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Non-Typical Influence of Adsorbed 1-Octanol on Electroreduction of 1-Nitropentane on Mercury Electrodes

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The electroreduction of 1-nitropentane in the absence and in the presence of 1-octanol was studied. In the absence of inhibitor, 1-nitropentane at concentrations near to saturation is adsorbed weakly on mercury electrodes. In the presence of smaller concentrations of inhibitors, such as 1-octanol, 1-nitropentane electroreduction is inhibited less than that of nitromethane under comparable conditions. This difference was explained by the larger affinity of 1-nitropentane to the alcohol-rich surface phase and nitromethane to the aqueous solution phase. The increased affinity of the reactant to the electrode surface phase at the 1-octanol relative concentration, c/c_s, exceeding 0.7, may explain the independence of the electroreduction rate constant of 1-nitropentane and, even, its increase when the bulk concentration of inhibitor approached the saturation.

Key words: electrochemistry of 1-nitropentane, inhibition by 1-octanol, adsorption, kinetics, reduction

Organic compounds adsorbed on the electrode surface usually inhibit the rate of electrode processes [1–11]. The efficiency of this inhibition, which occurs on the electrode surfaces covered by the oriented monolayers of organic molecules, depends on several parameters [12,13]. One of such important parameters is the affinity of reactant to the molecules of surfactant in the surface layer. Very frequently this affinity may be negligible both for the cationic and anionic inorganic reactants. Then on the electrode, fully covered with inhibitor molecules ($\theta \approx 1$), the measured reaction rate constant may be even several orders of magnitude lower than the constant found for the non-inhibited reaction and is dependent on the bulk inhibitor concentration according to [2,3]:

$$\log \frac{k_\theta}{k_{\theta=0}} = -\frac{r^{\neq}}{r_i} \log \frac{c}{c_s} + const \tag{1}$$

$r^{\neq}$ and r_i denote the numbers of solvent molecules replaced on the electrode surface by the activated complex and inhibitor molecule, respectively, during their adsorption, k_θ and $k_{\theta=0}$ stand for the rate constants in the presence of inhibitor and in the inhibitor free solution respectively, while c denotes the concentration related to the concentration in the saturated solution, c_s.

For the reactants with greater affinity to the surface phase, covered by organic molecules, the situation is more complicated. Such problem was considered earlier [9,12,13]. Experimentally for the electroreduction of nitromethane [14–17] and 1-nitrohexane [17], in the presence of 1-octanol or 1-decanol as inhibitors, it was found that the dependence of $\log k_\theta/k_{\theta=0}$ on $\log c/c_s$ is described by (1) only for the relatively low concentrations of inhibitors , $c/c_s < 0.35$. At concentration range $c/c_s = 0.35–0.5$ the rate constant was practically independent of the inhibitor concentration. Using higher concentrations of 1-octanol or 1-decanol, an increase of the reaction rates was even observed. Such behaviour was explained by the larger affinity of nitromethane and 1-nitrohexane to the alcohol-rich surface phase. In this case an important role is played by the distribution of the reactant between bulk ($[R]_b$) and surface phase ($[R]_s$), described by the partition coefficient P ($P = [R]_s/[R]_b$). Because of the large hydrophobic aliphatic chain, the P values should be larger for 1-nitrohexane than for nitromethane and, consequently, the penetration of the surface layer, populated by hydrophobic 1-octanol or 1-decanol molecules, should be easier for 1-nitrohexane than for more hydrophilic nitromethane.

To confirm this non-expected increase of the reaction rate of electroreduction of aliphatic nitrocompounds with the increase of the concentration of aliphatic alcohols we have investigated additionally the influence of the adsorbed 1-octanol on the electroreduction of 1-nitropentane (NP) on the mercury electrode in the acidic aqueous solutions containing 0.50 M $NaClO_4$ as a supporting electrolyte.

EXPERIMENTAL

Chemicals: Fluka manufactured 1-nitropentane was used as a reactant. As the inhibitor, 1-octanol (Reachim, Russia) was used. Sodium perchlorate ($NaClO_4 \times H_2O$ Fluka) and 70 vol. % perchloric acid (Fluka) were p.a. grade chemicals. Water from mili-Q served for preparation of the solutions. Solutions of 0.50 M $NaClO_4$ and 0.05 M $HClO_4$, prepared on purified water, were saturated during 4 days with 1-octanol, using a mechanical shaker at 25±0.1°C. The solutions, with lower content of the inhibitor, were prepared by mixing the appropriate quantities of such saturated solution and the stock solution of the supporting electrolyte.

Apparatus and experimental methods: The electrochemical studies were carried out in a three electrode cell. Static mercury drop electrode (Laboratorni Pristroje, Prague) was used as a working electrode, while the platinum foil (2 cm^2) served as a counter electrode. All potentials were measured against a calomel electrode (SSCE) with saturated sodium chloride. All experiments were carried out at 25±0.1°C in a cell with a water jacket. The electrode processes were investigated using voltocoulometry, a similar technique to the normal and reverse pulse polarography with charge, Q, instead of current recorded. Home made apparatus was used with the current integration times in the range from 4 to 100 ms. The kinetic parameters of the processes studied were determined from charge-potential waves, using the method based on the works of Koutecky [18], Randles [19] and Kimmerle and Chevalet [20]. The current integration was carried out (i) from the beginning of the pulse application, and (ii) with 1 ms delay after the pulse application, in order to reject a significant part of the double layer charging. In kinetic experiments, usually the later version (ii) was applied. In preliminary experiments cyclic voltammetry was also used.

RESULTS AND DISCUSSION

Electrode kinetics of electroreduction of 1-nitropentane (NP): Electrochemical reduction of NP in the 0.50 M $NaClO_4$ and 0.05 M $HClO_4$ solutions was studied using voltocoulometry with the current integration times: 16, 25, 36, 64, 81 and 100 ms, and cyclic voltammetry with scan rates ranging from 0.1 to 1 Vs^{-1}. On mercury electrodes in acidic solutions both with inhibitor and in the inhibitor free solutions NP was irreversibly reduced to derivative of hydroxylamine [14–17] according to:

$$C_5H_{11}NO_2 + 4e + 4H^+ \rightarrow C_5H_{11}NHOH + H_2O \qquad (2)$$

In voltocoulometric experiments we observed only one, well-developed, Q-E, cathodic wave. The cathodic curves were recorded in the potential range from –0.30 to –1.10 V. In the reverse pulse experiments, the electrode, kept usually at –1.10 V, was pulsed step by step to more anodic potentials; however, prior to the mercury oxidation no anodic wave was observed at this low pH (0.05 M $HClO_4$). The oxidation of the electroreduction product to nitrosoderivative was observed at mercury electrodes only at pH higher than 5.

The shape of the Q-E dependencies, recorded with the total charge measured from the pulse application, was practically similar to those obtained with 1 ms charge rejection, exhibiting regular Q-E waves (see Fig. 1). The regular, *i.e.* without any maximum shape of the waves, recorded with the rejection of 1ms charge, suggests [17,21] that, under the experimental conditions, 1-nitropentane may be only weakly adsorbed on the mercury electrode from its 5×10^{-4} M solutions, at the potential from

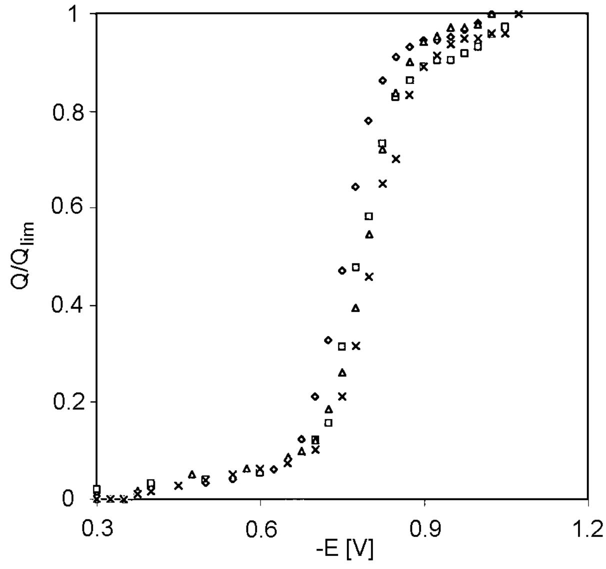

Figure 1. The dependence of electroreduction charges Q/Q_{lim} on potential for 5.3×10^{-4} M 1-nitropentane in aqueous solution containing 1-octanol in relative concentrations c/c_s equal to: 0.3 (◇), 0.5 ( ), 0.7 (x) and 0.9 (Δ). $t_p = 64$ ms. Supporting electrolyte: 0.50 M $NaClO_4$ with 0.05 M $HClO_4$.

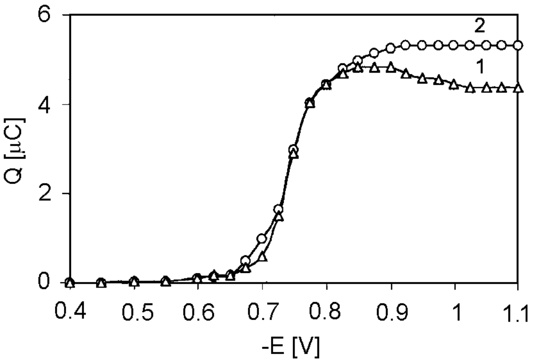

Figure 2. The charge-potential curves for 7.5×10^{-3} M 1-nitropentane in aqueous solution containing 0.50 M $NaClO_4$ and 0.05 M $HClO_4$. Curve (1) with rejection of the charge of first ms, curve (2) total charge, t_p = 9 ms.

which the pulse was initiated (–0.30 V). Also using less negative initial potentials –0.1÷–0.3 V such experiments did not point on a significant reactant adsorption. In our earlier investigations we have found that NP only at concentrations larger than 6×10^{-4} M is specifically adsorbed on mercury electrodes [10]. Also in the present work, when analysing NP at concentration c/c_s = 0.50 (7.05×10^{-3} M [21]), a small maximum at around –0.80 V on the voltocoulometric wave with rejection of the first millisecond charge was observed (Fig. 2 curve 1). On the adsorption of NP points also the shift of the cathodic voltocoulometric waves to more negative potentials with the increase of the NP concentration, shown in Table 1.

Table 1. Kinetic parameters for the electroreduction of 1-nitropentane in aqueous solutions containing: 1-nitropentane, 0.50 M $NaClO_4$ and 0.05 M $HClO_4$.

pulse time t_p [ms]	100		64		49		25	
relative 1- nitropentane concentration c/c_s	$-E_{1/2}$ [V]	$\frac{2.3\ RT}{\alpha nF}$ [mV]	$-E_{1/2}$ [V]	$\frac{2.3\ RT}{\alpha nF}$ [mV]	$-E_{1/2}$ [V]	$\frac{2.3\ RT}{\alpha nF}$ [mV]	$-E_{1/2}$ [V]	$\frac{2.3\ RT}{\alpha nF}$ [mV]
1.0	0.745	46.2	0.759	46.3	0.749	51.4	0.763	50.5
0.5	0.659	46.7	0.682	47.2	0.684	50.4	0.707	49.8
0.2	0.612	71.9	0.626	69.4	0.632	67.7	0.649	60.8
0.16	0.598	80.6	0.612	81.7	0.618	81.8	0.626	79.9
0.12	0.596	83.3	0.606	80.4	0.616	80.6	0.623	77.6
0.07	0.604	87.9	0.612	82.9	0.616	83.3	0.624	87.1
0.05	0.604	84.5	0.611	79.1	0.622	81.9	0.627	80.6
0.03	0.599	89.3	0.604	88.5	0.614	90.1	0.626	87.0
0.015	0.602	89.9	0.622	85.2	0.614	83.7	0.625	84.1

A weak adsorption of NP, even at 5×10^{-4} M occurs and may be confirmed by the cyclic voltammetric study. Such measurements carried out at different scan rates were analyzed in terms of the dependence of $I_p/v^{1/2}$ *vs.* $v^{1/2}$ [21] (I_p stands for the peak current). In the absence of adsorption and prevailing linear nature of diffusion the $I_p/v^{1/2}$ term should be independent of v [23]. Such independence of that parameter was found in the case of the electroreduction of 1-nitrobutane and lower aliphatic nitrocompounds. In opposite to that behaviour for NP, the $I_p/v^{1/2}$ term increased slightly and for 1-nitrohexane significantly with scan rate in the range of v from 2×10^{-2} to 1 Vs^{-1}, what is expected for the process of the adsorbed reactant [21].

The influence of inhibitor on the cathodic process (2) was investigated in aqueous solutions. The relative concentration of 1-octanol, c/c_S, in these solutions was equal to: 0, 0.10, 0.20, 0.3, 0.5, 0.6, 0.7, 0.9 and 1. In the presence of 1-octanol the charge was measured both (i) upon starting from the pulse application, and (ii) following 1 ms delay, using different pulse times in the 16 ms – 100 ms range. Also in the presence of inhibitors, the recorded cathodic waves of both types (i) and (ii) exhibited a well developed plateau.

A well-developed plateau of the limiting charge was observed also on curves with the total charge (Fig. 2 curve 2). Rather significant difference between limiting charges ΔQ of both type curves (with and without current integration during electrolysis in the first millisecond) is equal to [22]

$$\Delta Q = Q_{ad} + Q_1 + Q_{dl} \qquad (3)$$

where Q_{ad} and Q_1 denote the charges of adsorbed and diffusing reactant during first millisecond respectively, while Q_{dl} corresponds to the charging of the double layer when the potential of the electrode was changed from initial to the final value.

Table 2. Kinetic parameters for the electroreduction of 1-nitropentane in the presence of 1-octanol. Supporting electrolyte: 0.50 M $NaClO_4$ and 0.05 M $HClO_4$, NP concentration 5.3×10^{-4} M.

pulse time t_p [ms]	100			64			49			25		
relative 1- octanol concentration c/c_s	$-E_{1/2}$ [V]	$\frac{2.3RT}{\alpha nF}$ [mV]	αn	$-E_{1/2}$ [V]	$\frac{2.3RT}{\alpha nF}$ [mV]	αn	$-E_{1/2}$ [V]	$\frac{2.3RT}{\alpha nF}$ [mV]	αn	$-E_{1/2}$ [V]	$\frac{2.3RT}{\alpha nF}$ [mV]	αn
0.1	0.678	68	0.87	0.672	64	0.92	0.679	63	0.93	0.689	66	0.89
0.2	0.722	69	0.85	0.726	74	0.79	0.739	73	0.81	0.747	72	0.82
0.3	0.780	73	0.81	0.756	70	0.84	0.761	74	0.80	0.793	75	0.79
0.5	0.800	83	0.71	0.796	80	0.74	0.816	82	0.72	0.832	89	0.67
0.6	0.802	79	0.75	0.809	86	0.69	0.815	80	0.74	0.829	85	0.70
0.7	0.837	91	0.64	0.842	87	0.67	0.845	90	0.66	0.863	93	0.64
0.9	0.831	97	0.61	0.832	90	0.66	0.837	94	0.63	0.845	98	0.60
1.0	0.782	86	0.69	0.779	87	0.68	0.781	85	0.69	0.790	97	0.61

The cathodic waves obtained at different t_p and various c/c_s concentrations of n-octanol were at first analyzed in terms of the plots of log $(Q/Q_L - Q)$ *versus* electrode potential. All these dependencies were linear and from their slopes and intersections with the potential axis, the cathodic half-wave potentials, $E_{1/2}$ and the transfer coefficient αn were estimated. The obtained data are presented in Table 2. One can observe, that the electroreduction half-wave potential, $E_{1/2}$, of NP is more negative than that of 1-nitrohexane [17], but less negative than nitromethane [17] at the same pH (see Fig. 3). As expected, $E_{1/2}$ of the cathodic electroreduction of NP becomes more negative with the increase of 1-octanol concentration in the c/c_s range from 0 to 0.6. However, at higher concentration of inhibitor, $c/c_s > 0.7$ and constant pH, the half-wave potential of the electroreduction of $C_5H_{11}NO_2$ to $C_5H_{11}NHOH$ process was moved to less negative values with c/c_s. The shape of Q-E dependencies was practically not dependent on the pulse time, but the pulse time influenced the $E_{1/2}$ values in an expected way, *i.e.* these potentials were less negative at longer pulse times following the dependence [22]

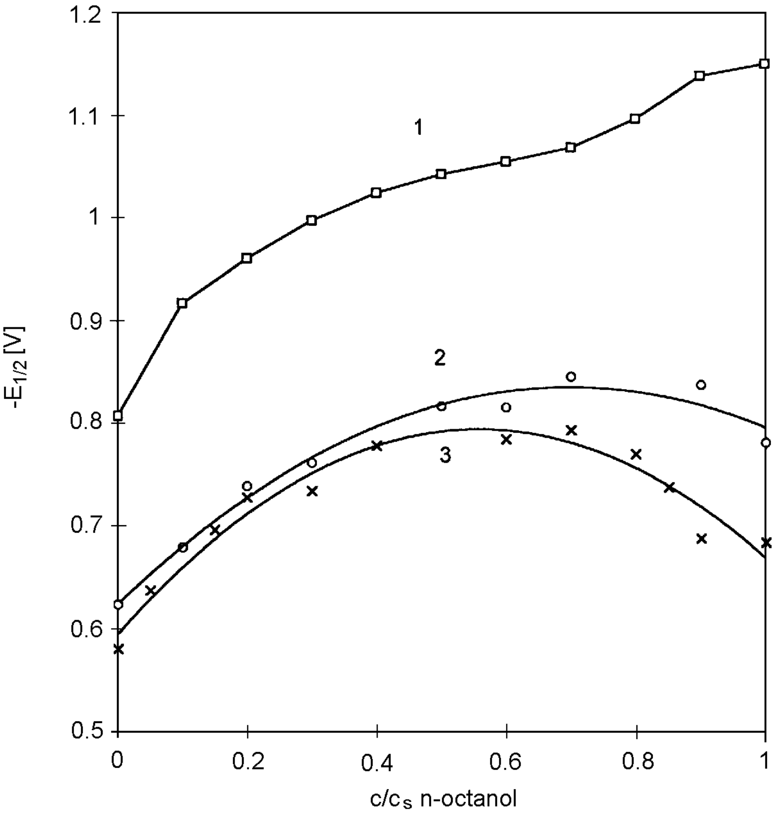

Figure 3. The dependence of the electroreduction half-wave potentials on the relative concentration of inhibitor. Reactants 5×10^{-4} M nitromethane (curve 1), 5×10^{-4} M 1-nitropentane (2) and 2×10^{-4} M 1-nitrohexane (3). $t_p = 49$ ms. Supporting electrolyte: 0.50 M $NaClO_4$ with 0.05 M $HClO_4$.

$$E^{1/2} = \text{const} + \frac{RT}{2\alpha nF}\ln t_p \tag{4}$$

From Q *vs*. E waves also the rate constants k_{fh} were obtained. In their calculation the diffusion coefficient of NP was assumed to 1.50×10^{-5} cm^2 s^{-1}, in all investigated solutions, as found for the reactant in an inhibitor-free solution [14,21]. The k_{fh} values calculated from the charge-potentials dependencies, recorded at different integration times for a given solution, were similar within the limits of the experimental error.

Cathodic Tafel plots constructed from the obtained data were linear in the case of all investigated solutions (with regression coefficient equal to 0.998), in the whole concentration range of 1-octanol. Typical plots are presented in Fig. 4. The values of the cathodic transfer coefficient αn, calculated from the Tafel slopes, are presented in Table 3. The αn values decrease with increase of 1-octanol concentration, but as expected, remain practically independent of the pulse time in the limits of the experimental error, as shown in Fig. 5. In Fig. 6 there are given the cathodic rate constants at fixed potentials, obtained from the Tafel plots, for various inhibitor concentrations. The reaction rate constant changed non-monotonically with concentration of the inhibitor, similarly to the change of $E_{1/2}$. Such behaviour is in variance with the theoreti-

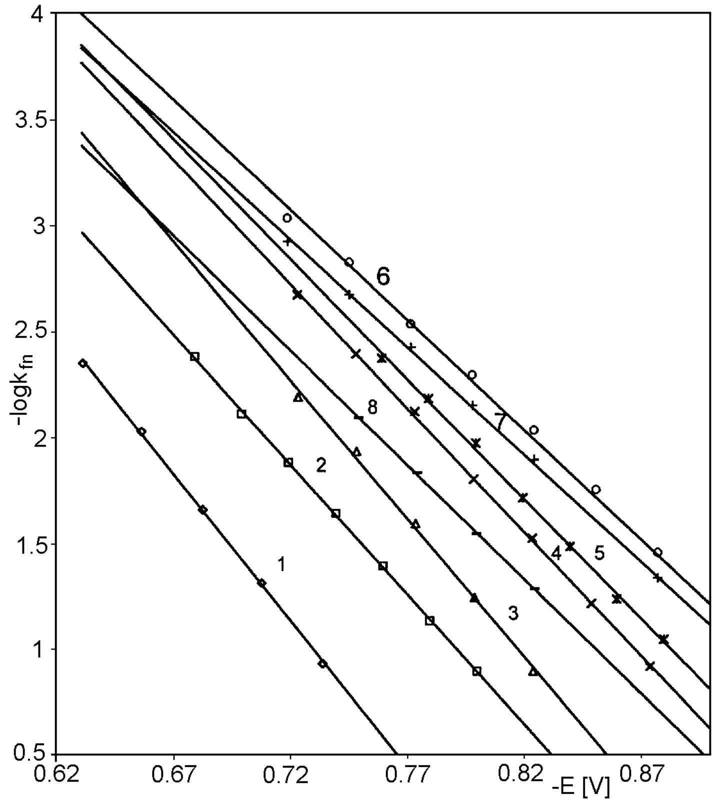

Figure 4. Tafel plots for electroreduction of 5.3×10^{-4} M 1-nitropentane in aqueous solutions in the presence of 1-octanol with concentrations c/c$_s$ equal to: curve 1 – 0.1, 2 – 0.2, 3 – 0.3, 4 – 0.5, 5 – 0.6, 6 – 0.7 and 8 – 1 at t_p = 64ms. Supporting electrolyte: 0.50 M $NaClO_4$ with 0.05 M $HClO_4$.

cal expectations and with the numerous experimental data on the inhibition of various electrochemical reactions [1–11]. In the concentration range of 1-octanol, $0 < c/c_s < 0.5$, k_{fh} decreases with the increase of c/c_s. For inhibitor concentrations, $0.5 < c/c_s < 0.7$, k_{fh} changed only slightly, but at $c/c_s > 0.7$ the reaction rate anomalous increased with the rise of the 1-octanol concentration.

1-nitropentane, as other n-nitroalkanes, is irreversibly reduced to hydroxyloamine derivatives on the mercury electrode in aqueous solutions. The reduction half-wave potentials (peak potentials) shift to more negative values with decrease of the pulse time and increase of scan rate, observed in the inhibitor free solutions and in the whole concentration range of inhibitors (see Table 2).

Table 3. Kinetic parameters for the electroreduction of 1-nitropentane in the presence of 1-octanol, $t_p = 49$ ms. Supporting electrolyte: 0.50 M $NaClO_4$ and 0.05 M $HClO_4$, NP concentration 5.3×10^{-4}M. A – at E = –0.70 V, B – calculated from the Tafel plots.

Concentration of 1-octanol, c/c_s	$-E_{1/2}$ V	$-\log k_{fh}^{A}$ cm s^{-1}	αn^{B}
0.0	0.623	0.86	0.72
0.1	0.679	1.42	0.85
0.2	0.739	2.17	0.81
0.3	0.761	2.52	0.74
0.5	0.816	3.05	0.68
0.6	0.815	3.08	0.68
0.7	0.845	3.22	0.61
0.9	0.837	3.12	0.58
1.0	0.781	2.58	0.61

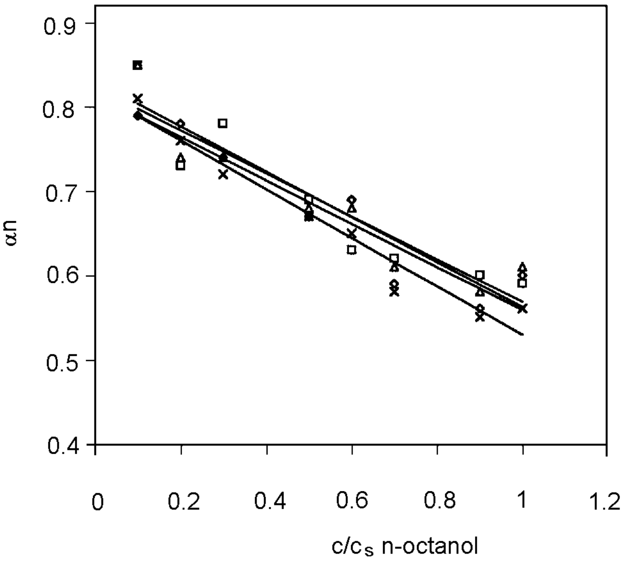

Figure 5. The dependence of cathodic transfer coefficient of the 5.3×10^{-4} M 1-nitropentane electroreduction on the relative n-octanol concentration at different pulse times: 100 ms (◇), 64 ms ( ), 49 ms (Δ) and 25 ms (x). Supporting electrolyte: 0.50 M $NaClO_4$ with 0.05 M $HClO_4$.

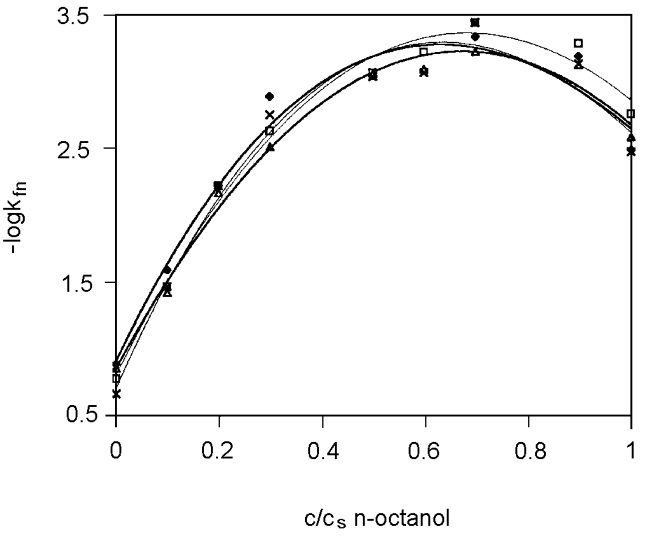

Figure 6. The dependence of the cathodic reaction rate of the 5.3×10^{-4} M electroreduction on the relative 1-octanol concentration at constant potential, E = –0.70 V for different t_p: 100 ms (◆), 64 ms (□), 49 ms (Δ) and 25 ms (x). Supporting electrolyte: 0.50 M $NaClO_4$ with 0.05 M $HClO_4$.

In the concentration range $0.1\le c/c_s \le 0.6$ of 1-octanol, the half-wave potential, $E^{ir}_{1/2}$, of the electroreduction of $C_5H_{11}NO_2$ was linearly dependent on the log (c/c_s) of the inhibitor (see Fig. 3). These changes can be described by the equation valid for the totally irreversible electrode processes, when the inhibitor fully covers the surface of the electrode ($\theta\approx1$) and the reactant practically does not interact with the adsorbed inhibitor [9]:

$$E^{ir}_{1/2} = E^f_o + const + \frac{RT}{\alpha nF}\ln k_{\theta=0}\left(\frac{c}{c_s}\right)^{-\frac{r^{\neq}}{r_i}} \tag{5}$$

E^f_o denotes the formal potential of the system, and other symbols were either described earlier in this work or have the usual significance. The slope, $\Delta E^{ir}_{1/2}/\Delta\log(c/c_s) = -2.3r^{\neq}RT/r_i\alpha nF$ was equal to –174 mV per decade of 1-octanol concentration. These and other data obtained in the present work show, that in the presence of 1-octanol the slope, $\Delta E^{ir}_{1/2}/\Delta\log(c/c_s) = -2.3r^{\neq}RT/r_i\alpha nF$ depends on the nature of n-nitroalkanes and changes in the order: –185 mV (nitromethane) [17] < –174 mV (1-nitropentane) < –155 mV (1-nitrohexane) [17]. This change can be caused by variation of α and $r^{\neq}$ parameters when the length of the aliphatic chain of n-nitroalkanes increases. Assuming that αn values for these compounds are similar under identical conditions, the change of that parameter may reflect the decrease of $r^{\neq}$ with the chain length, which in turn may be due to the increase of the penetration of the surface layer by the reactant.

At higher concentrations of 1-octanol ($c/c_s > 0.7$), the half-wave potential of electroreduction of NP is shifted to less negative values with the increase of c/c_s. In a similar direction there is also shifted, $E^{ir}_{1/2}$, of 1-nitrohexane [17], in opposite to nitromethane for which $E^{ir}_{1/2}$ is moved to more cathodic values. Such influence of 1-octanol at $c/c_s \geq 0.7$ on the electroreduction half wave potential of NP and 1-nitrohexane results probably from their large hydrophobic parts $-C_nH_{2n-1}$ and the higher affinity than that of nitromethane to the mercury electrode surface, practically covered by 1-octanol molecules.

The results presented in Table 3 show that also the reaction rate constant of 1-nitropentane changes non-motonically with concentration of the inhibitor. In the concentration range $0 < c/c_s < 0.5$, k_{fh}, decreases with the rise of 1-octanol in the solutions. In this case the influence of the inhibitor on the reaction rate can be described by (1). The dependence of $\log k_{fh}$, (at constant potential), on $\log c/c_s$ was linear only for $c/c_s < 0.5$ (see Fig. 7). The slope of the steric factor ($r^{\neq}/r_i$) was found to be 2.4. The value of the steric factor for the 1-nitropentane was only slightly higher than that found earlier for 1-nitrohexane ($r^{\neq}/r_i = 2.3$) [17]. It may point on the similar affinity of 1-nitropentane and 1-nitrohexane to the adsorbed layer of 1-octanol molecules on the mercury electrode.

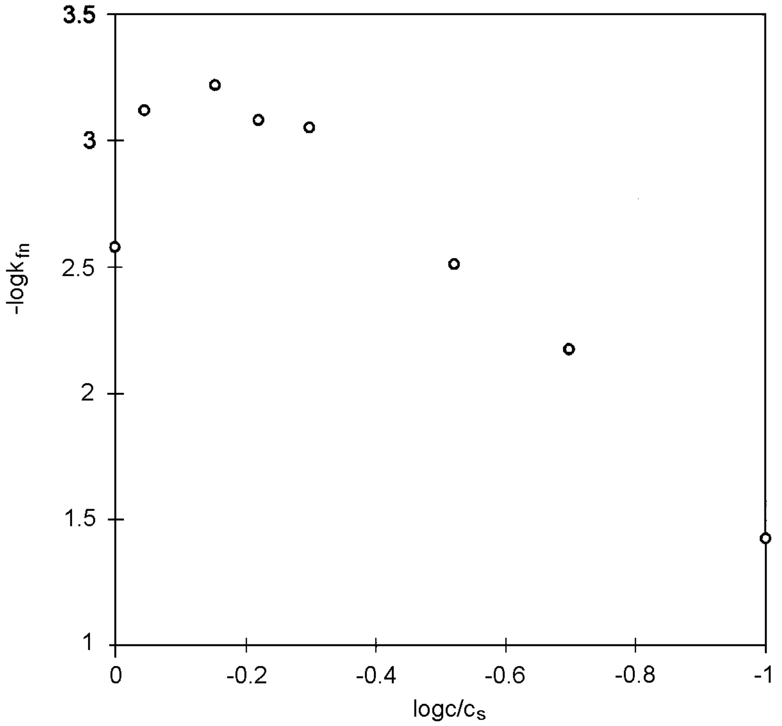

Figure 7. The dependence of the cathodic reaction rate constant for 1-nitropentane electroreduction on the relative $\log c/c_s$ 1-octanol concentration at a constant potential E = –0.70 V, t_p = 49 ms. Supporting electrolyte: 0.50 M $NaClO_4$ with 0.05 M $HClO_4$.

For higher concentration range of inhibitor $0.5 < c/c_s < 0.8$, k_{fh}, changes only slightly. A similar influence of adsorbed higher aliphatic alcohols on the electrode kinetics was observed for 1-nitrohexane [17]. Such behaviour has been predicted by Guidelli and Foresti [6] and by the more general model of Lipkowski and coworkers [24], who assumed that the chemical reaction of reactant with the adsorbed surfactant controls the process.

Formally the independence of the rate constant on the concentration of inhibitor may be also explained by the early model of inhibition represented by:

$$k_\theta = k_{\theta=0}(1-\theta)^a + k_{\theta=1}\theta^b \tag{6}$$

When $k_{\theta=0}(1-\theta)^a << k_{\theta=1}\theta^b$ (7)

which may be observed at the higher inhibitor concentration

$$\frac{c}{c_s} \approx \frac{1}{(1-\theta)^a} \tag{8}$$

then $k_\theta \cong k_{\theta=1}\theta^b$ (9)

Under the condition when $\theta \cong 1$, k_θ becomes virtually independent of the inhibitor concentration, $k_{\theta=1}$ in this simple model represents the rate constant of the process, which occurs on the inhibitor covered surface, while a and b are numerical coefficients.

In our case the limitation of the reaction rate may be explained by the limited solubility of the reactant in the surface layer. Further decrease of the free surface $(1-\theta)$ has no influence on the reaction rate, since θ, which now controls the kinetics, is virtually independent of the inhibitor concentration in this c/c_s range. Independently of the model assumed, there is observed the change of the mechanism of the reaction with c/c_s. This change is indicated not only by the deviation of the kinetics from the simple model (1), but also by the change of the αn parameter with the increase of the concentration of n-octanol. However, the independence of the rate of the c/c_s concentration occurs only in a very limited range of concentration, because already for $c/c_s > 0.7$ the increase of the rate constant with the inhibitor concentration is observed. The reasons of such a behaviour should be searched in the change of the properties of the surface layer, since the change of the bulk properties in this c/c_s range is negligible. (In the range of the relative concentration $0.7 < c/c_s \leq 1.0$ the bulk concentration of 1-octanol changes from 1.12×10^{-3} to 1.6×10^{-3} M [3]).

In the same time the changes, which occur in the surface phase, may be more significant. The decrease of $(1-\theta)$ as the concentration c/c_s increases leads to the drop of water content in the surface phase. Such change should in turn increase the solubility of 1-nitropentane in that phase and due to that also the rate of its electroreduction, what is experimentally observed.

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