

INVESTIGATIONS ON ORGANIC PEROXIDES BY APPLYING POLAROGRAPHIC METHODS, IV

FUROIL AND NICOTINOIL PEROXIDES

By

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Previous papers in this series have dealt with the polarographic analysis of benzoil [1] and lauroil [2] peroxides. It was found that the electrode process was diffusion-controlled and irreversible, involving a number of electrons of 2. The work presented here has been concerned with the polarographic behaviour of furoil and nicotinoil peroxides prepared from furan-2-carbonic acid and pyridine-3-carbonic acid, from the viewpoint of the acyl group differences. In the following, data of the character of the electrode process for furoil and nicotinoil peroxides obtained in different solvents will be described.

Experimental conditions

The conditions of the experiments are identical with those described in the previous studies [1, 2]. A RADELKIS 7-77-4/b type polarograph was used. As cathode a dropping mercury electrode and as anode a mercury pool was applied. The capillary constant values were 2.43 for furoil peroxide and 2.39 for nicotinoil peroxide. The measurements were carried out in a thermostat-controlled polished measuring cell of 15 ml capacity.

From the investigated solution the oxygen was expelled by oxygen-free nitrogen gas, which was first run through pyrogallol then a suitable solvent, applying a nitrogenation time of 10 minutes and a measuring temperature of 20 °C, maintained by an ultra-thermostate. For furoil and nicotinoil peroxides mercury levels were 38.5 cm and 65 cm, and dropping times were 2.90 and 2.84 s/drop, respectively. The measuring range was between 0 and -2 V. The half-wave potentials were established on the basis of the derived curves.

Furoil peroxide was prepared as indicated by MILAS [3]. Before use, it was dissolved in ether, shaken with the aqueous solution of Na₂CO₃, and dried on heated Na₂SO₄. After exhausting ther, it was dried in vacuum at room temperature. After recrystalling twice, identical melting points of 86 to 87 °C were obtained, as determined by Kofler's micro-method.

Nicotinoil peroxide could not be prepared either by MILAS [4], or by FORD's [5] method. From acid-chloride, the peroxide was prepared as follows:

To 2 g of sodium peroxide dissolved in 25 ml of icy water 6 g of acid-chloride was added at -1 to -3 °C. After stirring for 10 minutes, the precipitate was filtered, washed with icy water and dried in vacuum at room temperature.

Crystallization was performed in chloroform. The melting point was 87 °C to 89 °C as determined by KOFLER's method. The applied solvents were purified according to HOUBEN—WEYL [6]. Other applied chemicals were of analytical quality. The solvents were mixed in a ratio of 1 : 1 by volume.

Experimental results and their evaluation

1. Selection of the conducting salt and the maximum suppressor

In presence of different conducting salts, the peroxides gave a one-wave polarogram with a maximum (Figs 1a and 1b). Best evaluable waves were obtained with lithium chloride as basic electrolyte, therefore further evaluations were carried out by using this salt.

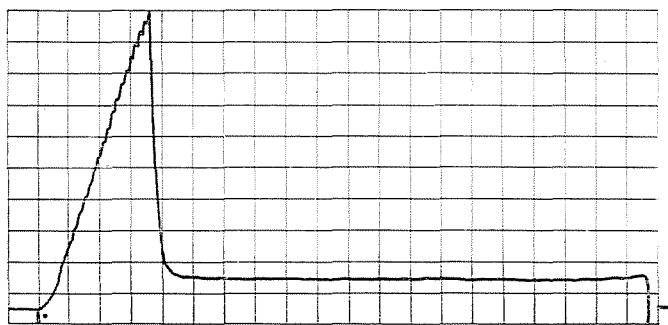


Fig. 1a. Polarogram of furoil peroxide. Depolarizer concentration: $1 \cdot 10^{-3}$ mol/l. Solvent: Mixture of benzene and methanol at 1 : 1 by vol. Basic electrolyte: 0.1 mol/l LiCl. Sensitivity: $1 \cdot 10^{-6}$ A/mm. Measuring range: 0 to -2 V

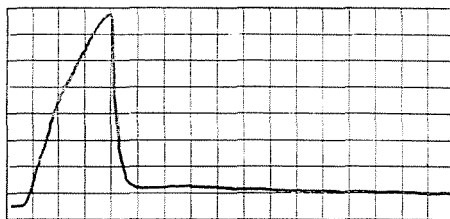


Fig. 1b. Polarogram of nicotinoil peroxide. Depolarizer concentration: $1 \cdot 10^{-3}$ mol/l. Solvent: Mixture of benzene and methanol 1 : 1 by vol. Basic electrolyte: 0.1 mol/l LiCl. Sensitivity: $8 \cdot 10^{-7}$ A/mm. Measuring range: 0 to -2 V

Upon increasing the concentration of the basic electrolyte, in case of nicotinoil peroxide the maximum diminished. In case of furoil peroxide, such decrease occurred after an initial rise (Fig. 2).

Upon raising the depolarizer concentration, the maximum (peak) increased (Fig. 3).

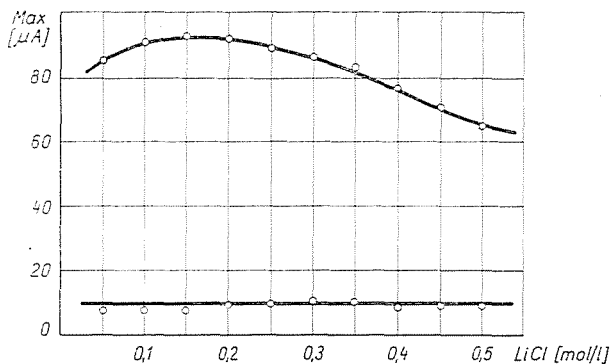


Fig. 2. Effect of the concentration of LiCl on the polarogram of furoil peroxide. Depolarizer: $1 \cdot 10^{-3}$ mol/l furoil peroxide. Solvent: Mixture of benzene and methanol at 1 : 1 by vol.

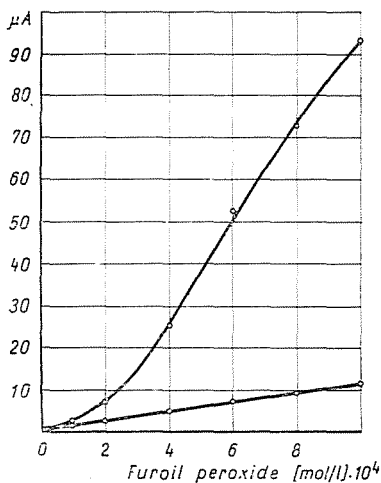


Fig. 3. Dependence of furoil peroxide peak on peroxide concentration. Solvent: benzene--methanol. Basic electrolyte: 0.1 mol/l LiCl

Polarograms of the peroxides are similar in character for different solvents. The peak heights and the ratios of peak to limiting current in the different solvents are compiled in Table I.

Under these experimental conditions, peaks can be suppressed.

The best maximum suppressing effects were obtained with methylene blue and fuchsine. Increasing the dosage of maximum suppressor exponentially reduced the peak heights (Figs 4, 5). Whereas the methylene blue suppressed the maximum less in a concentration by one order than fuchsine, this latter had been used to investigate the electrode process character, because its two waves (with the half-wave potentials of -0.865 and -1.315 V) did not disturb the evaluation of the peroxide waves (Fig. 6). On the contrary, superposition of the peroxide and the methylene blue waves did not permit accurate investigations on the behaviour of the peroxide waves to be carried out (Fig. 7).

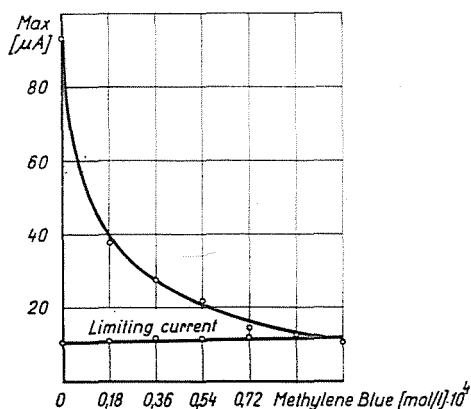


Fig. 4. Peak suppression with methylene blue. Depolarizer: $1 \cdot 10^{-3}$ mol/l furoil peroxide. Solvent: Mixture of benzene and methanol at 1 : 1 by vol. Basic electrolyte: 0.1 mol/l LiCl

Table I

The height of the first order maxima and the ratio of the maximum-limiting current for different solvents

Depolarizer concentration: $1 \cdot 10^{-3}$ mol/l. Mixture of methanol and the given solvent at 1 : 1 by volume. Basic electrolyte: 0.1 mol/l LiCl

Peroxide		Ethyl acetate	Methanol	Benzene	Dichloroethane	Dioxane	Acetic acid
Furoil	max. μA	141.0	104.3	95.0	118.5	88.5	70.0
	i μA	11.8	11.2	11.1	10.1	10.8	8.6
	$\frac{\text{max.}}{i}$	12.8	9.3	8.6	11.7	8.3	8.1
Nicotinoil	max. μA	118.0	76.0	58.0	110.0	100.0	—
	i μA	9.6	7.9	10.3	11.1	9.5	—
	$\frac{\text{max.}}{i}$	12.3	9.6	5.6	9.9	10.5	—

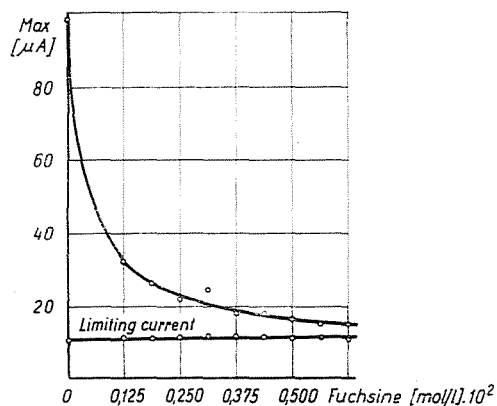


Fig. 5. Maximum suppression by fuchsine. Depolarizer: $1 \cdot 10^{-3}$ mol/l furoil peroxide. Solvent: Mixture of benzene and methanol at 1 : 1 by vol. Basic electrolyte: 0.1 mol/l LiCl

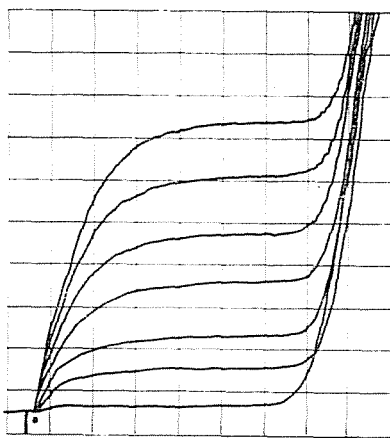


Fig. 6. Polarograms of fuchsine and furoil peroxide for different peroxide concentrations. Solvent: Dioxane—methanol. Basic electrolyte: 0.1 mol/l LiCl. Sensitivity: $1.5 \cdot 10^{-7}$ A/mm. Measuring range: 0 to -2 V. Curves in rising order:

$6.25 \cdot 10^{-3}$	mol/l fuchsine					
$6.25 \cdot 10^{-3}$	"	"	+	$1 \cdot 10^{-4}$	mol/l furoil peroxide	
$6.25 \cdot 10^{-3}$	"	"	+	$2 \cdot 10^{-4}$	"	"
$6.25 \cdot 10^{-3}$	"	"	+	$4 \cdot 10^{-4}$	"	"
$6.25 \cdot 10^{-3}$	"	"	+	$6 \cdot 10^{-4}$	"	"
$6.25 \cdot 10^{-3}$	"	"	+	$8 \cdot 10^{-4}$	"	"
$6.25 \cdot 10^{-3}$	"	"	+	$10 \cdot 10^{-4}$	"	"

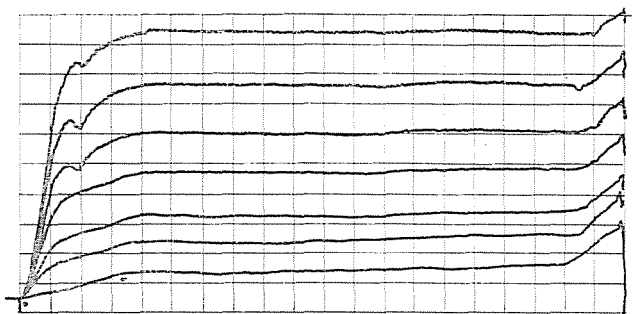


Fig. 7. Furoil peroxide polarograms for methylene blue and different peroxide concentrations. Solvent: Benzene—methanol. Basic electrolyte: 0.1 mol/l LiCl. Sensitivity: $1.5 \cdot 10^{-7}$ A/mm. Measuring range: 0 to -2 V. Curves in rising order:

$1.8 \cdot 10^{-4}$	mol/l methylene blue	+	$1 \cdot 10^{-4}$	mol/l furoil peroxide
$1.8 \cdot 10^{-4}$	+	$2 \cdot 10^{-4}$
$1.8 \cdot 10^{-4}$	+	$4 \cdot 10^{-4}$
$1.8 \cdot 10^{-4}$	+	$6 \cdot 10^{-4}$
$1.8 \cdot 10^{-4}$	+	$8 \cdot 10^{-4}$
$1.8 \cdot 10^{-4}$	+	$10 \cdot 10^{-4}$

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

In a concentration range of $1 \cdot 10^{-3}$ to $1 \cdot 10^{-4}$, of the different solvent mixtures depolarizer concentrations and wave-heights are in a linear relation (Tables IIa and b, Figures 8a, b, 6, 7), hence the polarographic method is suited to quantitatively determine the peroxides.

From Table II it is seen that within each concentration series the half-wave potentials are slightly, gradually shifted upon increasing the depolarizer concentration.

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

To establish the character of the electrode process, the effects of mercury level and of temperature on the wave-heights were investigated. The influence of the temperature on the limiting current is shown in Fig. 9. The temperature coefficients for furoil peroxide and nicitoinil peroxide are $0.60\%/^{\circ}\text{C}$ and $0.90\%/^{\circ}\text{C}$, respectively.

The $0.60\%/^{\circ}\text{C}$ temperature coefficient for furoil peroxide seems rather low even if it is considered that in case of organic solvents, the temperature coefficient of viscosity is about -1.6% as compared to that of water, i.e.

$$\frac{d\eta}{\eta dt} = 2.4\%.$$

Table IIa

Diffusion current and half-wave potential of furoil peroxide in function of the depolarizer concentration in various organic solvent mixtures
 Solvent: Mixture of methanol and the given solvent at 1 : 1 by vol. Basic electrolyte: 0.1 mol/l LiCl. Peak suppressor: $6.25 \cdot 10^{-3}$ 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
1		2	3	4	5	6	7
Ethylacetate	$i_d(\mu A)$	1.62	2.94	5.56	7.80	9.15	11.32
	$-\varepsilon_{1/2}(V)$	0.10	0.10	0.12	0.12	0.13	0.14
Methanol	$i_d(\mu A)$	1.50	2.55	4.80	6.75	9.15	10.95
	$-\varepsilon_{1/2}(V)$	0.08	0.09	0.11	0.12	0.12	0.11
Benzene	$i_d(\mu A)$	1.52	2.51	4.74	7.00	8.76	11.25
	$-\varepsilon_{1/2}(V)$	0.12	0.13	0.11	0.12	0.12	0.13
Dichloroethane	$i_d(\mu A)$	1.22	2.22	4.41	6.44	8.20	9.97
	$-\varepsilon_{1/2}(V)$	0.08	0.11	0.08	0.11	0.11	0.13
Dioxane	$i_d(\mu A)$	1.23	2.46	4.56	6.65	8.63	10.50
	$-\varepsilon_{1/2}(V)$	0.08	0.10	0.09	0.09	0.10	0.08
Acetic acid	$i_d(\mu A)$	0.99	1.98	3.60	5.24	7.05	8.55
	$-\varepsilon_{1/2}(V)$	0.13	0.13	0.15	0.16	0.16	0.15

Table IIb

Diffusion current and half-wave potential of nicotinoil peroxide in function of the depolarizer concentration in various organic solvent mixtures
 Solvent: Mixture of methanol and the given solvent at 1 : 1 by vol. Basic electrolyte: 0.1 mol/l LiCl. Peak suppressor: $6.25 \cdot 10^{-3}$ 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	$i_d(\mu A)(V)$	1.41	2.46	4.96	7.60	9.80	12.00
	$-\varepsilon_{1/2}$	0.06	0.08	0.08	0.09	0.11	0.11
Methanol	$i_d(\mu A)(V)$	0.75	1.48	2.80	4.20	6.00	7.40
	$-\varepsilon_{1/2}$	0.05	0.06	0.06	0.06	0.06	0.07
Benzene	$i_d(\mu A)$	1.20	2.20	4.15	6.20	8.20	10.40
	$-\varepsilon_{1/2}(V)$	0.06	0.06	0.06	0.06	0.06	0.06
Dichloroethane	$i_d(\mu A)$	1.30	2.40	4.60	6.80	9.00	11.10
	$-\varepsilon_{1/2}(V)$	0.06	0.06	0.06	0.07	0.07	0.07
Dioxane	$i_d(\mu A)$	1.08	1.98	3.92	5.70	7.60	9.60
	$-\varepsilon_{1/2}(V)$	0.05	0.05	0.06	0.06	0.06	0.06

Most probably, this is due to the decomposition of peroxide at higher temperatures.

The wave-height is in direct proportion to the square-root of the mercury level (Fig. 10).

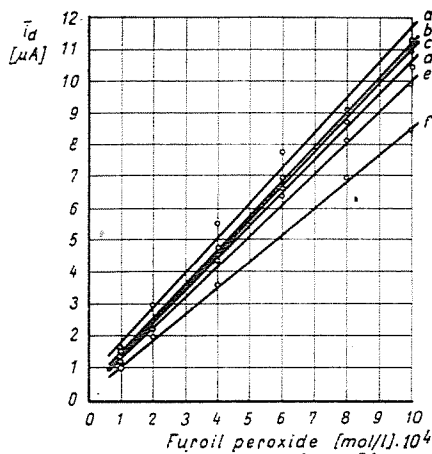


Fig. 8a. Dependence of the current waves of furoil peroxide on the peroxide concentration in different organic solvent mixtures. Basic electrolyte: 0.1 mol/l LiCl. Maximum suppressor: $6.25 \cdot 10^{-3}$ mol/l fuchsine. Solvent: a) ethylacetate—methanol, b) methanol, c) benzene—methanol, d) dioxane—methanol, e) dichloroethane—methanol, f) acetic acid—methanol

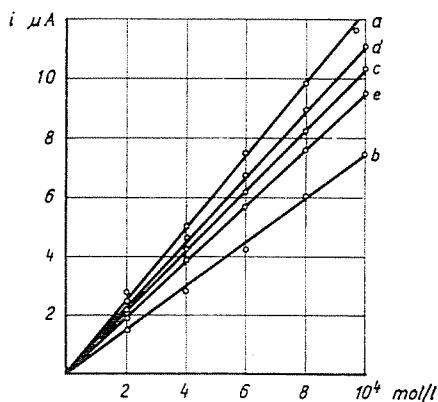


Fig. 8b. Dependence of the current waves of nicotinoil peroxide on the peroxide concentration in different organic solvent mixtures. Basic electrolyte: 0.1 mol/l LiCl. Peak suppressor: $3.20 \cdot 10^{-3}$ mol/l fuchsine. Solvent: a) mixture of ethylacetate and methanol at 1 : 1 by vol.; b) mixture of methanol; c) mixture of benzene and methanol; d) mixture of dichloroethane and methanol; e) mixture of dioxane and methanol

The linear correlation between the wave-height, the depolarizer concentration and the square-root of the mercury level makes it likely that the electrode process is diffusion-controlled.

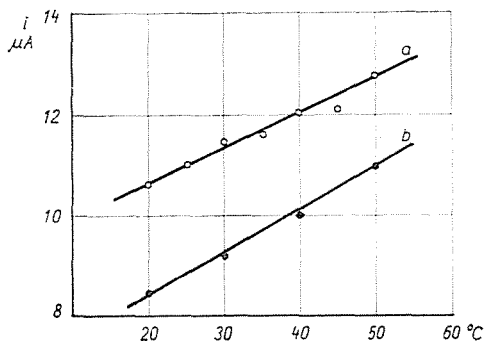


Fig. 9. Relationship between temperature and limiting current. Depolarizer: a) $1 \cdot 10^{-3}$ mol/l furoil peroxide, b) $1 \cdot 10^{-3}$ mol/l nicotinoil peroxide. Solvent: Mixture of benzene and methanol at 1 : 1 by vol. Basic electrolyte: 0.1 mol/l LiCl. Peak suppressor: $6.25 \cdot 10^{-3}$ mol/l for furoil peroxide; $3.20 \cdot 10^{-3}$ mol/l for nicotinoil peroxide

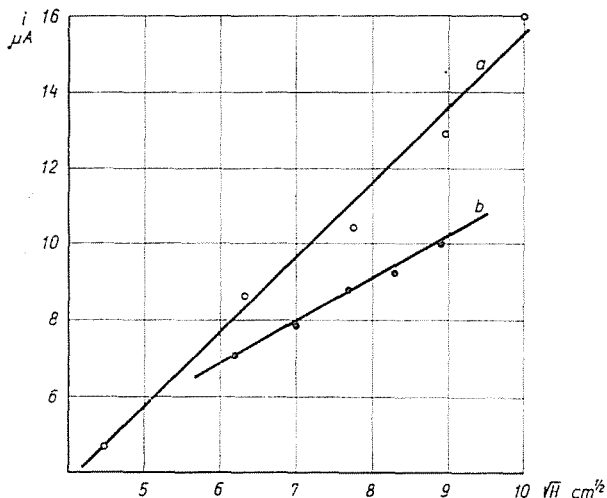


Fig. 10. Relationship between mercury level and limiting current. Depolarizer: a) $1 \cdot 10^{-3}$ mol/l furoil peroxide, b) $1 \cdot 10^{-3}$ mol/l nicotinoil peroxide. Solvent: Mixture of benzene and methanol at 1 : 1 by vol. Basic electrolyte: 0.1 mol/l LiCl. Maximum suppressor: $6.25 \cdot 10^{-3}$ mol/l fuchsine for furoil peroxide, $3.20 \cdot 10^{-3}$ mol/l fuchsine for nicotinoil peroxide

Table III shows the values of the transgressing factors α , determined by the method of logarithmic wave analysis. This relationship between the concentrations, the half-wave potential and the low α values supports the irreversibility of the electrode process.

In relation to the character of the electrode process, the reaction during the reduction was also examined by determining the electron numbers calculated according to the ILKOVIČ equation.

Table III

The values of $\frac{i_d}{c}$, diffusion current constant (I), $I_n^{1/2}$ and α of the peroxides in different solvent mixtures
 Solvent: Mixture of methanol and the given solvent at 1 : 1 by vol. Basic electrolyte: 0.1 mol/l LiCl. Maximum suppressor: Fuchsine for furoil peroxide $6.25 \cdot 10^{-3}$ mol/l. Fuchsine for nicotinoil peroxide $3.20 \cdot 10^{-3}$ mol/l

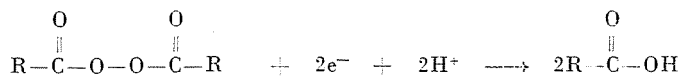
Peroxide		Ethyl- acetate	Methanol	Benzene	Dichloro- ethane	Dioxane	Acetic acid
Furoil peroxide	$\frac{i_d}{c}$	11.8	11.2	11.1	10.1	10.7	8.6
	I	4.84	4.61	4.56	4.17	4.39	3.55
	$I_n^{1/2}$	3.47	3.54	3.59	3.59	4.27	3.43
	α	0.20	0.25	0.22	0.21	0.18	0.27
Nicotinoil peroxide	$\frac{i_d}{c}$	12.3	7.9	10.3	11.1	9.5	—
	I	5.15	3.31	4.31	4.65	3.87	—
	$I_n^{1/2}$	3.70	1.95	3.39	3.93	3.76	—
	α	0.27	0.26	0.25	0.27	0.26	—

$$1 \frac{\mu A \cdot l}{\text{mmol}}$$

For furoil peroxide: $z = 2.11$ in methanol
 2.08 in benzene

For nicotinoil peroxide:
 $z = 1.55$ in methanol
 2.02 in benzene.

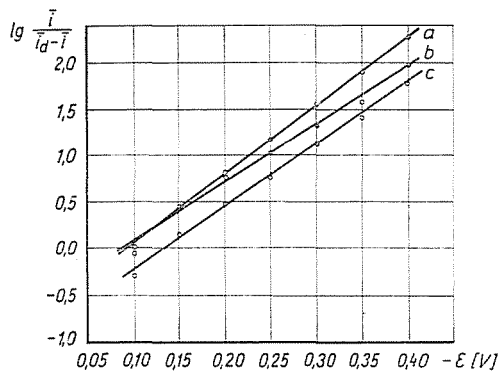
Accordingly, in the reduction of one peroxide molecule two electrons take part. As such, reduction takes place as follows:



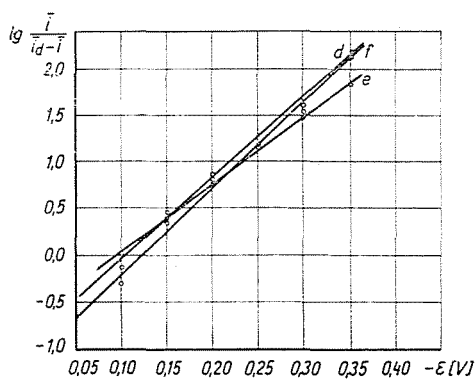
4. The effect of organic solvents upon the polarographic characteristics

The values of $\frac{i_d}{c}$, the constant of the diffusion current I, $I_n^{1/2}$, and α in different solvents are illustrated in Table III. In case of furoil peroxide the values of $I_n^{1/2}$ are identical within a range of 5% with the exception of dioxane-methanol solvent mixtures. With nicotinoil peroxide there is a 15% deviation, with the exception of methanol. Since viscosity values of solvent mixtures are

only approximative, these data may reveal that, with a few exceptions, some solvents only influence the diffusion constant of the depolarizers and thus the wave-height because of the difference in viscosity.



a



b

Fig. 11a and b. Logarithmic analysis of furoil peroxide waves. Depolarizer: $1 \cdot 10^{-3}$ mol/l LiCl. Basic electrolyte: 0.1 mol/l LiCl. Peak suppressor: $6.25 \cdot 10^{-3}$ fuchsine. Solvent: a) mixture of benzene—methanol at 1 : 1 by vol., b) mixture of dioxane—methanol at 1 : 1 by vol., c) mixture of ethyl acetate—methanol at 1 : 1 by vol., d) methanol, e) mixture of dichloroethane and methanol at 1 : 1 by vol., f) mixture of acetic acid and methanol at 1 : 1 by vol.

The data in Table II show that the different solvents slightly influenced the values of the half-wave potentials as well. Due to the absence of regular polarograms, however, and the half-wave potentials being gradually shifted within one series of concentration, variation of the half-wave potential values in different solvents cannot be related to some characteristic of the solvent (e.g. the dielectric constant value).

The different α values for each solvent — as determined by logarithmic wave-analysis — exhibited no regularity at all (Table III, Fig. 11), hence they

could not be attributed to the effect of the solvent on the reversibility of the electrode process.

Summary

In organic solvents, the furoil and nicotinoil peroxides give a one-wave polarogram with a maximum.

The electrode process is controlled by diffusion, there being a linear correlation between the limiting current, the depolarizer concentration and the square root of the mercury column height. The temperature coefficients are $0.90\%/^{\circ}\text{C}$ for nicotinoil peroxide and $0.60\%/^{\circ}\text{C}$ for furoil peroxide.

Upon increasing the depolarizer concentration the half-wave potentials are slightly shifted to the negative potential. A low transgression factor (α) proves the irreversibility of the electrode process. The electron number of the electrode process is two. The values of $I_{\frac{1}{2}}^{1/2}$ in different solvents are generally identical within a range of 10% . The half-wave potentials slightly differ for each solvent.

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