DETERMINATION OF THE RATE CONSTANT OF ELECTROCHEMICAL REACTION IN NONAQUEOUS MEDIUM BY THE POTENTIOSTATIC EQUILATERAL TRIANGLE PULSE METHOD

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The rate constant of the reaction $Li^+ + e + x\,Hg = LiHg_x$ in propylene carbonate was determined by the method of a single potentiostatic pulse in the form of an equilateral triangle. The determination was performed under exclusion of traces of water as well as with water additions, the influence of which on the accuracy of the determination and on the reaction kinetics was studied. To this purpose, a suitable analogue apparatus with compensation of the ohmic potential drop in the electrolyte was constructed. The triangular pulse method is more sensitive than the linear pulse method according to Matsuda.

We studied earlier[1] the automatic compensation of the ohmic potential drop in the electrolyte based on analogue circuits and determined the rate constant of the reaction $Li^+ + e + xHg = LiHg_x$ by the classical method of a linear potentiostatic pulse after Matsuda[3]. We derived also tables[2] for the determination of electrochemical rate constants by the method of a potentiostatic pulse in the form of an equilateral triangle, the practical application of which is the subject of the present work.

General Considerations

The characteristic parameters of current–voltage curves for an electrode polarized with a potentiostatic equilateral triangle pulse depend on the following dimensionless criteria (assuming a simple electrochemical reaction):

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

$$D_{2K} = nF(E_K - E_2)/RT \tag{2}$$

as well as on the transfer coefficient α. Here E_K denotes potential of the cathodic current peak, E_2 potential at which the rate of potential change dE/dt changes its sign, k_s electrochemical rate constant at standard potential, $v = |dE/dt|$; D_{ox} and

and D_{red} are diffusion coefficients of the oxidized and reduced forms. We assume that the electrode is polarized first cathodically and then anodically. The characteristic, experimentally accessible parameters of the current–voltage curves are:

$$D_{KR} = nF(E_{KR} - E_K)/RT, \qquad D_{AK} = nF(E_A - E_K)/RT, \qquad (3), (4)$$

$$D_{KKP} = nF(E_{KP} - E_K)/RT, \qquad Q_{KR} = (i_K/i_{KR})(v_R/v)^{1/2}, \qquad (5), (6)$$

$$Q_{AK} = i_A/|i_K|. \qquad (7)$$

Here E_A denotes potential of the anodic current peak, E_{KP} potential corresponding to one half of the rising portion of the cathodic peak, i_A anodic peak current density; i_{KR} and E_{KR} denote current density and potential of the cathodic peak corresponding to a low rate of potential change, v_R, at which the reaction is practically reversible. The dependence of the parameters (3)–(7) on the criteria α and Λ at constant $D_{2K} = 4$ was obtained by numerical solution[2] of the integral equation derived by Nicholson and Shain[4].

The determination of the rate constant is carried out with solutions containing only the oxidized form of the depolarizer, and the starting potential of the pulse must be sufficiently negative against the standard potential of the reaction. The rate constant can be calculated if any two parameters of (3)–(7) are found for one experimental current–voltage curve. Then two plots of α against Λ corresponding to the first and second chosen parameter, respectively, are constructed, their intersection giving the values of α and Λ corresponding to the experimental current–voltage curve. Finally, the rate constant is calculated from Eq. (1). The diffusion coefficient of the oxidized form can be calculated from the equation

$$\psi_K = |i_K|/nFc_{ox}(nFD_{ox}v/RT)^{1/2}, \qquad (8)$$

where ψ_K is a characteristic parameter tabulated[2] in dependence on α and Λ, and c_{ox} concentration of the oxidized form. The diffusion coefficient of the reduced form must be determined by an independent measurement.

The classical method after Matsuda is based on a study of the cathodic branch of the current–voltage curve and the electrode needs to be polarized only by a linear pulse. The calculation of the rate constant is based on the paremeter D_{KR} and either D_{KKP} or Q_{KR}. As follows from the definition of Q_{KR} and D_{KR}, the calculation of the rate constant is based either on two current–voltage curves, one of which is measured at a substantially lower rate of potential change than the other, or it is necessary to measure the standard potential of the reaction and both diffusion coefficients by other methods and the quantities E_{KR}, i_{KR} necessary for calculating the parameters D_{KR}, Q_{KR} must be calculated.

   With the triangular pulse method, the rate constant can be calculated from the anodic and cathodic branches of a single current–voltage curve. The parameters D_{AK} and Q_{AK} or D_{KKP} can be used for the evaluation. The dependences of D_{KR} and D_{AK} on α and log Λ are shown in Figs 1 and 2. To determine accurately the rate constant, the rate of potential change must be such that the derivative $\partial D_{KR}/\partial \log \Lambda$ or $\partial D_{AK}/\partial \log \Lambda$ is sufficiently large to match the resolving power of the oscilloscope. The first one increases with decreasing Λ to a certain constant limit corresponding to an "irreversible" reaction course; on the other hand it decreases with increasing α. The second one is practically independent of α, hence the triangular pulse method, in contrast to the Matsuda method, is practically equally sensitive for any value of α. It is obvious from Figs 1 and 2 that $\partial D_{AK}/\partial \log \Lambda$ is larger than $\partial D_{KR}/\partial \log \Lambda$ at the same value of Λ. Hence, the determination by the triangular pulse method is possible at lower rates of potential change, v, and the sensitivity is higher than with the Matsuda method (*cf.* the dependence of Λ on v, Eq. (*1*)).

   The dependences of Q_{KR} and Q_{AK} on α and log Λ are shown in Figs 3 and 4. The determination of α is with the use of Q_{KR} most accurate at small values of Λ, *i.e.* large v, where Q_{KR} does not depend any more on Λ and is proportional to $\sqrt{\alpha}$. Its relative change is proportional to the relative change of α:

$$\Delta Q_{KR}/Q_{KR} = (1/Q_{KR})\,(\partial Q_{KR}/\partial)\,\Delta\alpha = 0{\cdot}5\,\Delta\alpha/\alpha\,. \qquad (9)$$
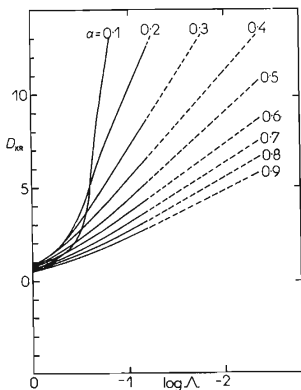
FIG. 1

Dependence of D_{KR} on α and log Λ
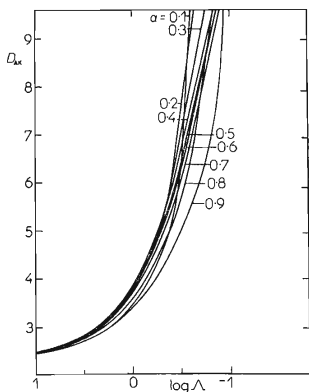
FIG. 2

Dependence of D_{AK} on α and log Λ

E.g., for $\alpha = 0.7$ and $\Delta\alpha = 0.1$ is $\Delta Q_{KR}/Q_{KR} = 0.0715$, *i.e.* the current must be measured with a higher accuracy than 7% if α has to be determined to within ± 0.1. From Fig. 4 it is possible to estimate the relative change of Q_{AK} due to a change of α, $\Delta Q_{AK}/Q_{AK} = (\partial \ln Q_{AK}/\partial\alpha) \Delta\alpha$ which in the range of Λ values suitable for measurement is little dependent on α and increases with decreasing Λ. Its value is always larger than the relative deviation of Q_{KR} at the same value of Λ. *E.g.*, for $\alpha = 0.7$, $\log \Lambda = -0.5$, $\Delta\alpha = 0.1$ is $\Delta Q_{AK}/Q_{AK} = 0.17$ which is larger than the value of Q_{KR}/Q_{KR} indicated above for the same α and $\Delta\alpha$ and for $\log \Lambda < -1$.

ELECTRICAL CIRCUIT

The circuit for polarization of an electrode with a pulse in the form of an equilateral triangle is shown in Fig. 5. The functions of the operational amplifiers are analogous as in the case of the circuit for polarization with a linear potentiostatic pulse[1]. A d.c. voltage component and a voltage proportional to the current passing through the electrode and measured in current detector F are added in adding circuit D to the voltage generated by integrator A. Amplifier E serves as potentiostat. Adjusting of positive feedback D, E, F, D was described previously[1]. The analogue part is supplemented by a two-bit memory Q_1, Q_2 consisting of Master-Slave flip-flop circuits. The dependence of the operation of the integrator on the memory content is as follows:

State	Q_1	Q_2	Integrator operation
0	0	0	generating negative pulse
1	1	0	—
2	0	1	generating positive pulse
3	1	1	zero output voltage

During generating a triangular pulse, the states 3, 0, 2, 3 follow one after another. A change of state 3 to 0 is achieved by feeding a clock pulse to the clock inputs of the flip-flop circuits. The clock pulse from an electric stop watch is shaped by Schmitt circuit S. A change from zero to 2 is achieved by feeding a logic 0 signal to the reset input of flip-flop circuit Q_2. This signal appears on the negated output of the comparator B_2 as soon as the absolute value of the voltage on the integrator output is equal to the voltage preset on helicoidal potentiometer P_2. The change of state 2 to 3 is accomplished by comparator B_1. Both comparators were described earlier[1]. The integrator is controlled by three electronic relays Re_1, Re_2, Re_3. Signals for their logical inputs are derived from the memory content. A signal for relay Re_2 is derived with the aid of a combination logical circuit from NAND gates. Relays Re_1 and Re_2 at a logic 1 signal on the logical input L_1 or L_2 connect voltage divider P_3 with a source of a positive or negative voltage of low output resistance. Silicon

transistors act as switching elements. Relay R_3 connects the analogue input with the analogue output if a logic 1 signal appears on the logical input; in the opposite case it connects the analogue input to the earth. Switching elements are MOS transistors with a P type channel (type MP 19A, A. S. Popov Research Institute, Prague).

EXPERIMENTAL

The reaction $Li^+ + e + x Hg = LiHg_x$ was studied in the medium of propylene carbonate containing $1M-(C_4H_9)_4NClO_4 + 4 . 10^{-4}M-Br^- + 8 . 10^{-3}M-Li^+$. Traces of water were eliminated as follows[5]: Propylene carbonate was dried for 48 hours by a molecular sieve of the type Potasit 3 (J. Dimitrov Chemical Works, Bratislava), whereby the content of water dropped to 15 p.p.m. The solvent was then transferred into an evacuated ampoule with an alloy of 65% K + + 35% Na and after 10 days distilled off in a closed evacuated system. Weighed amounts of salts dried in an exsiccator over P_2O_5 were further dried under high vacuum (10^{-6} Torr) at 75°C for 24 hours, the distilled propylene carbonate added and the solution transferred into the electrolytic vessel. The access of air was prevented and all vessels were predried under high vacuum. Electrolyses were performed on a dropping mercury electrode in an atmosphere of argon dried and deoxygenated with the K–Na alloy[5].

Potentiostatic pulses in the form of an equilateral triangle were applied to the electrode 20 or 10 s after breaking off of the preceding drop by a drop time controller. The capillary of an inner diameter of 0·1 mm was drawn out so that the rate of flow of mercury was $1·7—2·3 . 10^{-4}$ g/s. The electrolyte resistance between the indicator and reference electrode was about 500 Ω. A mercury pool in the electrolytic vessel served as a reference electrode; its potential was con-
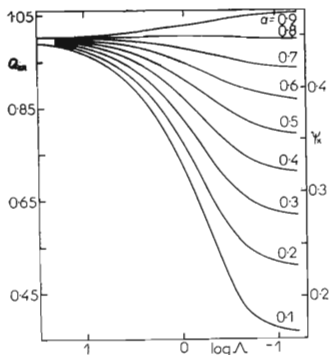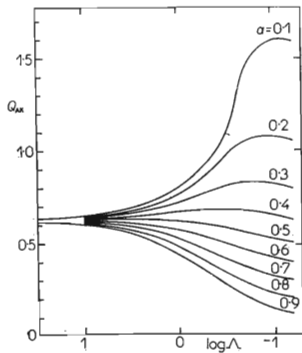

FIG. 3

Dependence of Q_{KR} on α and $\log \Lambda$

FIG. 4

Dependence of Q_{AK} on α and $\log \Lambda$

trolled by Br^- ions in solution. Another mercury pool served as a counter-electrode. The mercury reservoir, capillary and mercury were dried under high vacuum prior to use. Some measurements were performed in solutions containing a defined concentration of water added by means of
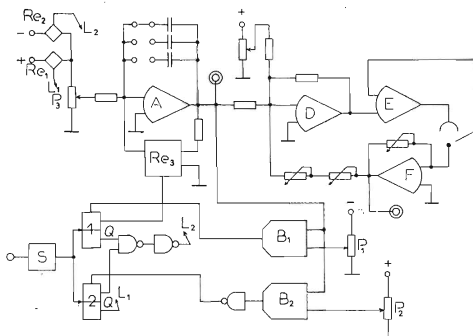

Fig. 5

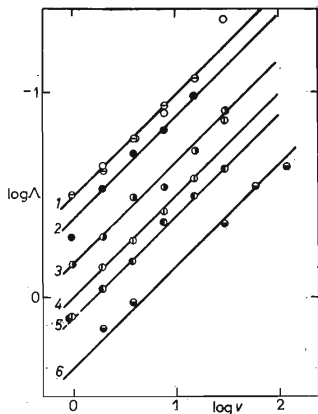Circuit for Polarization of Electrode with Equilateral Triangular Pulse

Fig. 6

Dependences of $\log \Lambda$ on $\log v$

Concentration of water (p.p.m.): *1* "0" (no H_2O added); *2* 215; *3* 645; *4* 1075; *5* 1505, *6* 1935.

a micropipette. Always several pulses with different rates of potential change were applied to the electrode in the same solution. The rates of potential change were 1—32 V/s in solutions without water and up to 128 V/s in solutions with water additions. The temperature of measurement was 25°C.

RESULTS AND DISCUSSION

For every oscillographic current–voltage curve the parameters D_{AK}, D_{KKP} and Q_{AK} (Eqs (4), (5) and (7)) were calculated. Further, plots of α against Λ corresponding to these parameter values were constructed for every curve, and the intersections of the curve $D_{AK}(\alpha, \Lambda) = (D_{AK})_{exper.}$ with $D_{KKP}(\alpha, \Lambda) = (D_{KKP})_{exper.}$ and $Q_{AK}(\alpha, \Lambda) = (Q_{AK})_{exper.}$ were found. Thus, the values of α an Λ for every current–voltage curve were determined. For solutions without water, the plots of α against Λ for D_{AK}, D_{KKP} and Q_{AK} intersected approximately in a single point. For other solutions, the values of α and Λ were calculated as average from two intersections. Afterwards, the value of ψ_K was found in tables[2] for every curve and the value of D_{ox} calculated from Eq. (8). The values of α and D_{ox} found at different rates of potential change were averaged for every electrolyte composition. The deviations were within ± 0.07 from the average for α and within $\pm 3 . 10^{-7}$ for D_{ox}. The results are summarized in Table I. With water-containing electrolytes, the deviations were larger than without water. The dependences of $\log \Lambda$ on $\log v$ (Fig. 6) are practically linear with a slope of -0.5. From their intersections with the $\log \Lambda$ axis, the rate constants of the reaction $Li^+ + e + x\, Hg = LiHg_x$ in electrolytes with various concentrations of water were calculated by Eq. (1) (Table I). The value of $D_{red} = 9.3 . 10^{-6}$ cm^2/s was taken from ref.[6].

TABLE I

Parameters of Reaction $Li^+ + e + x\, Hg = LiHg_x$ in Propylene Carbonate with Different Water Content

p.p.m. H$_2$O	$k_s . 10^2$ cm/s	α	$D_{ox} . 10^6$ cm^2/s
0	0·512	0·74	1·065[a]
0	0·480	0·75	1·029
215	0·625	0·76	1·012
645	0·948	0·82	1·003
1 075	1·606	0·82	1·003
1 505	2·202	0·80	1·004
1 935	3·00	0·69	0·805

[a] Drop time 10 s; in other cases 20 s.

The rate constant (Table I) increases with increasing concentration of water. This can be seen also from the current–voltage curves. In the absence of water, the curves show a relatively flat anodic peak, the potential of which is considerably different from the cathodic one. In the presence of water, the curves show much higher anodic peaks situated more closely to the cathodic ones. The differences in their cathodic branches are less conspicuous as a result of a relatively large transfer coefficient α. Since it is known from impedance measurements[7] that the structure of the double layer on mercury in the medium of propylene carbonate does not change appreciably with addition of water, the mentioned changes of the rate constant cannot be attributed to changes of ψ potential but rather to the formation of active complexes with the participation of a water molecule. Larger deviations of the current–voltage curves from their theoretical course in the presence of water can be attributed to complication of the electrochemical reaction by chemical reactions due to hydration of Li^+ ions. Based on the hydration constants[8], we calculated the fraction of hydrated Li^+ ions in the solutions used and found it to be less than 10% at water concentrations up to 500 p.p.m. The value of the rate constant found earlier[1] was higher than that in the present work in the absence of water since in the cited work no severe precautions for obtaining and maintaining a highly water-free medium were observed.

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