REACTOR WITH PULSE CONVECTION FOR FOLLOWING THE OXIDATION-REDUCTION REACTION KINETICS BY THE STOP-FLOW METHOD USING A SOLID INDICATOR ELECTRODE*

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A reactor for kinetic studies is described making use of the dependence of the nonequilibrium potential of a platinum electrode on time in the stop-flow method. For the model reactions, $Sn(II) + 2 Fe(III) = Sn(IV) + 2 Fe(II)$, $Sn(II) + 2 Ce(IV) = Sn(IV) + 2 Ce(III)$ and $V(IV) + Ce(IV) = V(V) + Ce(III)$ the following values were found at 20°C: $k_{V/Ce} = 959_M^{-1} s^{-1}$, $k_{Sn/Ce} = 18_M^{-1} s^{-1}$ in 2_N-H_2SO_4 and $k_{Sn/Fe} = 23_M^{-1} s^{-1}$ in 2.5_N-HCl. These values are in accord with the spectrophotometric data found in the literature as well as in the present work.

The preceding communication[1] dealt with results obtained from the study of potential–time (E–t) curves at zero current on a dropping mercury electrode during studies of oxidation–reduction reactions by the stop-flow method. Since the solution is stirred during the reaction by the periodically dropping mercury and the surface concentrations of the reactants are thus equalized with those in the bulk, the flow reactor is in this case very simple. However, the mercury electrode cannot be used in such cases where the oxidation agent reacts with mercury.

When a platinum electrode is used, the stop-flow method requires a modification of the reactor enabling a periodical motion of the liquid relative to the electrode so that the surface concentrations of the reactants might be equalized with those in the bulk. The description of such a reactor, its use in following the kinetics of oxidation–reduction reactions by the stop-flow method with a platinum electrode, and verification of the method of measurement[2,3] of the rate constant of a homogeneous red-ox reaction even in cases where the electrode does not behave ideally[3] form the subject of the present work.

EXPERIMENTAL

Chemicals

Iron(III) chloride of reagent grade (Lachema, Brno) in a concentration of approximately 0.1_M was dissolved in 2.5_M-HCl and its concentration was determined titanometrically with the use

of a potentiometric indication[4]. Tin(II) chloride (Polskie Odczyniki chem. Glivice) was dissolved also in 2·5M-HCl and determined potentiometrically with a solution of iron(III) chloride[4]. Its 0·2M solution was kept in an atmosphere of argon. Tin(II) sulphate was prepared by precipitating a saturated solution of tin(II) chloride in acetone with sulphuric acid; its 0·1M solution in 2N--H_2SO_4 was kept in an argon atmosphere and its concentration determined cerimetrically[4]. A solution of 0·1N-$Ce(SO_4)_2$ of reagent grade (Lachema, Brno) in 2N-H_2SO_4 was standardized potentiometrically with the use of Mohr salt. A solution of approximately 0·4N-$VOSO_4$ in sulphuric acid was prepared according to ref.[1].

Apparatus

Electrochemical measurement. The reactor was constructed as a five-way stopcock (Fig. 1) of dimensions $1·5 \times 5 \times 6$ cm machined from plexiglass. The inner diameter of the channels was 0·2 cm. It was provided with inlets of reaction components 1 and 2, a mixing compartment 3 from which the reaction mixture flowed into the indicator electrode compartment 4, then through the outlet 5, T-shaped tube with a side-arm for reference electrode 11, rubber joint 9 provided with arms of a clamp stirrer 10, to the inlet 7 and outlet 6. After stopping the flow, the reaction mixture continued to travel from the mixing compartment 3 directly to the outlet 8 while in the compartments 4—7, 9 and 11 a reaction took place under pulse stirring with the clamp 10, and the resulting changes of the electromotive force were measured with the electrodes 4 and 11. This design eliminates the inertia of the feeder during stopping the flow and enables to measure during the flow as well as when the flow is stopped, stirring of the reaction mixture relative to the electrode being very important in the latter case. After stopping the flow by turning the lever P and closing the joints 7—6 and 3—4, the compartment 4—6 (as well as 3—8 for free outflow of the pressed-in mixture) is united so that the reaction mixture can pulse freely against air or inert atmosphere (through the opening 6) after every pressing and loosening of the flexible tube by the clamp stirrer arms, one of which is stationary and the other movable by a revolving hexagonal cam mounted on the shaft of a motor. The *E–t* curves recorded at 3·2 and 4·8 pulsations/s were identical, an evidence that the pulse frequency was sufficiently high. Since the indicator electrode in the compartment 4 must be mounted hermetically and pressure-resistantly, a rotating or vibrating platinum electrode could not be used. The feeder with tempered 20 ml syringes had a linear shifting rate of 2·55 mm/s. The experimental set-up was similar as shown in Fig. 1 in the preceding
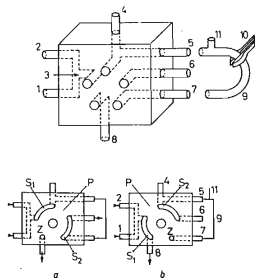

Fig. 1

Scheme of Reactor

P Switching lever; S_1, S_2 connecting channels in the body of the stopcock; Z place in the body of the stopcock closed by turning; *a* position during flow; *b* position after stopping the flow. See text for meaning of numbers.

communication[1] except that the whole reactor was dipped into a vessel filled with flowing water from a thermostat.
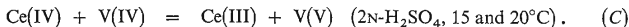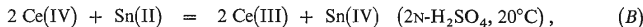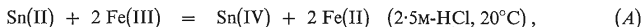
The indicator electrode was made from a platinum wire 0·2 mm in thickness and 3 mm in length, cemented in a plexiglass cylinder provided with a thread and screwed tightly in the orifice at 4. A saturated mercurous sulphate reference electrode with a salt bridge 11 was used when the reaction medium was H_2SO_4, and a saturated calomel one with a bridge when the medium was aqueous HCl. The electromotive force was fed through a high-resistance voltage divider ($R_1 = 10^7$ ohm, $R_2 = 10^4$ ohm) to an EZ 2 type pen-recorder whose polarographic filter was switched off. During the measurement, solutions of the reaction components were pressed into the mixing compartment 3 while the pen-recorder was in action. After turning the lever P the flow was stopped and the potential–time curve of the studied reaction recorded. Since the indicator electrode was placed closely to the point where mixing took place, the moment of stopping the flow was considered to be the beginning of the time scale. Changes of the ratio n = $[Ox_2(t = 0)]/[Red_1 . (t = 0)]$ were accomplished by diluting the starting solution of one of the components in the reserve vessel (2 or 3, Fig. 1 in ref.[1]) with the reaction medium from the reservoir. All solutions were kept in argon atmosphere.

The rate constant of the homogeneous red-ox reaction was determined from a set of E–t curves by plotting $t(1 - n')$ against log n' ($n' = nz_2/z_1$ as in ref.[5], z_1 and z_2 are stoichiometric coefficients of the reaction z_2 Red_1 + z_1 $Ox_2 = z_2$ Ox_1 + z_1 Red_2) determined from the intersections of the horizontal line E = const. with the set of E–t curves. The obtained dependence was then linearized by the methods described earlier[2,3] and from its slope the rate constant was calculated.

Spectrophotometrical measurements were carried out with the light ray parallel to the direction of flow both during flow and after stopping it. The apparatus and method of measurement will be described in a later communication[6].

RESULTS AND DISCUSSION

The following reactions were studied by the stop-flow method with the use of E–t curves in the current-less state:

$$Sn(II) + 2 Fe(III) = Sn(IV) + 2 Fe(II) \quad (2\cdot5\text{M-HCl, } 20°C), \qquad (A)$$

$$2 Ce(IV) + Sn(II) = 2 Ce(III) + Sn(IV) \quad (2\text{N-}H_2SO_4, 20°C), \qquad (B)$$

$$Ce(IV) + V(IV) = Ce(III) + V(V) \quad (2\text{N-}H_2SO_4, 15 \text{ and } 20°C). \qquad (C)$$

The obtained rate constants were compared with published data; in the case of the last reaction they were also checked by spectrophotometry. With reactions A and B, the platinum indicator electrode behaved as an ideal one (in the sense of ref.[2]) and the rate constant was determined from the slope of the linear dependence[2] of $t(1 - n')$ on $\mathfrak{z}$. In the case of reaction C, the properties of the platinum electrode depended on the parameter n as followed from the nonlinear dependence of $t(1 - n')$ on $\mathfrak{z}$, therefore a procedure valid for nonideal electrodes was used[3].

For illustration, a set of E–t curves for the reaction A and its evaluation based on the plot of $t(1 - n')$ against log n' and its linearization in the coordinates $t(1 - n')$, $\mathfrak{z}$ is shown in Fig. 2 as an example of an ideal behaviour of the platinum electrode. (Decadic logarithms were used.) This set of curves was recorded at constant concentration of the oxidized form, i.e. $[Fe^{3+}] = 8 \cdot 10^{-3}$M, and variable initial concentration of the reduced form (Sn^{2+}), therefore in this case the parameter n' was given by the ratio of $[Sn^{2+}(t = 0)]/[Fe^{3+}(t = 0)]$ and was in the range from 0.081 to 4.73 (Fig. 2). Two lines parallel to the potential axis were chosen on levels I and II denoted by arrows. From their intersection with the E–t curves the values of n' and t were determined, and the quantity $t(1 - n')$ was plotted as a function of log n' (open points) and as a function of $\mathfrak{z}$ log e (full points). The quantity $\mathfrak{z}$ was defined in ref.[2], Eq. $(2c_1)$. To simplify the calculation of $\mathfrak{z}$, only values of n' that could be expressed exactly to one decimal place were selected on the plots of $t(1 - n')$ against log n' when these dependences were linearized. Only the first eleven curves were evaluated, others lay below the level II.

The results for the reaction C are shown in Fig. 3 together with linearized beak-shaped plots of $t(1 - n')$ against $\mathfrak{z}$ (characteristic for a nonideal behaviour of the platinum electrode). Their linearization is based on the ratio of the slopes of both branches in the coordinates $(1 - n')\,t$, $\mathfrak{z}(nonid)$ (we used decadic logarithms, therefore the quantities $\mathfrak{z}$ log e and $\mathfrak{z}(nonid)$ log e were plotted). The E–t curves were recorded at constant concentration of the reduced form, i.e. $[VO^{2+}(t = 0)] = 9.114$. 10^{-4}M, and variable concentration of the oxidized form (Ce^{4+}) so that the para-

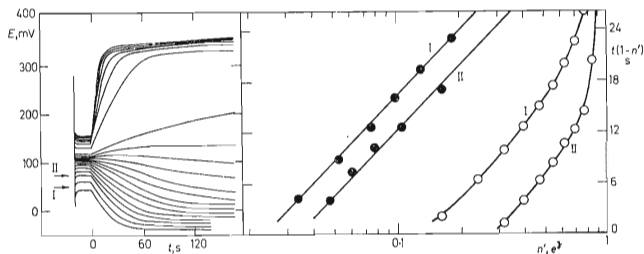
FIG. 2

Set of E–t Curves for Reduction of Fe^{3+} with Sn^{2+} Ions and its Evaluation

Values of n' beginning from the lowest E–t curve: 0.081, 0.161, 0.240, 0.318, 0.394, 0.470, 0.545, 0.619, 0.693, 0.765, 0.836, 0.907, 0.978, 1.045, 1.851, 2.586, 3.226, 3.788, 4.286, and 4.730. 2N-H_2SO_4 at 20°C. The abscissa is common for log n' and $\mathfrak{z}$ log e; a logarithmic scale was used.

meter $n' = [Ce^{4+}(t = 0)]/[VO^{2+}(t = 0)]$ was in the range from 0·046 to 1·118 (Fig. 3). Again two lines parallel with the E axis, I and II, were drawn on the diagram. The corresponding plots of $t(1 - n')$ against $\log n'$ are denoted by open points; joined by dashed lines show the dependences of $t(1 - n')$ on $\mathfrak{z} \log e$ with two branches forming a beak. Their linearization using the coordinate $\mathfrak{z}(\text{nonid}) \log e$ is denoted by full points. Only such values of n' that could be expressed correctly to one decimal place were chosen on the plots of $t(1 - n')$ against $\log n'$ to simplify the calculations of $\mathfrak{z}$ and $\mathfrak{z}(\text{nonid})$, and only the first twelve curves were evaluated.

With all three reactions, sets of E–t curves were recorded both at increasing and decreasing parameter n; the results were independent of the history of the electrode. The reactions were followed in such a concentration range that the product $[\text{Red}(t = = 0)] k$ was in the interval 0·1—0·8. The rate constants of the reactions A and C do not depend on dilution but with the reaction B there is a slight dependence (see below) suggesting that the simultaneous presence of Sn^{2+} and SO_4^{2-} ions is responsible for this effect, the other reaction component (Ce^{4+}) playing no role. The results are summarized as follows (with standard deviation δ):

The initial concentrations were in the range: Fe(III) (reaction A) $4 . 10^{-3} - 3.2 .$ $. 10^{-2}$M, Sn(II) (reaction B) $1 \cdot 4 . 10^{-3} - 1 \cdot 7 . 10^{-2}$M (in this case there was a slight dependence of k on concentration expressed empirically as k ($M^{-1} s^{-1}$) $= 23 \cdot 7 - - 447 \cdot C$), V(IV) (reaction C) $2 \cdot 7 . 10^{-4} - 9 . 10^{-4}$M. Brubacker[9] found for the reaction B at 20°C $53 \cdot 3 M^{-1} s^{-1}$, a value apparently too high, whereas the reported activation energy, $7 \cdot 6$ kcal/mol, appears too low with respect to ref.[5] and the present
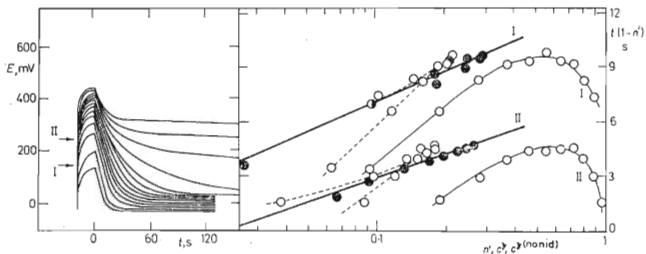

FIG. 3

Set of E–t Curves for Oxidation of VO^{2+} with Ce^{4+} Ions and its Evaluation

Values of n' beginning from the lowest E–t curve: 0·046, 0·093, 0·187, 0·278, 0·368, 0·457, 0·544, 0·629, 0·713, 0·769, 0·878, 0·959, 1·040, 1·118. 2N-H_2SO_4 at 20°C. The abscissa is common for $\log n'$, $\mathfrak{z} \log e$ and $\mathfrak{z}(\text{nonid}) \log e$; a logarithmic scale was used.

Reaction	$k_{20°} \pm \delta$, M^{-1} s^{-1}		
	E–t curves	spectroph. (lit.)	spectroph. (this work)
A	$23·4 \pm 0·2$	$23·5 \pm 0·8$ (ref.[5])	—
B	$18·0 \pm 0·7$	$18·3 \pm 1·4$ (ref.[5])	—
C	959 ± 40	815 ± 9 (ref.[7])	814 ± 19 (during flow)
C		957 ± 70 (ref.[8])	812 ± 34 (stopped flow)

work. Remick[10] studied the same reaction, but limited himself only to qualitative conclusions.

It follows from our results that the stop-flow method can be used safely during recording E–t curves with a platinum indicator electrode in the proposed reactor with pulse stirring to determine the rate constants of oxidation–reduction reactions reaching values of the order of 10^3M^{-1} s^{-1} regardless of whether the platinum electrode behaves ideally or reacts with one of the reaction components. At the same time, our results serve as a verification of the procedures for determining the rate constants of such reactions on the basis of the complete equations of the E–t curves derived in our previous communications for an ideal as well as for an nonideal electrode.

REFERENCES

1. Tockstein A., Skopal F.: This Journal, in press.
2. Tockstein A., Skopal F.: This Journal 39, 1518 (1974).
3. Tockstein A., Skopal F.: This Journal 39, 3016 (1974).
4. Čihalík J.: Potenciometrie. Academia, Prague 1961.
5. Tockstein A., Jaroš F.: This Journal 35, 2523 (1970).
6. Tockstein A., Skopal F.: Unpublished results.
7. Tockstein A., Matušek M.: This Journal 34, 27 (1969).
8. Rechnitz G. A., Rao G. R.: Anal. Chem. 39, 1192 (1967).
9. Brubacker C. H., Court A. J.: J. Am. Chem. Soc. 78, 5530 (1956).
10. Remick A. E.: J. Chem. Soc. 69, 94 (1947).

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