of voltage

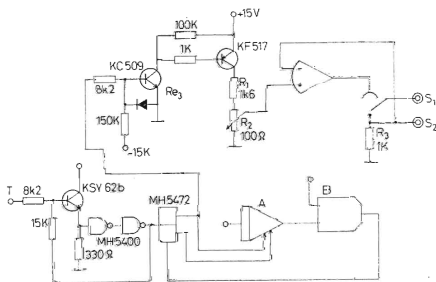


FIG. 3

Circuit for Measurement of Effective Electrolyte Resistance

for generating the pulse. This voltage is fed to divider R_1, R_2 and fixed by a potentiostat on resistance R_3 . Sockets S_1, S_2 are connected with differential inputs of an oscillograph. The relay is controlled by a flip-flop circuit "master-slave" MH 5742, to the clock input of which a starting clock pulse is fed, modified by a Schmitt circuit. The time of passage of the current through the electrode is equal to the time after which the output voltage from the integrator A attains the value preset on the comparator B. Both the integrator generating the linear pulse and the comparator are identical with the corresponding elements in Fig. 1. After the electrolyte resistance R is measured, the resistances R_6 and R_7 (Fig. 1) are set so that by leading the calibration current I into the current detector F (instead of the current from the indicator electrode) the voltage given by the potentiostat (part E) attains the value of IR . The apparatus was equipped with operating amplifiers Philbric Nexus PF 85 AU and Zeltex 134.

Other Apparatus and Chemicals

The rate constant of the reaction $\text{Li}^+ + e + x \text{Hg} = \text{LiHg}_x$ was measured in the medium of propylene carbonate containing $1\text{M}-(\text{C}_4\text{H}_9)_4\text{NClO}_4 + 4 \cdot 10^{-4}\text{M-Br}^-$; the concentration of Li^+ , c_{ox} , (as LiClO_4) was 4.6 and $8 \cdot 10^{-6} \text{ mol/cm}^3$. Tetrabutylammonium perchlorate was prepared by precipitating an aqueous solution of the iodide with perchloric acid, recrystallizing five times from 60% methanol, drying at 70°C in vacuum and then in an exsiccator with P_2O_5 . Lithium perchlorate was prepared by neutralization of the hydroxide with perchloric acid and drying at 220°C . Measurements were made on a dropping mercury electrode polarized by cathodic pulses of a slope of $4-1600 \text{ V/s}$ and on a hanging mercury drop at a rate of potential change of $6.6 \cdot 10^{-3} \text{ V/s}$. The drop was renewed after every pulse. To generate the pulse for hanging drop, the integrator was replaced by a polarograph; to record the curves, the oscillograph was replaced by a pen recorder of the type EZ 2 (Laboratorní přístroje, Prague). The electrolytic vessel is shown schematically in Fig. 4. The counterelectrode A and the reference electrode B were mercury; the potential of the latter was controlled by Br^- ions in the electrolyte. The starting potential was -1.2 V against the reference electrode B. The pulse was applied to the dropping

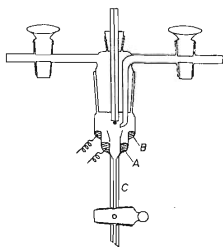


FIG. 4

Electrolytic Vessel

A Auxiliary electrode; B reference electrode; C measuring capillary.

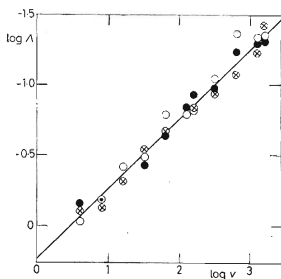


FIG. 5

Dependence of $\log A$ on $\log v$

$[v] = \text{V/s}$; conc. of Li^+ : \bullet $4 \cdot 10^{-6}$; \circ $6 \cdot 10^{-6}$; \otimes $8 \cdot 10^{-6} \text{ mol/cm}^3$.

electrode 10 s after breaking off of the preceding drop by a drop time controller. The surface area of the drop was calculated from the volume of a definite number of drops measured by a calibrated capillary C and was equal to $1.655 \cdot 10^{-2} \text{ cm}^2$ at the moment of measurement. The effective resistance of the electrolyte was 552Ω , mean rate of flow of mercury $2.734 \cdot 10^{-4} \text{ g/s}$; the surface area of the hanging drop $8.48 \cdot 10^{-2} \text{ cm}^2$ and effective electrolyte resistance 213Ω . The electrolyte was deaerated by argon. For every recorded current-voltage curve, the potentials E_K of the cathodic current peak and E_{KP} at which the current was one half as large were determined together with the absolute value of the cathodic peak current density, $|i_K|$ (Table I).

RESULTS

When a simple electrochemical reaction involving transfer of n electrons proceeds at the electrode and when the oxidized form of the electroactive substance is present in excess against the reduced one, the dependence of current density, i , on potential, E , during polarization with a linear cathodic potentiostatic pulse is given by

$$i(E) = -nFc_{ox}(nFvD_{ox}/RT)^{1/2} \Psi[nF(E_p - E)/RT], \quad (2)$$

where D_{ox} and c_{ox} denote diffusion coefficient and concentration of the oxidized form and E_p polarographic half-wave potential (reversible). The function Ψ is the solution of a Volterra integral equation and depends on two dimensionless parameters, α (cathodic transfer coefficient) and Λ defined as

$$\Lambda = k_s/(nFvD_{red}^\alpha D_{ox}^{1-\alpha}/RT)^{1/2}, \quad (3)$$

where k_s denotes reaction constant at standard potential and v absolute value of the rate of potential change. The function Ψ attains in the point X_K its maximum value Ψ_K corresponding to a cathodic current maximum (cathodic peak). Its coordinate and height for Λ increasing to infinity (reversible case) are further denoted as X_{KR} and Ψ_{KR} . The coordinate X_{KP} is defined by $\Psi(X_{KP}) = \frac{1}{2}\Psi_K$. The solution of the integral equation for various values of α and Λ gives $D_{KR} = X_K - X_{KR}$, $D_{KKP} = X_K - X_{KP}$, $Q_{KR} = \Psi_K/\Psi_{KR}$ as functions of α and Λ . The solution was found first by Matsuda and Ayabe¹, however, since their results were published only in the form of small diagrams we repeated their calculations. Our results are substantially in accord with the cited work¹ and will be published later. As follows from Eq. (2), the quantities D_{KR} , D_{KKP} and Q_{KR} can be calculated as

$$D_{KR} = (nF/RT)(E_{KR} - E_K), \quad D_{KKP} = (nF/RT)(E_{KP} - E_K), \quad (4), (5)$$

$$Q_{KR} = (i_K/i_{KR})(v_R/v)^{1/2}, \quad (6)$$

where E_K denotes potential of the cathodic maximum, E_{KR} same for the reversible case, E_{KP} potential at which the current, i , is one half of the cathodic current peak

TABLE I
Experimentally Found Values

v V/s	$ i_k $ mA/cm	$-E_K$ mV	$-E_{KP}$ mV	D_{KR}	D_{KKP}	Q_{KR}	$-\log A$			α	
							D_{KKP}	Q_{KR}	av.	D_{KKP}	Q_{KR}
$4 \cdot 10^{-6} \text{ mol/cm}^3$											
4	1.79	1 765	1 704	0.97	2.37	0.961	0.17	0.15	0.16	0.700	0.675
8	2.47	1 769	1 704	1.13	2.53	0.938	0.20	0.19	0.195	0.635	0.625
16	3.42	1 776	1 710	1.40	2.57	0.918	0.33	0.30	0.315	0.645	0.600
32	4.93	1 782	1 716	1.44	2.57	0.936	0.44	0.42	0.430	0.665	0.640
64	7.04	1 794	1 727	2.10	2.61	0.945	0.64	0.66	0.650	0.685	0.700
128	9.59	1 810	1 745	2.73	2.53	0.910	0.90	0.80	0.850	0.730	0.650
160	11.1	1 816	1 745	2.96	2.76	0.942	0.92	0.96	0.940	0.670	0.705
320	15.0	1 823	1 751	3.23	2.80	0.900	0.99	0.98	0.985	0.660	0.650
640	21.3	1 841	1 773	3.93	2.65	0.904	1.28	1.20	1.240	0.700	0.605
1 280	30.8	1 847	1 778	4.17	2.69	0.924	1.30	1.30	1.300	0.690	0.690
1 600	34.7	1 850	1 776	4.28	2.88	0.932	1.27	1.38	1.325	0.645	0.700
$6 \cdot 10^{-6} \text{ mol/cm}^3$											
4	2.80	1 761	1 698	0.82	2.45	0.961	0.01	0.04	0.035	0.610	0.650
8	3.94	1 767	1 705	1.05	2.41	0.956	0.20	0.18	0.190	0.700	0.670
16	5.57	1 780	1 716	1.56	2.49	0.956	0.42	0.43	0.425	0.685	0.700
32	7.62	1 786	1 718	1.79	2.65	0.925	0.49	0.50	0.495	0.645	0.650
64	11.0	1 807	1 735	2.61	2.80	0.943	0.77	0.82	0.795	0.655	0.700
128	15.0	1 808	1 739	2.65	2.69	0.910	0.81	0.78	0.795	0.675	0.650
160	16.6	1 812	1 741	2.80	2.76	0.900	0.84	0.81	0.825	0.660	0.635
320	23.5	1 826	1 759	3.34	2.61	0.902	1.08	1.01	1.045	0.695	0.650
640	34.4	1 843	1 780	4.01	2.45	0.933	1.43	1.30	1.365	0.765	0.700
1 280	46.9	1 850	1 781	4.28	2.69	0.900	1.37	1.30	1.335	0.695	0.655
1 600	52.3	1 856	1 782	4.52	2.88	0.897	1.35	1.35	1.350	0.650	0.650
$8 \cdot 10^{-6} \text{ mol/cm}^3$											
4	3.87	1 763	1 700	0.69	2.45	0.980	0.09	0.14	0.115	0.650	0.725
8	5.27	1 766	1 702	1.01	2.57	0.944	0.13	0.15	0.140	0.605	0.630
16	7.43	1 777	1 708	1.44	2.69	0.941	0.29	0.35	0.320	0.580	0.660
32	10.7	1 785	1 723	1.75	2.41	0.958	0.57	0.55	0.560	0.750	0.730
64	14.5	1 800	1 730	2.34	2.73	0.918	0.67	0.69	0.680	0.650	0.665
128	19.9	1 812	1 746	2.80	2.57	0.894	0.89	0.81	0.850	0.690	0.630
160	22.7	1 810	1 745	2.73	2.53	0.909	0.90	0.80	0.850	0.790	0.645
320	30.8	1 826	1 756	3.35	2.82	0.872	0.98	0.92	0.950	0.640	0.700
640	45.6	1 831	1 760	3.54	2.76	0.913	1.08	1.09	1.085	0.660	0.665
1 280	64.9	1 849	1 776	4.24	2.84	0.919	1.22	1.24	1.230	0.665	0.680
1 600	72.6	1 856	1 788	4.51	2.65	0.920	1.45	1.41	1.430	0.700	0.685

i_K , and i_{KR} value of i_K for the reversible case. The values of D_{KR} , D_{KKP} and Q_{KR} calculated for the measured current-voltage curves are in Table I. These quantities can be regarded as functions of α and A ; if they are kept constant and equal to their experimentally found values they define three implicit functions in α and A as variables. Diagrams of α against A corresponding to these three functions were constructed; the resulting curves should theoretically intersect in a single point giving the experimental values of α and A . To compensate for errors of measurement, the values of α and A were calculated from the intersections of the $\alpha - A$ functions corresponding to D_{KKP} and Q_{KR} with that corresponding to D_{KR} and their arithmetic mean values were taken (Table I). The average value of the transfer coefficient α was calculated as 0.668 (from all intersections). The experimental dependence of $\log A$ on $\log v$ is a straight line with a slope of 0.5 (Fig. 5); its intersection with the ordinate $\log v = 0$ enables to calculate the rate constant at standard potential from Eq. (3) as $k_s = 2.15 \cdot 10^{-2}$ cm/s. The value of $D_{ox} = 8.03 \cdot 10^{-7}$ cm²/s was determined from the peak current density at $6.66 \cdot 10^{-3}$ V/s (assuming reversible reaction course); the average from values found at different concentrations of Li⁺ was taken. The value of $D_{red} = 9.3 \cdot 10^{-6}$ cm²/s was found in the literature².

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