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## DETERMINATION OF THE NATURE OF ANODIC CURRENTS OF N-VINYLPYRIDINE ELECTRIC OXIDATION

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**Abstract:** the article shows the characteristics of the electron donation of a solution of n-vinylpyrrolidone (n-VPP) in acetic acid, n-propanol, DMF, DMSO and in their mixtures with acid-base properties of background electrolytes.

**Keywords:** n-vinylpyrrolidone, acetic acid, n-propanol, background electrolyte, titer, reagent, anodic current, electro-oxidation

To optimize the conditions for the amperometric titration of metal ions, along with other factors affecting the shape of the curves and the results of determination, it is also necessary to establish the nature of the anodic currents of electrooxidation of n-vinylpyrrolidone (n-VPP) in the non-aqueous and mixed solutions used.

It is known that the nature of currents of mixed and kinetic nature is extremely necessary and that it is important to strictly thermostat the analyzed n-VPP solution and observe certain formalities. Therefore, a logarithmic analysis was carried out in order to establish and reveal the reversibility and irreversibility of the processes occurring in the solution, as well as to establish the nature of the influence of the rotational speed of the disk microelectrode and the temperature of the n-VPP solution under study on the limiting current and other parameters of the electrochemical oxidation of n-VPP.

In order to establish the kinetics of the electrode processes of oxidation of n-VPP on a platinum disk microanode in non-aqueous and mixed media, a logarithmic analysis of the voltammograms of n-VPP

obtained in a series of experiments was performed. For each such curve, the value  $Y = \log I / I_d - I$  was calculated for 10-15 equidistant values of the potential in the region of the n-runway wave. Then, according to the obtained values, a graph was plotted in Y-X coordinates, where X are the values of the potential. As a rule, in all cases, these plots turned out to be practically rectilinear, however, their slopes to the potential axis were always less than could be expected for a reversible process with the number of electrons participating in it, which indicates the irreversibility of the corresponding electrode process. Data in Table 1. Parameters a and b were calculated based on the experimental values of  $y_i$  and  $x_i$  by the least squares method using the formulas:

$$a = \frac{\sum x_i^2 \sum y_i^2 - \sum x_i y_i}{P \sum x_i^2 - (\sum x_i)^2};$$

$$b = \frac{P \sum x_i y_i - \sum x_i \sum y_i}{P \sum x_i^2 - (\sum x_i)^2}$$

Where P is the number of used values  $x_i$  and  $y_i$

From the found values of the parameters a and b, the values of the half-wave potentials ( $E_{1/2}$ ) and the product  $\alpha n$  were calculated, where  $\alpha$  is the transfer coefficient, and n is the number of electrons

participating in the process. The calculations were carried out according to the formulas:

$$E_{1/2} = -a/b; \alpha n = 0,0584$$

The number of electrons taking part in the electrode reaction, determined from the slope of the straight line, is much less than the true number-2, which was determined by the coulometric method, which also indicates the irreversibility of the process. On the other hand, in accordance with the values (Table 1), it can be concluded that in all background electrolytes and investigated protolytic solutions, n-VPP proceeds completely irreversibly.

Table 1.

Logarithmic analysis of voltammograms of n-PPP oxidation on a platinum disk microanode in non-aqueous media and backgrounds

Protolyticsolvent	Nature and concentration of background electrolyte mol / L	Electroderotationspeed, rpm	$E_{1/2}$	P	$X_i = -E; y = a + bx; y_i = I/I_d - I$	An
Aceticacid	0,25 KCH <sub>3</sub> COO	390	1,12	11	$y = -2,436 + 1,394x$	0,59
	0,20 LiClO <sub>4</sub>	390	1,37	12	$y = -1,984 + 1,078x$	0,35
	0,15 LiNO <sub>3</sub>	390	1,24	10	$y = -3,980 + 2,792x$	0,54
n-propanol	0,25 KCH <sub>3</sub> COO	750	1,03	13	$y = -4,563 + 6,976x$	0,37
	0,20 LiClO <sub>4</sub>	750	1,31	10	$y = -3,980 + 5,087x$	0,78
	0,15 LiNO <sub>3</sub>	750	1,08	11	$y = -4,980 + 4,178x$	0,91

### Electrooxidation of n-VPP at different speeds of rotation of the microdisk electrode and temperatures of the studied solution.

The electrode processes of n-VPP oxidation, which do not accompany the formation of a new phase, in nonaqueousprotolytic media have been

studied extremely poorly. Meanwhile, the study of such processes would make it possible to more fully establish the laws of electrochemical kinetics. To determine the nature of the anodic oxidation current of the n-runway, it was necessary to study the dependence of the limiting current on the number of revolutions of the disk microanode. The study carried out at 25 ° C and various electrode revolutions (380; 725; 1085 and 1400 rpm) showed that the value of the limiting oxidation current of n-runway is proportional to the number of revolutions of the disk microelectrode. Since the nature of the anodic currents of the depolarizer in all background electrolytes of protolytic solvents is the same, Table 2 shows the results of the effect of temperature on the value of the limiting oxidation current of n-VPP only for acetic acid media on different backgrounds. Experiments have shown that when studying the dependence of the limiting oxidation current of n-VPP in protolytic media on the square root of the rotational speed of the disk microanode, all four experimental points corresponding to different electrode velocities fit very well on a straight line passing through the origin, which once again confirms the diffusion nature of the limiting oxidation current of n-HPP on a platinum disk microanode. The detected limitation of the limiting current of electrooxidation of the reagent by the rate of mass transfer was found for all investigated background electrolytes and protolytic solvents.

The revealed fact allows us to consider that for the rate of the process of anodic oxidation of n-VPP it is possible to apply the convective diffusion equation for a rotating disk electrode [1-3]. The experimental data obtained allow us to

conclude that the rate of anodic oxidation of the studied depolarizer in non-aqueous protolytic media, on background electrolytes of different acid-base properties, is limited by diffusion to the electrode.

Table 2.

Dependences of the value of the limiting current of oxidation of n-HPP on a platinum microdisk anode in acetic acid media and various background electrolytes on the temperature of the test solution

The nature of the solvent	Nature and background concentration, mol/l	Current limiting temperature coefficient	Test solution temperature, °C	Limiting current value, μA	
				2·10 <sup>-4</sup> M	4·10 <sup>-4</sup> M
Acetic acid	0,25CH <sub>3</sub> COOK	3,32	24,0	4,05	8,07
	0,25CH <sub>3</sub> COOK	3,43	30,0	4,85	9,71
	0,25CH <sub>3</sub> COOK		40,0	6,55	13,12
	0,20 LiClO <sub>4</sub>	4,15	24,0	7,80	15,58
	0,20 LiClO <sub>4</sub>	3,66	30,0	9,77	19,52
	0,20 LiClO <sub>4</sub>		40,0	13,41	26,82
	0,15 LiNO <sub>3</sub>	4,18	24,0	4,27	8,56
	0,15 LiNO <sub>3</sub>	3,24	30,0	5,45	10,78
	0,15 LiNO <sub>3</sub>		40,0	7,15	14,34

The linear relationship established by us between the concentration of the reagent in the test solution and the limiting current in the range of its oxidation potentials allows us to recommend the use of n-VPP as analytical titrants for ions of various metals in non-aqueous amperometric titrations.

The diffusion nature of the anodic oxidation currents of n-VPP was also confirmed by the found average value of the temperature coefficient of the limiting current of its oxidation at a disk microelectrode rotation speed equal to 1085

rpm in the temperature range 24-40°C, which is 3.0-5.6% per degree (Table 2).

The values of the temperature coefficient of the limiting anode current of the n-runway were calculated according to the equations and method [4-8]:

$$K = [(I_d)_{t_2} - (I_d)_{t_1}] \cdot 100 / (t_2 - t_1) \cdot (I_d)_{t_1}, \%$$

where  $(I_d)_{t_2}$  – is the limiting current at  $t_2$ ;  $(I_d)_{t_1}$  – limiting current at  $t_1$ .

In a wider temperature range, the experiments were not carried out, since below 24°C, the background electrolytes used in the work partially precipitated due to their limited solubility in the used non-aqueous protolytic media, and above 40°C, the gel of the connecting bridge dissolved.

Based on our studies, we can conclude that the proportional relationship between the value of the limiting current and the concentration of the investigated reagent-n-VPP for all studied non-aqueous protolytic solvents and their mixtures with some inert solvents, as well as background electrolytes, is quite well observed in the concentration range  $2 \cdot 10^{-3} - 4 \cdot 10^{-5}$  mol/l.

It was found that the nature of the polarization curves of the oxidation of n-VPP, recorded at different temperatures of the studied solution and the turnover numbers of the platinum disk microanode in all studied background electrolytes and solvents, is diffusion, and its irreversible nature was revealed by the method of logarithmic analysis. Based on the polarization curves, it was found that, when the electrooxidation process of the studied depolarizer on a platinum disk microanode in the studied nonaqueous media is irreversible, the electrode process is accompanied by the release of two electrons, followed by transformation into

simpler substances, the nature of which has not yet been identified.

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