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RESEARCH ARTICLE

ELECTROCHEMICAL BEHAVIOR OF N-VINYL PYRIDINE ON A PLATINUM DISK MICROANODE.

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Abstract

The article shows the influence of the nature of background electrolytes on electro-oxidation of n-vinylpiperidine (n-VPP) and determined the number of electrons during electro-oxidation, also determined the nature of the current currents at different speeds of the rotation of the disk electrode and the temperature of the test solution. It was established that n-VPP can be successfully used as a specific analytical reagent for ions of various metals in non-aqueous amperometry.

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Introduction:-

When developing AT techniques with one or two solid indicator electrodes in any (aqueous, non-aqueous and mixed) medium, it is necessary to know the peculiarities of the voltammetric behavior in it on the corresponding electrode of not only the detected ions, but also the reagent and its complex used in order to choose the optimal titration conditions.

Of considerable analytical interest is the class of organic reagents, which form strong complex compounds with cations of heavy and other metals that are insoluble in water but generally soluble in many organic solvents.

Due to the fact that n-vinylpiperidine (n-VPP) in aqueous, non-aqueous and mixed media has not yet been widely used as an analytical reagent for various cations in the amperometric indication of CTT, it was necessary, first of all, to use it in non-aqueous amperometry, to study the current-voltage behavior of this depolarizer on a platinum microdisk electrode in a protolytic solvent (acetic acid) in the presence of background electrolytes of a different nature and concentration.

The effect of the nature of background electrolytes on the electrooxidation of n-runway. When studying the electrochemical properties of n-runways on a platinum microdisk electrode in a protogenic solvent of acetic acid and 0.25 M sodium and potassium acetates, perchlorate, chloride and lithium nitrate, we found that it produces one anode wave with half-wave potentials equal to for these backgrounds, respectively: 1.18; 1.17; 1.50; 1.31 and 1.22 V (Fig. 1).

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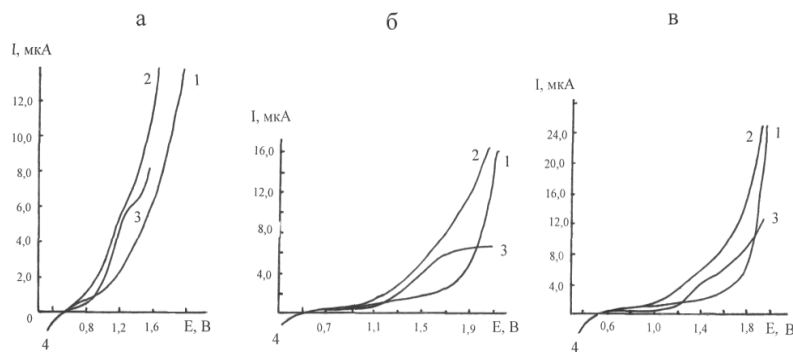


Fig 1:- Voltammograms of n-VPP ($2 \cdot 10^{-4}$ mol / l) in various background electrolytes in acetic acid: a) 0.25 M potassium acetate; б) 0.20 M lithium perchlorate; B) 0.15 M lithium nitrate; 1 — background current, 2 — reagent wave uncorrected for background current, 3 — reagent wave corrected for background current, 4 — oxygen reduction wave.

A directly proportional relationship between the limiting current value of n-runway and its concentration for the studied non-aqueous solutions and background electrolytes is fairly well observed in the concentration range $2 \cdot 10^{-2}$ - $2 \cdot 10^{-5}$ M. Considering the values of the half-wave potentials of oxidation of n-runway, that the oxidation half-wave potential of the depolarizer shifts to the side of less positive values of the potentials during the transition from acidic (lithium perchlorate) to neutral (lithium nitrate and chloride), and then to the main (potassium and sodium acetates) backgrounds.

Determination of the number of electrons during the electrooxidation of n-runway. In studying the mechanism of the electrode process of oxidation of n-runways, first of all, it was necessary to determine the value of "n" - the number of electrons given during its electrooxidation.

In the case of a reversible process determined by diffusion, the number of electrons can be found from the slope of the plot of E versus E , but due to the fact that the electrooxidation of n-runway on a platinum disk microanode on background electrolytes with different acid-base properties and the studied protolytic medium is irreversible, then the definition "n" by the above method is not possible [1]. The number of electrons can also be determined by the known concentration of the depolarizer and its diffusion coefficient, but in this case this method is also unsuitable due to the lack of data on the diffusion coefficient of this reagent in the studied non-aqueous and mixed solutions [2].

It is known that in electrochemical processes with the transfer of several electrons, especially in cases when depolarizers with large complex molecules take part in them, the above methods also do not allow obtaining unambiguous results [3]. Therefore, the number of electron donations during the oxidation of one n-runway molecule was determined coulometrically by the method of determining the amount of electricity from the curve of the current versus time (by the area enclosed under the current – time curve).

The essence of the method is to conduct electrolysis at a constant value of the potential of the working electrode under conditions that exclude the simultaneous occurrence of extraneous processes, and to measure the amount of matter that has reacted to the electrode and the amount of electricity expended on it. The number of electrons was then calculated directly by the Faraday formula:

$$n = \frac{Q \cdot M_i}{F \cdot P}$$

where P is the mass of the substance oxidized or reduced on the electrode, mg; M is its molecular weight, kg / mol; Q - the amount of electricity spent on the electrode reaction, mC; F - Faraday constant (96 487), C / mol. The mass of electrooxidized n-runway was found by the difference in values between the taken amount of the reagent and the remaining amount after electrolysis, in accordance with the formula:

$$P = C_0 V_0 - C_K V_K, \text{ mg}$$

where C_0 is the molar concentration of N-runway (mol / l) before electrolysis, V_0 is the volume of the solution of n-runway (ml) in the electrolyzer, S_k - the remaining molar concentration of n-runway in the solution obtained by its quantitative transfer from the electrolyzer (after electrolysis) to the volumetric flask and diluting it to the mark (mol / l), V_c is the volume of this solution (ml).

The amount of electricity was found by graphically integrating the values of the current strength corrected for the background current (from zero to the end of electrolysis), that is, by determining the area of the figure bounded by the curves of the current strength versus time during electrolysis of the n-runway solution (cr. 1 in Fig. 2.) and background electrolysis (kr.2 in Fig. 2.) and ordinates $t = 0$ and $t = t_e$ (t_e is the electrolysis time). In fig. 2. This area is shaded. Denoting the area of the obtained figure by S_i (mm²), the scale of the values for current and time, expressed in mA / mm and s / mm, respectively, through Q and b , then for the amount of consumed electricity we get the formula:

$$Q = S_i \cdot a \cdot b,$$

where Q is expressed in mC.



Fig 2:-The time dependence of the current strength during potentiostatic electrolysis of the n-runway solution (cr. 1) and the background solution (cr. 2).

Substituting the expressions for P and Q in equation (1) we obtain the final formula for determining the number of electrons - n [4]:

$$n = \frac{S_i \cdot a \cdot b \cdot M}{F(C_o V_o - C_k V_k)}$$

The values of S_i , a , b , C_0 , V_0 , C_k , V_k and the numbers of electrons found from them during the oxidation of n-WFP in the studied protolytic medium and the results of determining the number of electrons participating in the oxidation of one molecule of n-WFP on a platinum microdisk anode in acetic acid and background electrolytes of various nature ($V_0 = 80.0$ ml, $V_c = 250$ ml, $a = 12.5$ s / mm, $b = 0.047$ mA / mm) are presented in table 1.

Table 1.

The results of determining the number of electrons involved in the oxidation of one n-runway molecule on a platinum microdisk anode.

Solvent	The nature and concentration of the background electrolyte, mol / l	S_i , mm ²	E , B	C_o , mol / L	C_c , mol / l	"n"
Acetic acid	0,25 CH ₃ COOK	1009	1,11	0,1809	0,1099	0,97
	0,25 CH ₃ COONa	1012	1,20	0,1737	0,1087	0,98
	0,15 LiNO ₃	11405	1,24	0,1431	0,0722	1,01
	0,15 LiCl	12241	1,41	0,1539	0,0804	1,02
	0,20 LiClO ₄	11496	1,52	0,1607	0,0901	1,03

Thus, it was found that the number of electrons emitted during the oxidation of one n-WFP molecule on a platinum electrode in CH₃COOH and the studied background electrolytes is close to unity (Table 1).

To determine the number of electrons participating in the electrode reaction during the electrooxidation of n-runway on a platinum microanode and to prove the reversibility or irreversibility of this process, we used a logarithmic analysis of its current-voltage curves in background electrolytes with different acid-base properties and non-aqueous protolytic medium - acetic acid. For each such curve, the dependence was calculated for 10-15 equally spaced potential values in the region of the n-runway wave, and then a graph was plotted based on the obtained values. In all cases, these dependences were almost straightforward.

However, the slopes of the potentials direct to the axis of the axis, as a rule, were always much smaller than would be expected for a reversible process with the number of electrons participating in it equal to 1, which indicates poor reversibility (irreversibility) of the corresponding electrode process.

The equations of all the straight lines $y = a + bE$ we obtained are shown in Table 2, the parameters a and b in these equations were calculated on the basis of the experimental values of "y" and "E" using the least squares method using the formulas:

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

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

where P is the number used to calculate the values;

$$y = \lg \frac{I}{I_d - I}$$

$x_i = -E$ и

Using these values of parameters a and b , the most probable half-wave potentials $E_{1/2}$ and the product αn were calculated, where α is the transfer coefficient and n is the number of electrons participating in the process. The calculations were carried out according to the formulas:

$$E_{1/2} = -\frac{a}{b}$$

и $\alpha n = 0,0584 \cdot b$

The results of a logarithmic analysis of voltammograms of the oxidation of n-runway on a platinum microanode.

Solvent	The nature and concentration of the background, mol / l	Electrode rotation speed, rpm	P	$y = a + bE$ $y = \lg \frac{I}{I_d - I}$ $x_i = -E;$	$E_{1/2}, B$	αn
CH ₃ COOH	0,25 CH ₃ COOK	1085	12	$y = -4,9831 + 3,2461 \cdot x$	1,10	0,16
	0,25 CH ₃ COONa		13	$y = -3,5302 + 3,0173 \cdot x$	1,19	0,17
	0,15 LiNO ₃		13	$y = -2,7165 + 2,1732 \cdot x$	1,23	0,12
	0,15 LiCl		11	$y = -3,8882 + 2,8562 \cdot x$	1,40	0,18
	0,20 LiClO ₄		12	$y = -5,0600 + 3,5391 \cdot x$	1,51	0,20

As can be seen from the illustrated data (Table 2), the number of electrons participating in the electrode reaction established by the slope of the straight line is much smaller than the true number (1) obtained by the coulometric method, which once again indicates the irreversibility of the electrooxidation of n-runways in the studied acetic acids environments.

The reason for the slow progress of the electrochemical reaction, apparently, is the slow conversion of the depolarizer into its more active form, capable of electron exchange, which is associated with the expenditure of a certain activation energy. In such cases, the limiting oxidation current of the reagent, as a rule, is diffusive.

Establishing the nature of the anode currents at various rotational speeds of the microdisk electrode and the temperatures of the test solution. Electrode processes that are not accompanied by the formation of a new phase in non-aqueous and mixed solutions are extremely poorly studied. Meanwhile, the study of such processes would more fully establish the laws and anomalies of electrochemical kinetics.

To determine the nature of the anodic oxidation current of n-runway, first of all, it was necessary to identify the dependence of the limiting current of the depolarizer on the number of revolutions of the disk microanode. A study conducted at 24 ° C and various electrode revolutions (380, 725, 1085, 1400 rpm) showed that the limiting value of the reagent oxidation current is directly proportional to the number of revolutions of the disk microanode (Fig. 3.).

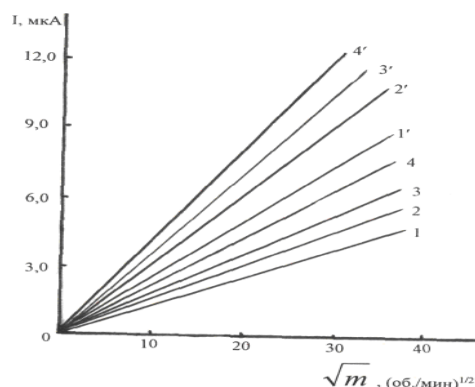


Fig 3:-Dependence of the limiting oxidation current of n-runway on $(r / \text{min})^{1/2}$ in CH_3COOH . Background concentration, mol / L: 1; 1' - 0.20 M LiNO_3 ; 2; 2' - 0.25 M CH_3COOK ; 3; 3' - 0.20 M LiClO_4 ; 4; 4' - 0.15 M LiCl . The concentration of n-runway, mol / l: 1; 2; 3; 4, - $2 \cdot 10^{-4}$, 1'; 2'; 3'; 4' - $4 \cdot 10^{-4}$.

In Fig. 3. As an example, the dependence of the values of the limiting oxidation current of n-runway in acetic acid on the square root of the rotation speed of the microanode in all the studied backgrounds is given. Table 3.

Results and dependences of the limiting current strength of electrooxidation of one n-runway molecule on a platinum microdisk anode

The nature and concentration of the background, mol / l	Electrode rotation speed, rpm	\sqrt{m} , (об/мин) ^{1/2}	The value of the limiting current, μA	
			$2 \cdot 10^{-4} \text{ M}$	$4 \cdot 10^{-4} \text{ M}$
1	2	3	4	5
0,25 CH_3COONa	380	19,49	3,96	7,94
	725	26,93	5,12	10,25
	1085	32,94	6,18	12,36
	1400	37,42	7,06	13,98
0,25 CH_3COOK	380	19,49	4,05	8,11
	725	26,93	5,21	10,43
	1085	32,94	6,27	12,55
	1400	37,42	7,15	14,31
0,15 LiCl	380	19,49	4,44	8,85
	725	26,93	6,00	11,97
	1085	32,94	7,16	14,26
	1400	37,42	8,24	16,43

0,15 LiNO ₃	380	19,49	4,40	8,81
	725	26,93	5,96	11,93
	1085	32,94	7,12	14,22
	1400	37,42	8,20	16,39
0,20 LiClO ₄	380	19,49	7,78	15,56
	725	26,93	10,65	21,24
	1085	32,94	12,66	25,32
	1400	37,42	15,51	29,02
1	2	3	4	5
0,15 KNO ₃	380	19,50	4,60	8,91
	725	26,97	5,76	12,03
	1085	32,98	7,82	14,32
	1400	37,48	15,91	29,42
0,20 KClO ₄	380	19,60	4,50	8,85
	725	26,63	5,66	11,96
	1085	32,64	7,72	14,27
	1400	37,62	15,81	29,16

As can be seen from the dependence of the limiting current of n-WFP oxidation on $(r / \text{min})^{1/2}$ in CH₃COOH (Fig. 3.) and the results and the dependence of the limiting current of electrooxidation of one n-WFP molecule on a platinum microdisk anode in an acetic acid medium in the presence of various by the nature of the background electrolytes from the square root of the number of revolutions of the electrode per min. (Table 3.), all four experimental points corresponding to different speeds of rotation of the electrode fit well on the straight line passing through the origin, which indicates the diffusion nature of the limiting current of electrooxidation of the n-runway on a platinum disk microanode.

Table 4:-Results of the dependence of the limiting oxidation current of n-runway on a microdisk anode on the temperature of acetic solutions.

The nature and concentration of the background, mol / l	Temperature coefficient of limiting current	The temperature of the test solution, 0C	The value of the limiting current, μA	
			2.10-4M	4.10-4M
0,25 CH ₃ COONa	3,37	24,0	4,08	8,12
0,25 CH ₃ COONa	3,38	30,0	4,90	9,76
0,25 CH ₃ COONa	3,41	40,0	6,60	13,17
0,25 CH ₃ COOK	3,39	24,0	4,12	8,16
0,25 CH ₃ COOK	3,51	30,0	4,94	9,80
0,25 CH ₃ COOK	3,65	40,0	6,64	13,21
0,15 LiCl	4,27	24,0	4,36	8,65
0,15 LiCl	3,33	30,0	5,44	10,87
0,15 LiCl	3,21	40,0	7,24	14,43
0,15 LiNO ₃	4,23	24,0	4,32	8,61
0,15 LiNO ₃	3,29	30,0	5,40	10,83
0,15 LiNO ₃	3,12	40,0	7,20	14,39
0,20 LiClO ₄	4,20	24,0	7,85	15,63
0,20 LiClO ₄	3,71	30,0	9,82	19,59
0,20 LiClO ₄	3,43	40,0	13,46	26,87

The detected limitation of the limiting anode current of n-WFP oxidation by the mass transfer rate was established for all studied background electrolytes and the used protolytic solvent - CH₃COOH. This conclusion is also confirmed by the found average value of the temperature coefficient of the limiting current of oxidation of the n-runway, which is found in the temperature range 24-40 ° C and is equal to 3.5 - 4.5% per degree (Table 4).

No experiments were performed at wider solution temperature ranges, since below 24 ° C, the used backgrounds in the studied protolytic media, due to their limited solubility, partially precipitated, and above 40 ° C, the agar-agar gel

of the connecting bridge was dissolved. Based on the studies, it was found that during the electrooxidation of one n-runway molecule on a platinum microdisk anode in protolytic non-aqueous media, depending on the nature of the background and medium, the half-wave ($E_1 / 2$) potential of the reagent oxidation shifts to the region of more positive potentials upon transition from less acidic to more acidic backgrounds.

It has been shown that a direct proportional relationship between the limiting current value and the concentration of the reagent used for all studied nonaqueous solutions and background electrolytes is fairly well observed in the concentration range $2 \cdot 10^{-2}$ - $2 \cdot 10^{-5}$ mol / l.

Based on the polarization curves of the oxidation of n-runways, taken at different solution temperatures and revolutions of the platinum disk microanode in all the studied backgrounds and non-aqueous solutions, the diffusion nature of the reagent electrooxidation current was established, and its irreversible nature was established by logarithmic analysis.

The revealed patterns are important for clarifying the need for thermostating of the analyzed solutions. It was established that the process of electrooxidation of n-runway on a platinum disk microanode in all studied media is irreversible and is accompanied by the recoil of one electron.

The data obtained suggest that n-runway can be successfully used as a specific analytical reagent for ions of various metals in non-aqueous and mixed amperometric titrations.

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