POLAROGRAPHIC INVESTIGATIONS ON ORGANIC PEROXIDES, III

5-BR-FUROYL- AND FURYL ACRYLIC-ACID-PEROXIDE

By

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(Received November 30, 1967)

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In previous publications the authors reported of studies made by polarographic method on benzoyl [1], and lauroyl [2]-peroxide. It was stated that the electrode process was controlled by diffusion and was irreversible. The number of electrons of the electrode process was 2. This study was aimed at investigating two other peroxides to determine the differences of the polarographic behaviour of the acyl groups. Below, an account will be given of the results obtained in testing with different solvents the characteristics of the electrode process in case of Br-furoyl and furyl-acrylic acid-peroxide, produced from 5-Br-furane-2-carboxylic acid and β-furylcarboxylic acid.

Experiments

The experimental conditions were identical with those mentioned in the previous publications [1, 2]. A 7-77-4/b-type Radelkis polarograph was used. For cathode, a dropping mercury electrode and for anode, a mercury pool was used. With Br-furoyl-peroxide and with furyl-acrylic acid-peroxide the values of the capillary constant were 2.39, and 2.53, respectively. Measurements were carried out in a thermostat-controlled, well-ground measuring cell of 15 ml capacity. Oxygen was expelled from the test solution by bubbling oxygen-free nitrogen gas through pyrogallol solution then through the tested solvent. Bubbling time was 10 min. By an ultrathermostat, the temperature was kept at 20° C. In case of Br-furoyl-peroxide and of furyl-acrylic acid-peroxide mercury levels of 65 and 37 cm, resp. were applied with a dropping time of 2.84 sec for both. Degree of damping was 4, the capacitive current-compensation was 1. The recording speed was 2, and the measurements ranged from 0 to —2V, excepted for specially indicated tests. Half-wave potentials were evaluated from the derived curve.

There are no references available on 5-Br-furoyl-peroxide. It was produced by the following steps: furfurol, furane-2-carboxylic acid, bromation. The 5-Br-furane-2-carboxylic acid was converted into acid-chloride by thyonilchloride and from this compound peroxide was produced by adding sodium peroxide. A solution of 21 gr of acid-chloride in 100 ml of ether was drip-fed to a solution of 7.8 gr of sodium peroxide dissolved in 100 ml of icy water at 0 to —2° C, in one hour. After having it agitated for 60 min., the formed precipitate was filtered, rinsed in water at 0° C, and dried in a vacuum at room temperature. The pure product was obtained by repeated re-crystallizations of the produced peroxide. Prior to use, the peroxide was dissolved in chloroform, shaken with an aqueous solution of Na_2CO_3 and precipitated with methanol. Filtered, dried in vacuum, at room temperature. Twice re-crystallization resulted unchanged melting points. The melting point determined by KOFLER's procedure was 125—126° C.

Br-furoyl-peroxide — its formula being $C_{10}H_4O_6Br_2$ — is a water-insoluble crystalline material, light yellow in colour. It is readily soluble in chloroform. In polar solvents, however, it is difficult to dissolve.

Furyl-acrylic acid-peroxide was produced by MILAS' method [3], then purified. The melting point determined by KOFLER's method was 97 to 99° C. The applied solvents were purified according to HOUBEN—WEYL [4]. The other types of chemicals were of pro analysis quality. The solvents were mixed in a ratio of 1 : 1 by volume.

Test results and evaluation

In the presence of different types of conducting salts, 5-Br-furoyl- and furyl-acrylic acid-peroxide gives a polarogram containing first and second order maxima (Figs 1*a*, and *b*). Steps, which were the easiest to evaluate were obtained by LiCl conducting salt, the more detailed investigations were carried out by its application.

Change of the heights of the maxima in function of the concentration of LiCl is in good agreement with those found with benzoyl-peroxide[1]. By increasing the concentration of the base electrolyte, height of the first order maximum will diminish, while the second order maximum increases. By increasing the concentration of the depolarizers, the maxima will increase in the range of 1.10^{-4} to 1.10^{-3} mol/l. The polarograms of the peroxides in different solvents are similar in character. The heigth of the maxima and the maximum to limiting current ratio varies with each solvent, and this is illustrated in Table I.

In the given experimental conditions the maxima can be flattened and— by increasing the quantity of the maximum supressor, their heights will exponentially diminish. Though with both peroxides, the optimum maximum-suppressing effect was obtained by methylene blue used in a concentration of $2 \cdot 10^{-4}$ mol/l, in case of Br-furoyl-peroxide, fuchsine at a concentration of

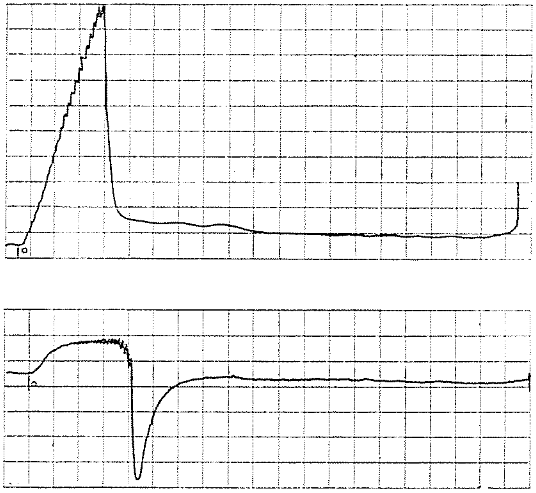


Fig. 1a. Polarogram of 5-Br-furoyl-peroxide. Concentration of depolarizer: 1.10^{-3} mol/l; Solvent: benzene—methanol mixture of ratio 1 : 1 by volume; Basic electrolyte: 0.1 mol/l LiCl; Measuring range: 0 ⟶ —2V; Sensitivity: 1.10^{-6} A/mm. Sensitivity at recording the derived curve: 4.10^{-4} A/mm

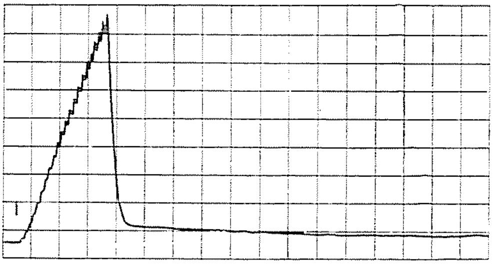


Fig. 1/b. Polarogram of furyl-acrylic acid-peroxide. Concentration of depolarizer: 1.10^{-3} mol/l; Solvent: benzene—methanol mixture of ratio 1 : 1 by volume; Basic electrolyte: 0.1 mol/l LiCl; Sensitivity: 8.10^{-7} A/mm; Measuring range: 0⟶ —2V

Table I

The height of the first order maxima and the ratio between the maximum and the limiting current in various solvents

Concentration of depolarizer: 1.10^{-3} mol/l. Solvent: Tabulated solvents are in 1 : 1 ratio by volume mixed with methanol. Basic electrolyte: 0.1 mol/l LiCl

Peroxide		Ethylacetate	Methanol	Benzene	Di-chloro-ethane	Dioxane	Acetic acid
Br-furoyl	Max. μA	56.0	36.5	94.0	65.0	40.0	21.0
	i μA	10.0	7.2	9.6	8.8	7.2	5.2
	Max./i	5.6	5.1	9.8	7.4	5.6	4.0
Furyl-acrylic acid	Max. μA	43.0	—	65.0	36.0	32.0	—
	i μA	6.2	—	8.4	5.2	3.8	—
	Max./i	7.0	—	7.7	7.0	8.4	—

$2.96 \cdot 10^{-3}$ mol/l was used as maximum-suppressor to investigate the properties of the electrode process, and with furyl-acrylic acid-peroxide $4.45 \cdot 10^{-3}$ mol/l of concentration was applied, owing to the fact that its two steps (—0.865 and —1.315 V potentials) did not interfere with the evaluation of the peroxide steps.

Polarograms of the peroxides after the suppression of the maxima are shown in Figs 2*a* and *b*.

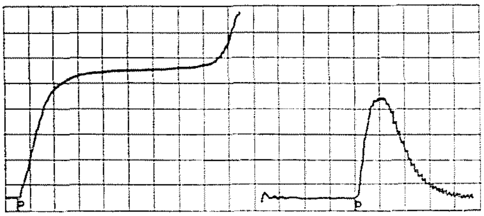


Fig. 2a. Polarogram of 5-Br-furoyl-peroxide after maximum suppression. Concentration of depolarizer: 1.10^{-3} mol/l; Solvent: benzene—methanol; Basic electrolyte: 0.1 mol/l LiCl; Maximum-suppressor: fuchsine of $2{,}96 \cdot 10^{-3}$ mol/l; Sensitivity: 2.10^{-7} A/mm. Sensitivity at recording the derived curve: 4.10^{-8} A/mm

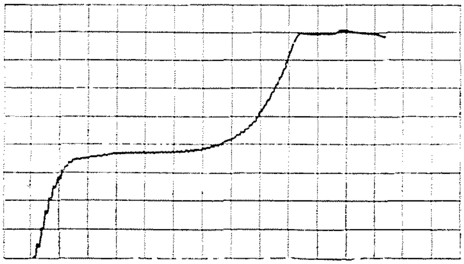


Fig. 2b. Polarogram of furyl-acrylic acid-peroxide after maximum suppression. Concentration of depolarizer: 1.10^{-3} mol/l; Solvent: benzene—methanol mixture of ratio 1 : 1 by volume; Basic electrolyte: 0.1 mol/l LiCl; Maximum suppressor: fuchsine of $4.45 \cdot 10^{-3}$ mol/l; Sensitivity: A/mm

1. *Variation of the limiting current and of the half-wave potential in function of the peroxide concentration*

Since the polarograms of 5-Br-furoyl-, and nicotinyl-peroxides have no basic current, the polarogram crosses the 0-line of the galvanometer from the anodic side (Figs 2*a* and *b*), the steps were investigated beginning with —0.2V. As it is seen in Fig. 3, on the anodic side, — upon the effect of the peroxides — a wave of constant height — independent of the concentration peroxide — will form, whereas in the negative voltage range the cathodic wave-height will depend on the peroxide concentration. No detailed analysis was made of the wave formed on the anodic side, due probably to the anodic oxidation of the mercury caused by the peroxides. Further on, it has been returned to 0 V starting potential and the wave-heights were measured between the 0-line of the galvanometer and the limiting current.

As Table II and Figs 4*a* and *b* indicate, in the various mixed solvents, in the concentration range of $1 \cdot 10^{-4}$ to $1 \cdot 10^{-3}$ mol/l, the concentration of the depolarizers and the wave-height are linearly related. Hence, quantitative determination of the peroxides is possible by the polarographic method. Within the given concentration series, the half-wave potentials will slightly gradually displace (Table II).

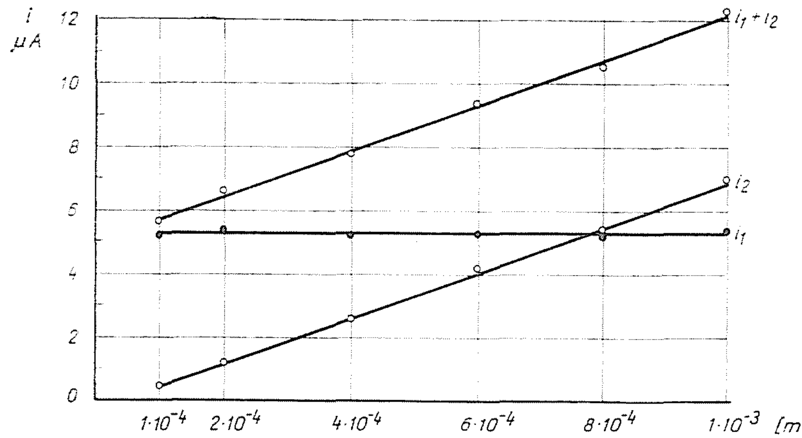


Fig. 3. Dependency on concentration-limiting current in a potential range of +0.2 —2V in case of Br-furoyl-peroxide. Solvent benzene—methanol mixture of ratio 1 : 1 by volume; Basic electrolyte: 0.1 mol/l NH_4NO_3; Maximum suppressor: fuchsine of $2.96 \cdot 10^{-3}$ mol/l; i_1 — limiting current + 0.2 ⟶ OV measuring range, i_2 — limiting current + 0 ⟶ —2V measuring range

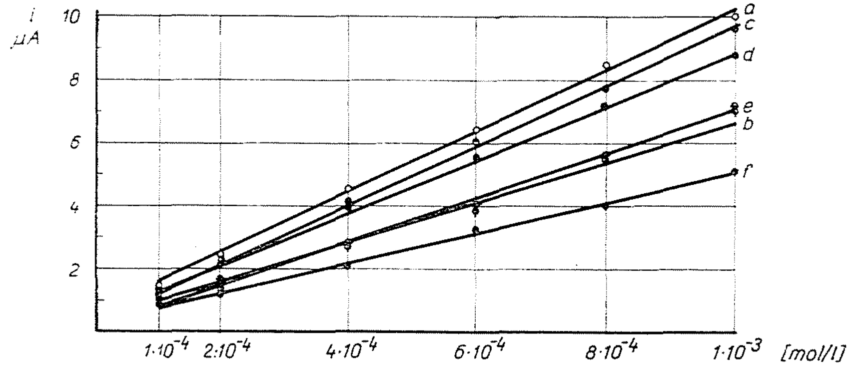


Fig. 4a. Dependency of the current waves of 5-Br-furoyl-peroxide on the peroxide concentration in various organic solvents. Basic electrolyte: 0.1 mol/l LiCl; Maximum suppressor: fuchsine of $2.96 \cdot 10^{-3}$ mol/l; Solvent: *a)* ethylacetate—methanol mixture of ratio 1 : 1 by vol. *b)* methanol; *c)* benzene—methanol mixture of ratio 1 : 1 by vol.; *d)* di-chloro-ethane methanol mixture of ratio 1 : 1 by vol.; *e)* dioxane—methanol mixture of ratio 1 : 1 by vol. *f)* acetic acid—methanol mixture of ratio 1 : 1 by vol.

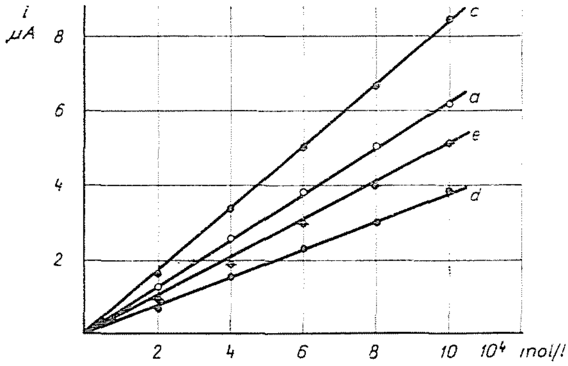


Fig. 4b. Limiting current of furyl-acrylic acid-peroxide wave depolarizer vs. concentration in various organic colvent mixtures. Basic electrolyte: 0.1 mol/l LiCl; Maximum suppressor: $4.45 \cdot 10^{-3}$ mol/l fuchsine; Solvent: *a)* ethyl-acetate—methanol mixture of ratio 1 : 1 by volume; *c)* benzene—methanol mixture of ratio 1 : 1 by volume; *d)* di-chloro-ethane—methanol mixture of ratio 1 : 1 by volume; *e)* dioxane—methanol mixture of ratio 1 : 1 by volume

Table IIa

Relationship between diffusion current and half-wave potential of 5-Br-furoyl-peroxide and the concentration of the depolarizer in various organic solvent mixtures
Solvent: Tabulated solvents in 1 : 1 vol. ratio mixed with methanol. Basic electrolyte: 0.1 mol/l LiCl. Maximum-suppressor: $2.96 \cdot 10^{-3}$ mol/l fuchsine

Solvent		$1 \cdot 10^{-4}$ mol/l	$2 \cdot 10^{-4}$ mol/l	$4 \cdot 10^{-4}$ mol/l	$6 \cdot 10^{-4}$ mol/l	$8 \cdot 10^{-4}$ mol/l	$10 \cdot 10^{-4}$ mol/l
Ethylacetate	i_d μA	1.50	2.43	4.56	6.40	8.48	10.00
	$-\varepsilon_{1/2}$V	0.060	0.07	0.08	0.09	0.10	0.10
Methanol	i_dμA	1.01	1.71	2.84	3.95	5.55	7.20
Benzene	i_dμA	1.11	2.15	4.16	6.10	7.73	9.60
Di-chloroethane	i_dμA	1.28	2.28	4.00	5.60	7.20	8.80
	$-\varepsilon_{1/2}$V	0.05	0.06	0.07	0.07	0.09	0.10
Dioxane	i_d μA	0.92	1.38	2.76	4.10	5.55	7.20
	$-\varepsilon_{1/2}$V	0.05	0.06	0.06	0.07	0.08	0.08
Acetic acid	i_d μA	0.93	1.26	2.16	3.30	4.05	5.20
	$-\varepsilon_{1/2}$V	0.06	0.07	0.08	0.09	0.10	0.11

2. Character of the electrode process and the mechanism of reduction

To elucidate the character of the electrode process, the influence of the temperature and the height of the mercury column upon the wave-heights was considered. Fig. 5 clearly indicates that with both peroxides, the wave-height is in proportion to the square root of the height of the mercury column.

Table IIb

Dependency of the diffusion current and half-wave potential of the furyl-acrylic acid-peroxide on the concentration of the depolarizer in different organic solvent mixtures

Solvent: The solvents in the Table mixed with methanol in 1 : 1 ratio by volume

Maximum-suppressor: 4.45 · 10^{-3} mol/l fuchsine. Basic electrolyte: 0.1 mol/l LiCl

Solvent		$1 \cdot 10^{-4}$ mol/l	$2 \cdot 10^{-4}$ mol/l	$4 \cdot 10^{-4}$ mol/l	$6 \cdot 10^{-4}$ mol/l	$8 \cdot 10^{-4}$ mol/l	$10 \cdot 10^{-4}$ mol/l
Ethylacetate	i_d μA	0.68	1.28	2.58	3.60	5.10	6.15
	$-\varepsilon_{1/2}$ V	0.05	0.06	0.06	0.07	0.07	0.08
Benzene	i_d μA	0.76	1.56	3.36	5.00	6.60	8.40
	$-\varepsilon_{1/2}$ V	0.07	0.08	0.09	0.10	0.01	0.10
Di-chloroethane	i_d μA	0.48	0.96	1.88	2.80	4.00	5.20
	$-\varepsilon_{1/2}$ V	0.06	0.07	0.08	0.08	0.08	0.10
Dioxane	i_d μA	0.32	0.68	1.48	2.28	3.00	3.80
	$-\varepsilon_{1/2}$ V	0.05	0.06	0.07	0.07	0.08	0.08

Fig. 6 illustrates the effect of the temperature upon the limiting current. It is seen that by increasing the temperature the limiting current will diminish, that is, the peroxides will decompose at higher temperatures. Dependency on the temperature, therefore, will allow no conclusions on the character of the electrode process. By considering the fact, however, that a linear relation exists between the wave-height, the concentration of the depolarizer and the square root of the mercury column, it can be concluded that the electrode process is of a diffusion character.

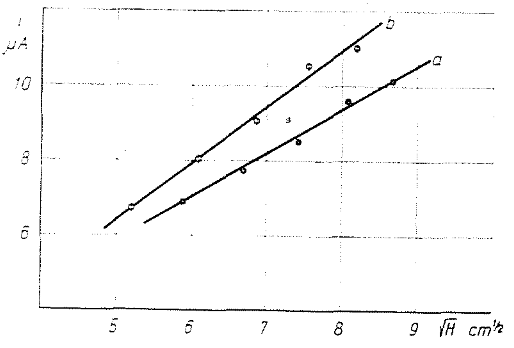


Fig. 5. Depolarizer: Mercury level vs. limiting current diagram: *a)* 1.10^{-3} mol/l Br-furoyl-peroxide; *b)* 1.10^{-3} mol/l furyl-acrylic acid-peroxide; Solvent: benzene—methanol mixture of ratio 1 : 1 by vol.; Basic electrolyte: 0.1 mol/l LiCl; Maximum-suppressor: *a)* 2.96 · 10^{-3} mol/l fuchsine; *b)* 4.45 · 10^{-3} mol/l fuchsine

Table III represents the values of the factors of transgression α determined by the logarithmic wave-analysing method. Dependency of the low

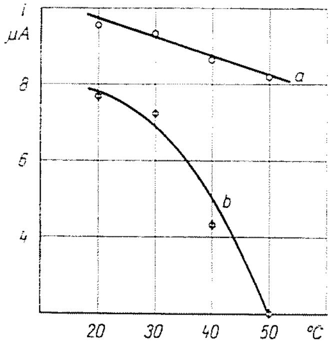


Fig. 6. Depolarizer: Temperature vs. limiting current diagram; *a)* 1.10^{-3} mol/l Br-furoyl-peroxide; *b)* 1.10^{-3} mol/l furyl acrylic acid-peroxide; Solvent: benzene—methanol mixture of ratio 1 : 1 by volume; Basic electrolite: 0.1 mol/l LiCl; Maximum suppressor: *a)* $2.96 \cdot 10^{-3}$ mol/l fuchsine; *b)* $4.45 \cdot 10^{-3}$ mol/l fuchsine

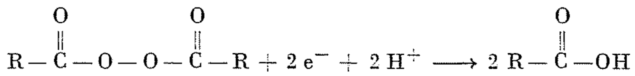
α values and the half-wave potentials on the concentration prove the irreversibility of the process.

In relation to the character of the electrode process, the transformation during the reduction was investigated as well, by determining the number of electrons. The number of electrons z was calculated on the basis of the ILKOVIČ's equation, giving with Br-furoyl-peroxide and with furyl-acrylic acid-peroxide z values of 1.67 in methanol and 2.03 in benzene and 1.60 in benzene, respectively. Hence, two electrons will contribute to the reduction of one molecule of peroxide. Accordingly, reduction will take place as follows:

Table III

Values i_d/c of peroxides, the diffusion current constant (I), $I_\eta^{1/2}$ and α in different solvent mixtures Solvent: Tabulated solvent mixed with methanol in 1 : 1 ratio by volume. Basic electrolyte: 0.1 mol/l LiCl. Maximum-suppressor: $2.96 \cdot 10^{-3}$ mol/l fuchsine with Br-furoyl-peroxide $4.45 \cdot 10^{-3}$ mol/l fuchsine with furyl-acrylic acid-peroxide

Peroxide		Ethylacetate	Methanol	Benzene	Di-chloro-ethane	Dioxane	Acetic acid
Br-furoyl-peroxide	i_d^1/c	9.6	6.3	9.3	9.5	6.9	4.9
	I	4.02	2.64	3.88	3.56	2.89	2.05
	$I_\eta^{1/2}$	2.89	2.03	3.07	3.01	2.81	1.99
	α	0.26	0.27	0.26	0.27	0.26	0.25
furyl-acrylic acid-peroxide	i_d^1/c	6.2	—	8.4	5.2	3.8	—
	I	2.46	—	3.32	2.06	1.51	—
	$I_\eta^{1/2}$	1.77	—	2.52	1.74	1.47	—
	α	0.28	—	0.24	0.31	0.32	—
	l	μA/l/mmol					



$$R-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-R+2\,e^{-}+2\,H^{+}\longrightarrow 2\,R-\overset{\overset{O}{\|}}{C}-OH$$

3. Influence of organic solvents on the polarographic properties

The values of $\frac{i_d}{c}$, of the diffusion current constant I and $I\eta^{1/2}$ in various solvents are compiled in Table III. In case of Br-furoyl-peroxide, the values of $I\eta^{1/2}$ — with the exception of methanol and acetic acid—methanol solvent — are identical within a range of 5%. Taking into account the approximative calculation of the viscosity value of the mixed solvents, these data indicate that the solvents affect the diffusion constant of the depolarizers and hence the wave-height only because of their different viscosities. With furyl-acrylic acid-peroxide, the $I\eta^{1/2}$ values are quite different. In this paper, no concern has been given to the cause of the low $I\eta^{1/2}$ values.

Values of the half-wave potential are also slightly influenced by the different solvents (Table II). In lack of regular polarograms, however (starting with no basic current) and — within one series of concentration — with regard to the gradual shifting of the half-wave potentials, no relationship between the variations of the half-wave potentials in different solvent mixtures and any characteristic of the latter (e.g. the value of the di-electric constant) could be established.

Summary

In an organic medium, 5-Br-furoyl-, and furyl-acrylic acid-peroxides will give cathodic (reduction) wave with a maximum.

The electrode process has a diffusion character, owing to the fact that the limiting current, the depolarizer concentration and the square root of the height of the mercury column are linearly related. The temperature coefficients are of negative value. The electrode process is irreversible since by increasing the concentration of the depolarizer the half-wave potential will displace in negative sense and the value of the transgression factor α is low. Number of electrons of the electrode process is 2. The $In^{1/2}$ values have been determined in various solvents. The half-wave potentials changed but slightly in each solvent.

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