

THE USE OF ROTATING DISC ELECTRODES FOR THE STUDY OF THE KINETICS OF SORPTION PROCESSES ION-EXCHANGE OF IRON III ON DOWEX 50W X8 IN ACID MEDIA

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Dedicated to honour the memory of Professor J. Hanuš on the occasion of the centenary of his birthday.

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It has been found that both film and gel kinetics can be operative according to experimental conditions. Exchange rate constants and the activation energy for the film kinetic process have been calculated. The method seems well suited for following sorption kinetics.

Generally, the study of the kinetics of chemical or physico-chemical processes in solution depends on following the time-dependent concentration of one of the reactant or product species. Most methods employed for this purpose (*e.g.* spectrophotometry) are severely hindered by the presence of a suspended phase and thus can only be used for those sorption processes which proceed sufficiently slowly for sampling techniques. An exception is the high frequency conductometric method used by Eliášek and Talášek¹, which measured the hydrogen or hydroxide ions released from catex or anex resp. The accuracy of such a method cannot be expected to be very great in work with acidic or basic solutions. The rotated disk method proposed by Vydra² would seem to be particularly well suited for this purpose. It measures directly the concentration of one of the reacting species (*e.g.* the cation exchanged), and thus does not depend on the mechanistic assumptions implied in the measurement of hydrogen ion concentration. It can be used for studying the sorption of electroactive species, the voltammetry of which is well characterized in the medium to be employed. The results are unaffected by the presence of a solid phase.

The voltammetry of iron(III) in perchloric acid has been studied at the rotated glassy carbon disk electrode³, and the waves have been found to be near-reversible. (Apparent standard rate constants are greater than 10^{-2} cm/s). Thus the current at sufficient overpotentials will be diffusion controlled and its value will respond rapidly to changes in the iron (III) concentration. Further it has been found that the current at a given potential decreases only slightly and linearly with time.

EXPERIMENTAL

Reagents and Apparatus

The iron solutions used were prepared from Merck pure $\text{Fe}_2(\text{SO}_4)_3$ and were standardized by EDTA titration. All other solutions were prepared from reagent grade chemicals. The catex used was Dowex 50W X8, 50/100 mesh, H + cycle (The Dow Chemical Co., U.S.A.) (Grain radius centres around $1.1 \cdot 10^{-2}$ cm).

The rotated disk electrode was a glassy carbon rod G. C. 20, (Tokay Electrode Manuf. Co., Japan) 3 mm in diameter, fixed into a Teflon tube 15 mm in diameter. The electrode rotation apparatus was designed in the workshops of the Polarographic Institute. The electrode was rotated at 2800 r.p.m., as measured with the Hand-Tachometer H 6, (VEB Meßgerätewerk, G.D.R.). Current and potential measurements were made on the Polarograph OH 102 (Radelkis, Hungary) with *I.R* compensation using a platinum plate 54 mm² in area as a counter electrode, and with a saturated calomel reference electrode. The inherent error in current measurements is 1%.

Before each measurement, the electrode surface was polished using metallographic papers 2/0 and 5/0 (SIA, Switzerland). For temperature studies, a thermostated voltammetric cell was used, in conjunction with the constant temperature bath type WHM 100/50-6311/8 (VEB Elektromotorenwerke, G.D.R.). The solutions were magnetically stirred using the stirrer "LM II" (Dioptra, Czechoslovakia).

Procedure

The electrolyte was first deaerated with purified nitrogen. Then the voltammetric curve was recorded from +0.70 to 0 volts, the potential scan-recorder gears were decoupled, and the current-time curve at 0 volts was recorded, using a chart speed of 0.5 cm/s. After an appropriate time, usually about 30 s, during which a linear current-time dependence was established, a Dowex 50W X8 suspension was added all at once through a wide neck funnel, the tip of which was suspended over the surface of the solution. The solution was continuously stirred by the rotation of the electrode and by the magnetic stirrer, the bar of which was placed sufficiently far from the electrode surface to prevent interference of the magnetic field with the electrode polarization (about 2–3 cm). After the current had dropped to less than one half the original value, the current base line

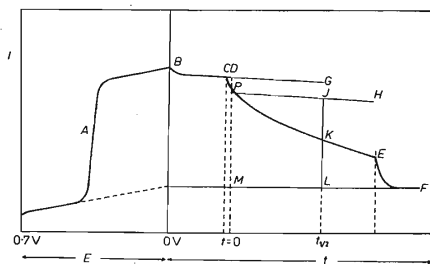


FIG. 1

Schematic Representation of Experimental Curves

A Reduction wave of iron (III); B potential scan-chart gears decoupled; B—C current-time variation at constant potential (0V vs SCE); C—D adsorbent added in suspension; C—D adsorbent addition time (~ 1 s). Current drop corresponds to electrolyte dilution by adsorbent suspension; P—E current drop due to adsorption of iron(III); E addition of reducing or complex agent; F base line ($I = 0$); D—G parallel to pH; J—K = K—L; K corresponds to $t_{1/2}$; P—M corresponds to $[\text{Fe}^{3+}]_{t=0}$.

was determined by adding a complexing (EDTA) or reducing (ascorbic acid) agent for iron(III), depending on the pH. Fig. 1 shows schematically the appearance of the resulting curve. When required, both the electrolyte solution and the Dowex suspension were prethermostated. The temperature was, in all cases, measured both before and after the experimental procedure. The amount of Dowex added was measured as the underwater volume, and was then suspended by vigorous shaking in 10 ml of the base electrolyte (e.g. 0.1M-HClO₄). All measurements were performed in triplicate.

RESULTS AND DISCUSSION

The rate of the exchange process was followed at various concentrations of iron(III) and using various volumes of Dowex 50WX8 from 2 to 8 cm³ (total electrolyte volume = 100 ml before addition of Dowex). The variation of exchange half-times is shown in Fig. 2. At sufficiently high concentrations of Dowex (i.e. when the concentration of iron(III) is well below the catex capacity), $t_{1/2}$ is independent of the concentration of both Dowex and iron(III).

According to Helfferich⁴, gel kinetics is the rate controlling process at low concentrations of adsorbent, high concentrations of adsorbate, and with fast stirring. With higher concentrations of adsorbent, low concentrations of adsorbate, and slow stirring, film kinetics become the controlling factor. The rate of stirring was intermediate, and thus the other two factors will determine the type of kinetics observed, all other factors being constant. Helfferich⁴ gives the relation between the instantaneous concentration of adsorbate and time for film kinetics (t) and for

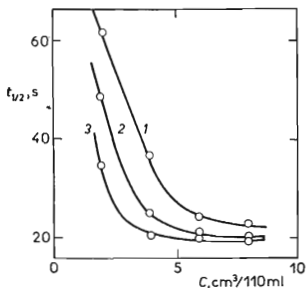


FIG. 2

Variation of $t_{1/2}$ with Volume of Dowex and Concentration of Iron

22°C, iron(III) conc.: 1 $1.0 \cdot 10^{-3}$ M, 2 $5.0 \cdot 10^{-4}$ M, 3 $1.0 \cdot 10^{-4}$ M, pH 2.

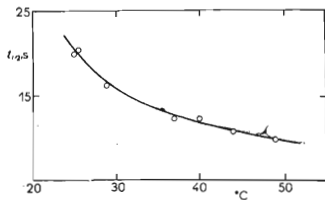


FIG. 3

Variation of $t_{1/2}$ with Temperature

$1.0 \cdot 10^{-4}$ M-Fe³⁺, 0.1M-HClO₄, 6 cm³ Dowex in a final volume of 110 ml.

gel kinetics (2)

$$\ln(1 - U) = -k_F t, \quad (1)$$

and

$$U = k_G t^{1/2}, \quad (U < 0.05), \quad (2)$$

where U is the fractional adsorption (e.g. of iron (III)) at time t , k_F is the heterogeneous rate constant for the film process, and k_G is that for the gel process, equal to $6\bar{D}^{1/2}/\pi^{3/2}r^0$ where \bar{D} is the diffusion coefficient in the grain and r^0 is the grain radius.

The kinetic curves for the sorption of 10^{-3} molar iron(III) on 2 cm³ of Dowex and of 10^{-4} molar iron(III) on 6 cm³ of Dowex (in a final volume of 110 ml) were tested for conformation to equations (1) and (2). In the former case, gel kinetics was found, with a value of $k_G = 2.1 \cdot 10^{-2} \text{ s}^{-1/2}$, giving $\bar{D} = 4.6 \cdot 10^{-8} \text{ cm}^2/\text{s}$. In the latter case, film kinetics was observed, giving $k_F = 3.15 \cdot 10^{-2} \text{ s}^{-1}$. Agreement between duplicates was excellent, the variation in k_F being $\pm 0.03 \cdot 10^{-2} \text{ s}^{-1}$ for a series of three measurements. These findings are in agreement with the theoretical predictions of the effect of adsorbent and adsorbate concentrations.

The Effect of Temperature on the Film Kinetics

The kinetic curves for the adsorption of 10^{-4} molar iron (III) on 6 cm³ Dowex (final volume = 110 ml) were recorded for various temperatures between 25 and 50°C. The $t_{1/2}$ values decreased non-linearly with temperature (Fig. 3). Curves at all temperatures were found to conform to the film-kinetic equation (1) and to give non-linear U vs $t^{1/2}$ plots (non-conformity with the gel-kinetic equation (2)). Values of k_F calculated from the $\log(1 - U)$ vs t plots are given in Table I. A plot of k_F vs temperature is non-linear. However, a plot of $\log k_F$ vs $1/T$, in accordance with the Arrhenius equation, is linear. The slope yields a value for the activation energy of 6.2 kcal/mol for the film kinetic process in 0.1 molar HClO₄.

TABLE I

Variation of k_F with Temperature

$1 \cdot 10^{-4} \text{ M-Fe}^{3+}$ 0.1M-HClO₄, Dowex conc. = 6 cm³ in a final volume of 110 ml.

°C	$k_F 10^2, \text{ s}^{-1}$	°C	$k_F 10^2, \text{ s}^{-1}$
25.4	3.15	40.0	5.44
29.0	3.50	44.0	5.71
38.0	5.03	49.0	6.40

The Effect of Acid Concentration

The kinetic ion exchange curves were studied for the adsorption of 10^{-4}M Fe^{3+} on 6 cm^3 Dowex in a total volume of 110 ml at acid concentrations from 0.1 to 3.0 molar. Figs 4 and 5 show that, at lower acid concentrations, the process is film-kinetic controlled, but that at higher acid concentrations, gel kinetics becomes the controlling factor. In Table II are shown the values of k_F and k_G calculated from the slopes of these plots. In both cases, the best fit is observed for a linear dependence of k on the first power of the acid concentration.

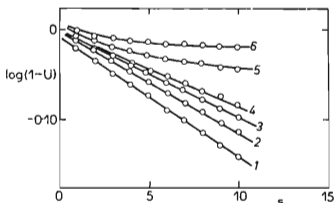


FIG. 4

Variation of $\log(1-U)$ vs t Plot with Acid Concentration (Film Kinetics)

$1 \cdot 10^{-4}\text{M-Fe}^{3+}$, 6 cm^3 Dowex in a final volume of 110 ml. Acid conc.: 1 0.1, 2 0.5, 3 1.0, 4 1.5, 5 2.0, 6 3.0 mol/l.

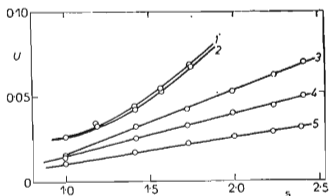


FIG. 5

Variation of U vs $t^{1/2}$ Plot with Acid Concentration (Gel Kinetics)

$1 \cdot 10^{-4}\text{M-Fe}^{3+}$, 6 cm^3 Dowex in a final volume of 110 ml. Acid conc.: 1 1.0, 2 1.5, 3 2.0, 4 2.5, 5 3.0M.

TABLE II

Variation of k_F and k_G and \bar{D} (diffusion coefficient in grain) with Concentration of Perchloric Acid

Adsorption of $1 \cdot 10^{-4}\text{M-Fe}^{3+}$ on 6 cm^3 Dowex X8 in a total volume of 110 ml.

HClO_4 mol/l	$k_F 10^2, \text{s}^{-1}$	$k_G 10^2, \text{s}^{-1/2}$	$\bar{D}, \text{cm}^2/\text{s}$
0.1	3.12	—	—
0.5	2.68	—	—
1.0	2.29	—	—
1.5	1.88	—	—
2.0	—	3.80	$1.5 \cdot 10^{-7}$
2.5	—	2.50	$6.5 \cdot 10^{-8}$
3.0	—	1.57	$3.3 \cdot 10^{-8}$

Helfferich⁴ gives the fraction

$$(X\bar{D}\delta/CDr_0)(5 + 2T_B^A), \quad (4)$$

as the controlling factor in determining whether film or gel kinetics are followed. Here, X is the concentration of Dowex at $t = 0$, in the same units as C , the concentration of iron at $t = 0$, D is the diffusion coefficient in the film, \bar{D} and r_0 are defined as previously, δ is the film thickness, and T_B^A is the adsorption factor depending on the concentration ratio of adsorbent to adsorbate. Thus (4) is a dimensionless number. When (4) $\gg 1$ film kinetics is observed; if (4) $\ll 1$, gel kinetics is operative.

With varying acid concentration, XC , r_0 , and T_B^A are constant, being fixed by the experimental conditions, and δ depends on the rate of stirring; *i.e.* δ may be expected to be independent of acid concentration, except for viscosity effects. Thus the change in kinetics can most probably be attributed to a change in the ratio \bar{D}/D . Both \bar{D} and D decrease with decreasing k_G and k_F , resp. (Values of \bar{D} calculated from k_G at various acid concentrations are shown in Table II). Thus \bar{D} will be larger than D at $H^+ < 2.0$ molar and smaller at $H^+ \geq 2.0$ molar. Consequently, either \bar{D} decreases more rapidly with $[H^+]$, or else the decrease of D with $[H^+]$ becomes less pronounced after $[H^+] \geq 2.0$ molar. The latter interpretation would entail a change of film "quality" at higher acid concentrations.

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