

Electrochemical fluorination of organic compounds.

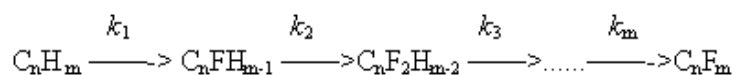
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5. Stages of the process of electrochemical fluorination of organic compounds.

A high overvoltage of elemental fluorine evolution when the value η in the Tafel's equation reaches 4 V is an evidence of a low value of the exchange current and a low rate of the electrochemical stage of fluorine ion discharge. Values of the logarithmic coefficient in this equation on carbon and nickel anodes [15,56] adsorbing fluorine radical [13,15,58] in the electrolysis in AHF medium are more than twice higher than those for platinum [15,59] nonreacting with fluorine. Taking into account a rather low bond energy in F_2 molecule, one can suggest that the controlling stages of ECF are interactions of the adsorbed fluorine radical with organic substrate. Because the latter is subjected to almost exhausting fluorination prior to its removal from an electrolyzer, electrochemical fluorination is a multistage electrode process with several sequential delayed stages of fluorination parallel with the electrochemical stage of the fluorine ion discharge. At a constant anodic potential controlling the fluorine radical concentration on the anode surface and a constant concentration of protonated cation complexes in fluorine ion in the electrolyte, the process of fluorination itself can be described by the following scheme with the rate constants k_i for every stage :



The rate of the first stage of fluorination expressed in electric units such as the partial current density i_1 can be written (from concepts of formal kinetics) as:

$$i_1 = k_1 [C_nH_m] \delta [C_nH_m] / \delta t,$$

At a steady feeding of starting substrate at a rate $\Delta [C_nH_m] / \Delta t = \dot{O}$, the full concentration derivative is

$$d[C_nH_m] / dt = \dot{O} \delta [C_nH_m] / \delta t = \dot{O} - k_1 [C_nH_m],$$

Solving this differential equation by means of the variable exchange $[C_nH_m] = \dot{E} * \exp(-k_1 t)$:

$$d[C_nH_m] / dt = d x / dt * \exp(-k_1 t) - x k_1 * \exp(-k_1 t) = \dot{O} - k_1 [C_nH_m]$$

$$\text{ord } x / dt * \exp(-k_1 t) - x k_1 * \exp(-k_1 t) = \dot{O} - x k_1 * \exp(-k_1 t),$$

from which

$$dx = c \cdot \exp(-k_1 t) dt$$

and we obtain after integration $x = c \cdot \exp(-k_1 t) / k_1 + \text{const}$,

or $[o_n H_m] = c / k_1 + \text{const} \cdot \exp(-k_1 t)$, then under the boundary conditions: $t = 0$; $[o_n H_m] = [o_n H_m]_0$ we obtain for $\text{const} = [o_n H_m]_0 - c / k_1$, from which

$$[C_n H_m] = \frac{c}{k_1} - \frac{c - k_1 [C_n H_m]_0 \cdot \exp(-k_1 t)}{k_1}$$
, then the partial current density for the first stage is equal to:

$$i_1 = \dot{O} - (\dot{O} - k_1 [o_n H_m]_0) \exp(-k_1 t).$$

For the second stage it should be written:

$$i_2 = k_2 [o_n F H_{m-1}] = \delta [C_{nF} \hat{I}_{m-1}] / dt = i_1 - \delta [C_{nF} \hat{I}_{m-1}] / t = i_2$$

Because the concentration of the first intermediate increases by means of its appearance in the first stage and reduces by means of its consumption in the second stage, its full derivative is added from partial derivatives for 1 and 2 stages and is equal to the difference of the partial currents for these stages:

$$d [C_{nF} H_{m-1}] / dt = \delta [C_{nF} \hat{I}_{m-1}] / t = i_1 - i_2 = \dot{O} - (\dot{O} - k_1 [o_n H_m]_0) \exp(-k_1 t) - k_2 [o_n F H_{m-1}]$$

Solving this equation under the boundary conditions when at $t = 0$, $[o_n F H_{m-1}] = 0$ and with the variable exchange

$[o_n F H_{m-1}] = \dot{E} \cdot \exp(-k_2 t)$ we obtain for

$$[o_n F H_{m-1}] = \left\{ \dot{O} / k_2 - (\dot{O} - k_1 [o_n H_m]_0) \exp(-k_1 t) / (k_2 - k_1) - k_1 (\dot{O} - k_2 [o_n H_m]_0) \exp(-k_1 t) / k_2 (k_1 - k_2) \right\}$$

and for

$$i_2 = \dot{O} - k_2 (\dot{O} - k_1 [o_n H_m]_0) \exp(-k_1 t) / (k_2 - k_1) - k_1 (\dot{O} - k_2 [o_n H_m]_0) \exp(-k_1 t) / (k_1 - k_2)$$

Similarly one can solve the equation for the subsequent stages of fluorination, for the third stage in particular:

$$i_3 = \frac{c - k_2 k_3 (c - k_1 [C_n H_m]_0) \exp(-k_1 t)}{(k_2 - k_1)(k_3 - k_1)} - \frac{k_1 k_3 (c - k_2 [C_n H_m]_0) \exp(-k_2 t)}{(k_1 - k_2)(k_3 - k_2)} - \frac{k_1 k_2 (c - k_3 [C_n H_m]_0) \exp(-k_3 t)}{(k_1 - k_3)(k_2 - k_3)}$$

Accordingly the partial current density for the last stage of the process or the rate of the end product formation will be expressed by the equation:

$$i_m = c - \sum_{x \neq y} \exp(-k_x t) (c - k_x [C_n H_m]_0) \prod_{m} \frac{k_y}{(k_y - k_x)}$$

, where x is not equal to y .

The rates of the last stage will be influenced only by decelerated stages of the process for which $k_y \gg k_x$. Under these conditions constants k_y existing in the fractional products will be contracted and one

can neglect the exponential terms with constants differing by an order of magnitude from the constants of the decelerated stages.

If the process includes only one decelerated stage (obviously, electrochemical one) , the equation becomes considerably more simple and reduces to the equation: $i_m = \frac{d[C_nH_m]}{dt} = (i_0 - k_A[C_nH_m]_0) \exp(-k_A t)$

similar to the given one for the partial current density for the first stage. In this case the rate of the last stage and consequently the current yield of the end product will increase monotonically with time asymptotically approaching $\dot{O} = d[C_nH_m]/dt$ as it is shown in **Fig.8**.

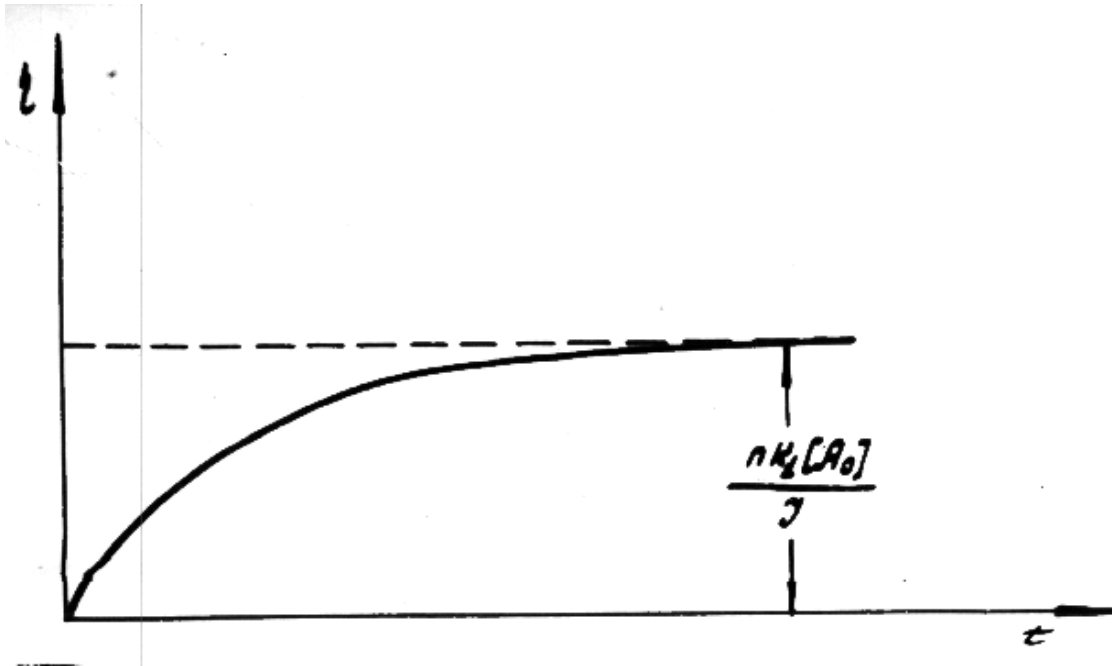


Fig.8 Current yield versus electrolysis time at one slowed down process stage

In the absence of the starting substrate feeding during the electrolysis, when the concentration of the starting substrate decreases with its consumption in fluorination, i.e. at $c=0$ the equation is expressed as follows:

$$i_m = \frac{[C_nH_m]_0 \cdot k_x \cdot \exp(-k_x t)}{k_y - k_x}$$

At $t=0$ $i_m=0$ in accordance with the boundary conditions , at $t \rightarrow \infty$, the exponent with the negative index tends to zero and hence, $i_m \rightarrow \frac{k_x [C_nH_m]_0}{k_y - k_x} > 0$. In reality this takes place at a finite instant when the electrolyte has been exhausted and the concentration of the organic substrate and intermediates aim at zero. In conformity with the Roll theorem, at finite values of the multistage process rate, the partial current density of the last stage is to have a maximum at a some value t .

The current yield of a process of electrochemical fluorination involved z electrones is $A = zF d[C_nH_m]/dQ$, where Q is the amount of electricity passed. The electrolysis current J is equal to dQ/dt and hence, at a constant electrolysis current , the current yield is equal to:

$$A = \frac{zF}{J} \cdot \frac{d[C_nH_m]}{dt}$$

Evidently, the derivative of the end product concentration with respect to time is the rate of this product formation, i.e. the rate of the last stage of the electrolysis process. The current yield may be expressed as a ratio of the amount of electricity consumed for the given end product to the total amount of electricity passed, % . It is not difficult to calculate this value in case of the formation of an individual product when the amount of expendable Faradays is known. But in electrochemical fluorination there is produced a lot of products due to a variety of accompanying processes, so it is not always possible to calculate the current yield and in this case it is evaluated in g/A-hour.

According to the analysis performed, in the absence of the starting substrate feed, methyl-3-methoxypropionate in particular, in the electrolysis with electrolyte exhausting the experimental dependence of the current yield in g/A-hour has a form of a rather symmetrical curve with a maximum given in Fig.9.

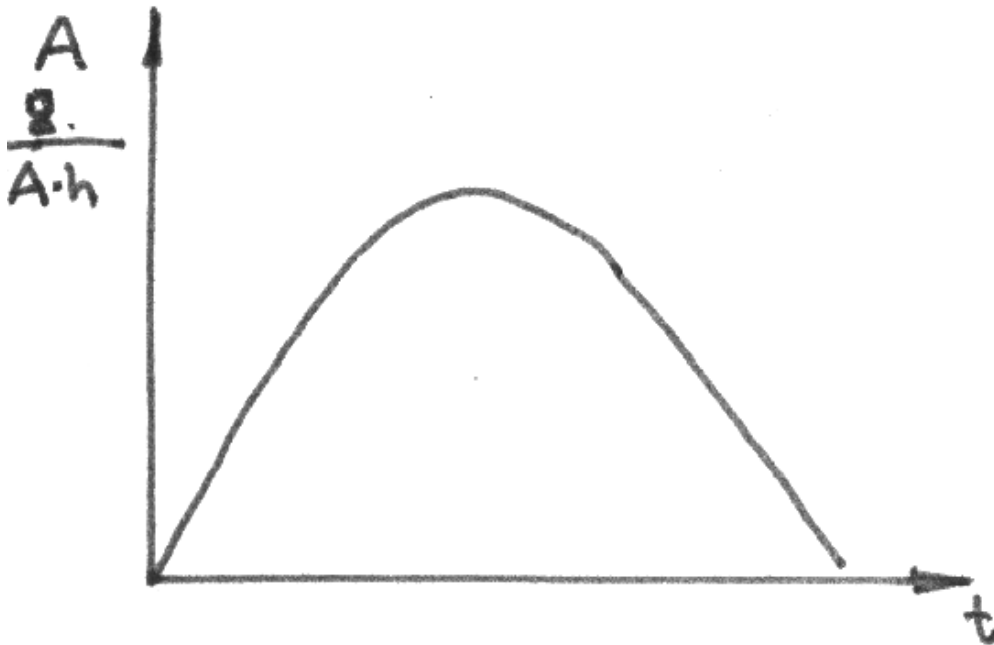


Fig.9 Current yield versus electrolysis time at two (at least) slowed down stages of the process without starting substrate feed during the course of ECF ($c = 0$)

In the lasting continuous electrolysis with the starting substrate feed to the electrolyzer to keep a stationary electrolyte concentration, the current yield will conform to the equation:

$$A = \frac{z \cdot j_m}{J} = \frac{z}{J} \left\{ c - \sum_m \exp(-k_x t) (c - k_x [C_n H_m]_0)^4 \prod_m \frac{k_x}{(k_y - k_x)} \right\}$$

At $\dot{O} = k_1 [O_n H_m]_0$ when the starting substrate feed to the electrolyzer is equal to its consumption in the first stage and its concentration is not changing during the course of the process, the equation for the current yield can be written:

$$A = \frac{z \cdot k_1 [C_n H_m]_0}{J} \left\{ 1 - \sum_m \exp(-k_x t)^2 \prod_m \frac{k_x}{(k_y - k_x)} \right\}$$

and at $t = 0$ $A = 0$ according to the boundary conditions, $t \rightarrow \infty, A \rightarrow z \cdot k_1 [O_n H_m]_0$ similarly to the

time given in Fig.10.

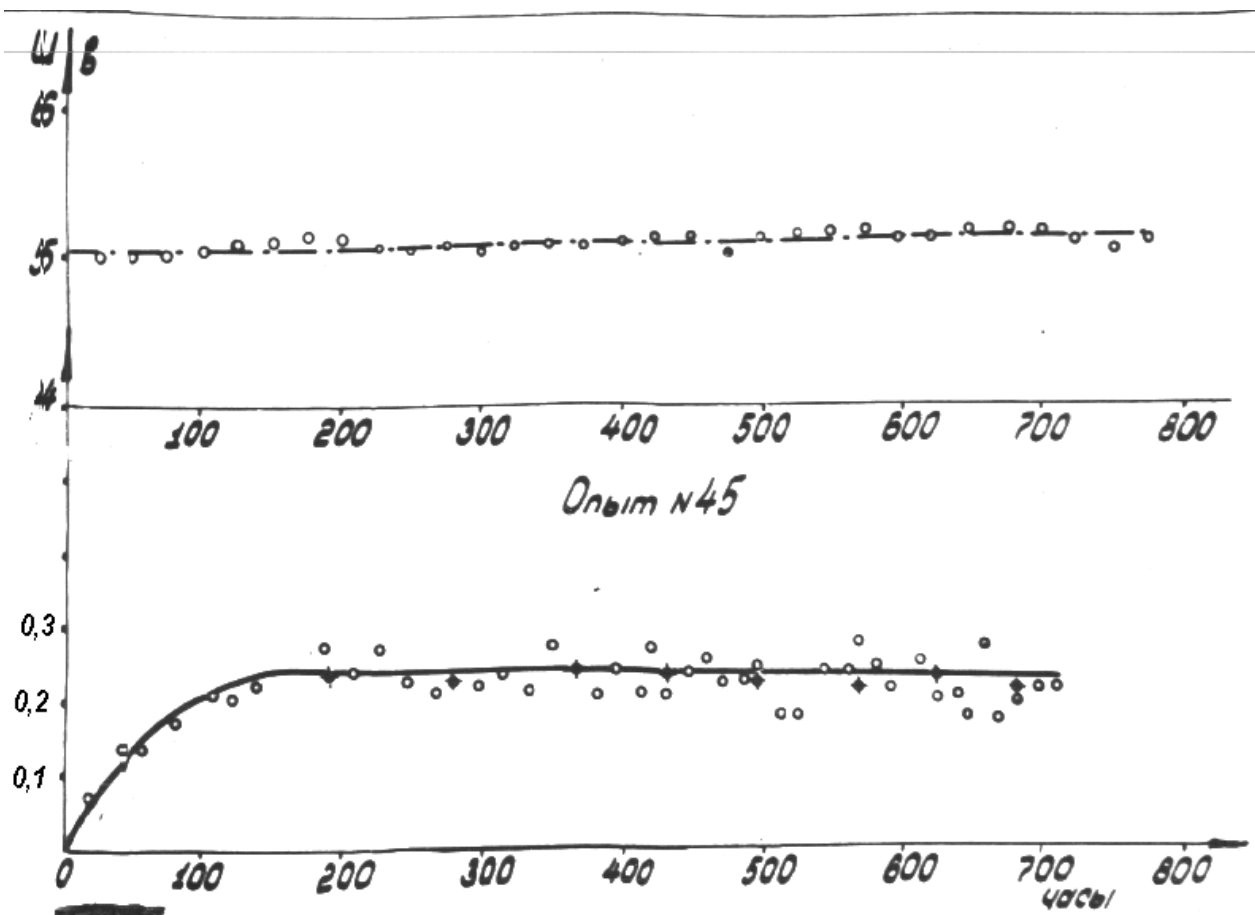


Fig.10 Experimental curve of current yield R_FCOF (g/ A-h) in ECF of $CH_3OCH_2CH_2COOCH_3$ under steady-state conditions

The value k_1 can not be determined strictly due to a variety of reactions of destruction, cyclization, isomerisation and so on, which probably precede the fluorination . That is why one has to calculate the value of starting compound feed "c" in accordance with the electricity consumption for fluorination in the electrolysis with one-time loading. Usually, such a calculated value is slightly lower than $k_1 [C_nH_m]_0$ because in this electrolysis an instant comes when there is no starting substrate in the electrolyte and the current is still consuming for fluorination of intermediates and this value is to be refined experimentally.

In conformity with mathematical analysis, at $c < k_1 [C_nH_m]_0$ the current yield at a real conditions passes through a maximum reducing with time due to the electrolyte exhaustion as it is shown in Fig.11 .

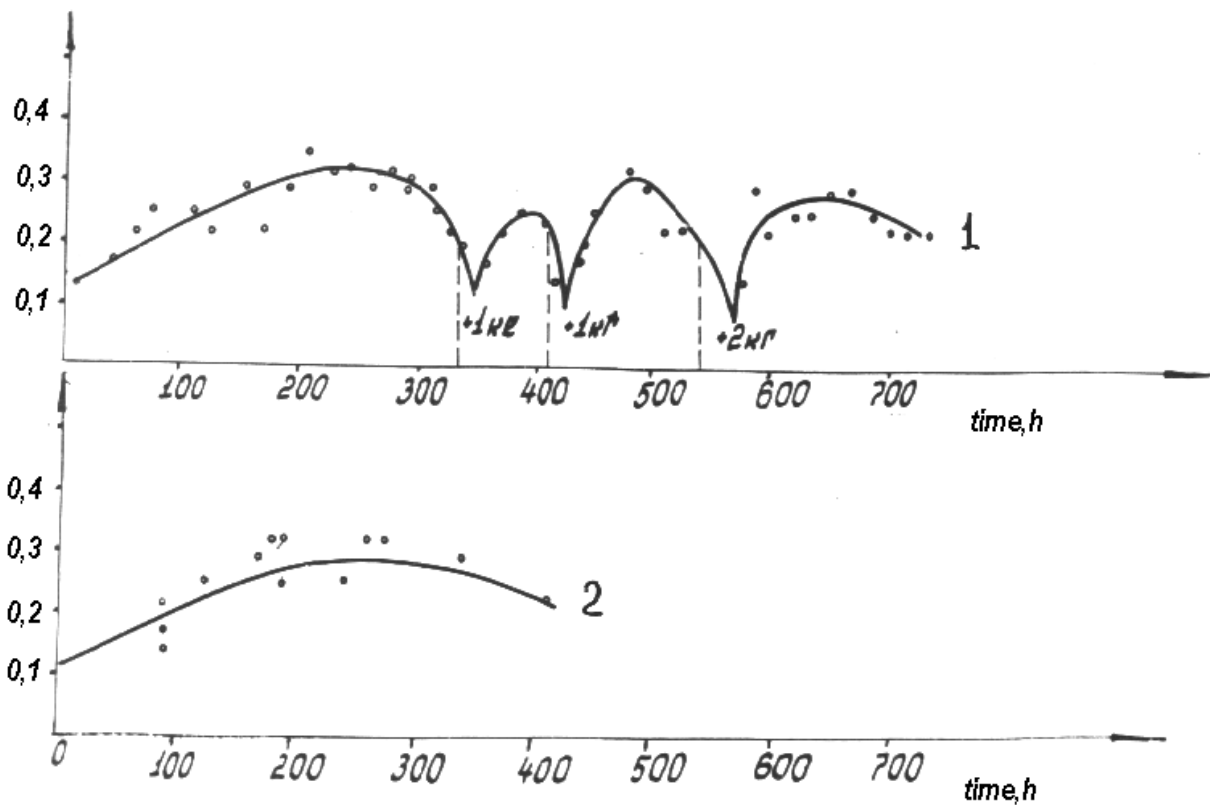


Fig.11 Curve 2: experimental curve of the current yield $R_{F\text{COF}}$ (g/A-h) at deficient feed of the starting substrate; curve1: the same curve with a correction of feed deficiency by additions of the starting substrate portions

The attempts to correct the electrolyte content by one-time additions of the starting product surprisingly resulted in a considerable reduction in the current yield as it follows from Fig.11.

The analysis of the given equation for the current yield indicates that if a slowed down stage of the process is the first one, at a change of the concentration $[\acute{o}_n H_m] \Delta \acute{o}_n H_m$ due to an increase of the partial current density of this stage when the total current density is fixed by the electrolysis current, then there will proceed their corresponding redistribution in the subsequent stages. As a result, the current yield has to drop sharply as it is shown in Fig.12

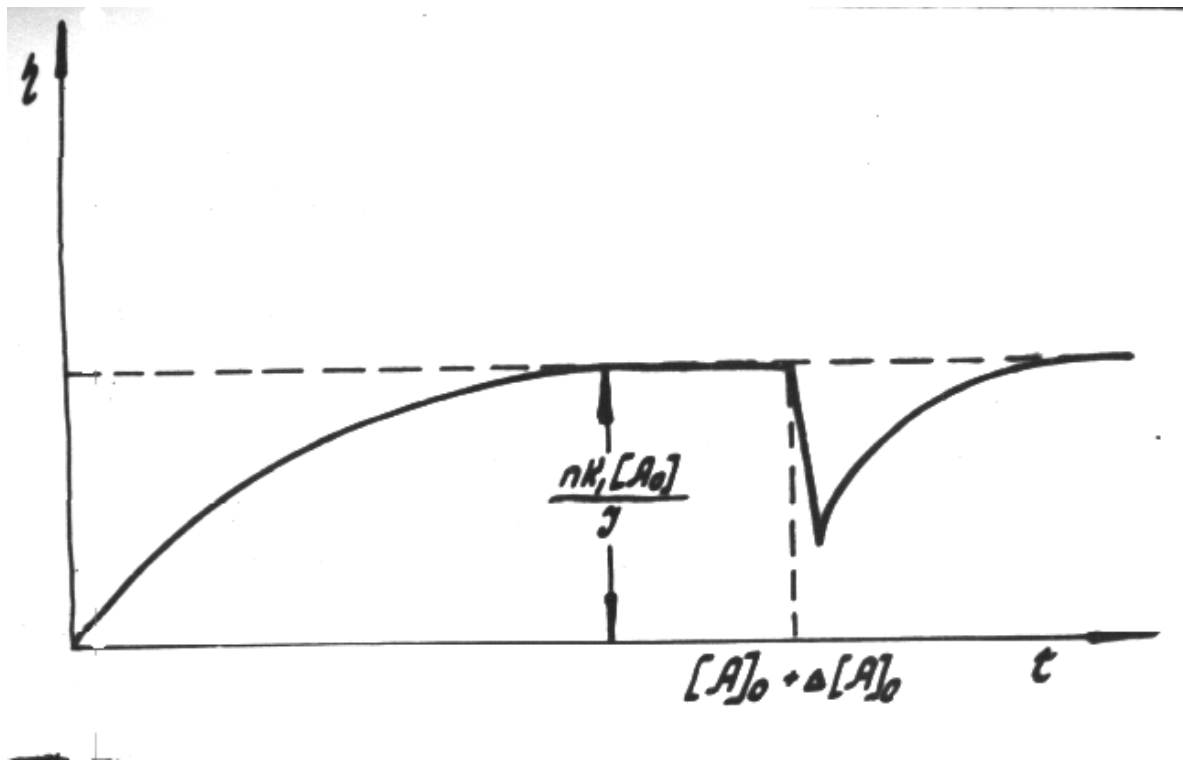


Fig.12 Plot of current yield function at $c = k_1 [C_nH_m]_0$ and $[C_nH_m] = [C_nH_m]_0 \Delta [C_nH_m]$ and confirmed by the experimental curve in Fig.13.

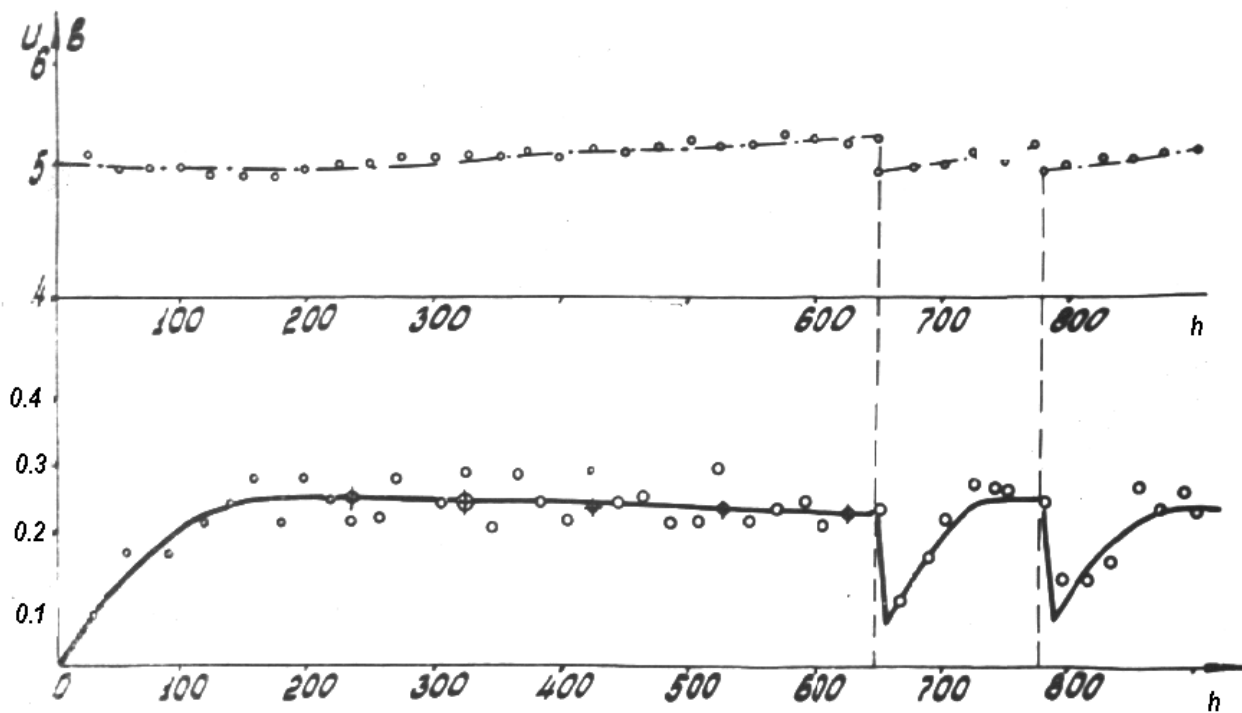


Fig.13 Experimental curve of current yield R_FCOF (g/A-h) in ECF of $CH_3OCH_2CH_2COOCH_3$ under steady-state conditions after additions of the starting substrate

Such an extreme drop in the current yield of the end products at one-time correction results in a reduction in the average current yield and hence, in the electrolyzer capacity. Also this brings to a noticeable scatter of the values to be determined, which is associated with batch nature of the starting

product feed into the electrolyzer in the lasting continuous process. This phenomena is not observed at continuous feed by a dozing pump.

Overfeeding the starting product resulted also in a reduction in the current yield due to an accumulation of resin type high molecular products in the electrolyte, but this is a subject of a special consideration.

Thus, the performed formal kinetic analysis of multistage nature of ECF has been convincingly confirmed in the electrochemical fluorination of methyl-3-methoxypropionate and some other oxygen-containing compounds and may be probably used in continuous electrolysis of different compounds.

Conclusions

1. Usually, dissolution of organic compounds in anhydrous hydrogen fluoride is accompanied by their protonation with formation of cations which can not participate the electrode process on the surface of the positively charged nickel anode.
2. The nickel anodic polarization in AHF medium is accompanied by anode passivation due to a formation of a nickel fluoride film, on whose surface at high anodic potentials fluorine ion discharge takes place with adsorption of fluorine radicals on nickel fluoride that prevents their molization.
3. Evidently, organic compounds in AHF medium are able to be deprotonated forming complex compounds with nickel fluoride. This determines Simons' ECF specificity when fluorine radicals in adsorbed state in a phase film of nickel fluoride interact with the structure of organic molecules.
4. The nature of the organic substrate and its interaction with nickel fluoride on the anode surface produce a determining influence on processes of fluorination, destruction and other structure transformations accompanying ECF of organic compounds.
5. The formal kinetic analysis of the multistage ECF process, in which slowed down stages are not only the electrochemical stage of discharge but also consequent chemical stages of fluorination, indicates that for successful realization of the lasting continuous process it is required to keep strictly a steady concentration of the substrate to be fluorinated in the electrolyte.

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