ELECTROCHEMICAL BEHAVIOR OF DIETHYLAMINO-4-METHYL-HEXIN-OL-4 ON A PLATINUM DISK MICROANODE IN NON-AQUEOUS MEDIA

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ABSTRACT: The article shows the influence of the nature of background electrolytes on electro-oxidation of diethylamino-4-methyl-hexin -2-ol-4 (DEMGO) and determined the number of electrons during electro-oxidation, also determined the nature of the anode current at different speeds of the rotation of the disk electrode and the temperature of the test solution. It was established that DEAMHO can be successfully used as a specific analytical reagent for ions of various metals in non-aqueous amperometry.

KEYWORDS: dietilamino-4-metil-hexin-2-ol-4, solution, acetic acid, perchlorate lithium, nitrate lithium, background electrolytes, electrolysis time, concentration.

INTRODUCTION

When developing amperometric titration methods 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 not only of the detected ions, but also the reagent and its complex used in order to correctly select the optimal titration conditions.

Of considerable interest from an analytical point of view is the class of organic reagents, which form with the cations of heavy and other metals durable complex compounds, insoluble in water, but generally well soluble in many organic solvents.

Due to the fact that diethylamino-4-methyl-hexin-2-ol-4 (DEAMHO) 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 titration endpoint, in order to use it in non-aqueous amperometry, it was necessary, first of all, to investigate the current-voltage behavior of this depolarizer on a platinum microdisk electrode in a

protolytic solvent medium (acetic acid) in the presence of different in nature and concentration of background electrolytes.

The influence of the nature of background electrolytes on electro-oxidation DEAMHO. When studying the electrochemical properties of DEAMHO on a platinum microdisk electrode in protogenic solvent acetic acid against 0.25 M sodium and potassium acetates, perchlorate, lithium nitrate, we found that it gives one anodic wave with half-wave potentials equal to backgrounds respectively: 1.18; 1.17; 1.50; 1.31 and 1.22 V (Fig. 1).
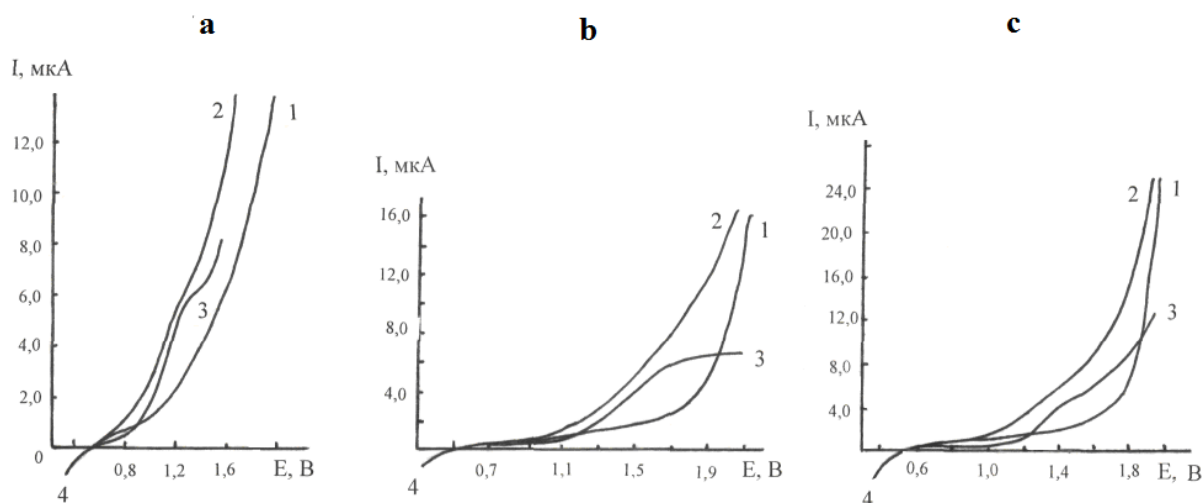

Fig.1. Voltamperogram DEAMHO ($2 \cdot 10^{-4}$ mol/l) in various background electrolytes in acetic acid: a) 0.25 M potassium acetate; b) 0.20 M lithium perchlorate; c) 0.15 M lithium nitrate; 1 is the background current, 2 is the reagent wave uncorrected to the background current, 3 is the reagent wave corrected to the background current, 4 is the oxygen reduction wave.

The direct proportional relationship between the magnitude of the current of DEAMHO and its concentration for the studied non-aqueous solutions and background electrolytes is fairly well observed in the concentration range of $2 \cdot 10^{-2}$ - $2 \cdot 10^{-5}$ M. Considering the values of the half-wave oxidation potential, it can be noted that the depolarizer oxidation half-wave potential shifts towards less positive potentials when going from acidic (lithium perchlorate) to neutral (lithium nitrate and lithium chloride), and then to basic (potassium and sodium acetates) backgrounds.

Determination of the number of electrons during electro-oxidation DEAMHO. When studying the mechanism of the electrode process of DEAMHO oxidation, first of all, it was necessary to determine the value of "n" - the number of electrons released during its electro-oxidation.

In the case of a reversible process determined by diffusion, the number of electrons can be found from the slope of the plot of dependence of $\lg \dfrac{I}{I_d - I}$ on E, but due to the fact that electro-oxidation of DEAMHO on a platinum disk microanode on different acid-base properties of the background electrolytes and the studied protolytic medium is irreversible, the definition of "n" by the above method is not possible.

The number of electrons can also be determined from 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.

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 to obtain unambiguous results. Therefore, the number of electron donations during the oxidation of one DEAMHO molecule was found coulometrically by the method of determining the amount of electricity from the current vs. time curve (over the area enclosed by 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 reacted on the electrode and the amount of electricity expended on it. The number of electrons was then calculated directly using the Faraday formula:

$$n = \frac{Q \cdot M_i}{F \cdot P} \ , \qquad\qquad (1)$$

where P is the mass of the substance oxidized or reduced on the electrode, mg; M is its molecular weight, kg / mol;

Q is the amount of electricity spent on the electrode reaction, mCl;

F is the Faraday constant (96487), Cl/mol.

The mass of electro-oxidized DEAMHO was found from the difference in values between the amount of reagent taken and the amount remaining after electrolysis, in accordance with the formula:

$$P = C_o V_o - C_к V_к, \ мг \qquad\qquad (2)$$

where C_o is the molar concentration of DEAMHO (mol / l) before electrolysis,

V_o is the volume of the DEAMHO solution (ml) in the electrolyzer,

C_k - the remaining molar concentration of DEAMHO in the solution obtained by its quantitative transfer from the electrolyzer (after the end of electrolysis) into a volumetric flask and diluting it to the mark (mol/l),

$V_К$ - 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 time-current curves during electrolysis of the DEAMHO solution (Fig. 1).) and electrolysis of the background (curve 2 in Fig. 2) and ordinates t = 0 and t = t_e (t_e - electrolysis time). In fig. 2 this area is shaded. Having designated the area of the obtained figure as S_i (mm^2), the scales of values for current and time, expressed in mA / mm and s / mm, respectively, through Q and b, then for the amount of electricity consumed we obtain the formula:

$$Q = S_i \cdot a \cdot b, \qquad (3)$$
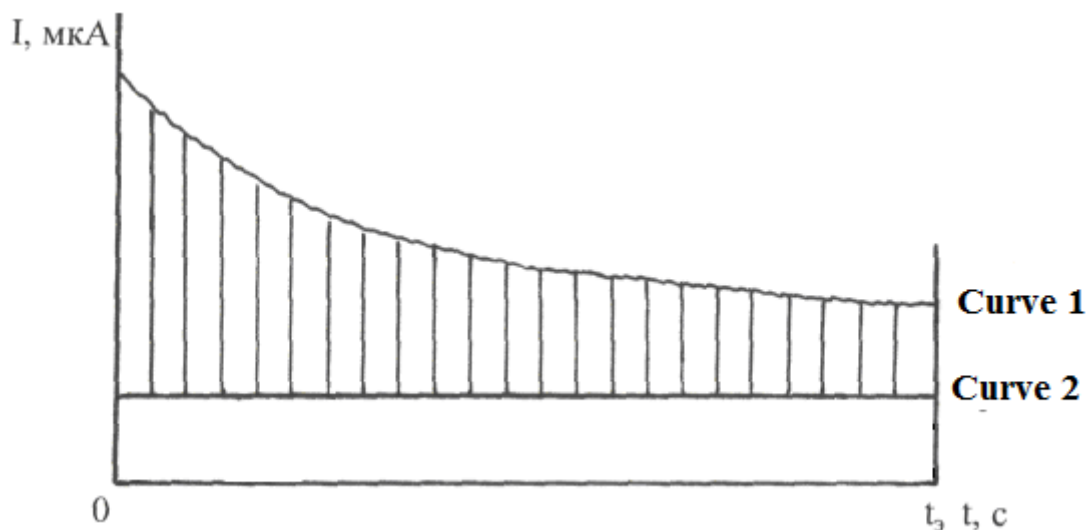
where Q is expressed in mCl.

Fig.2. The curve of current values versus time in the potentiostatic electrolysis of the DEAMHO solution (curve 1) and the background solution (curve 2).

Substituting the expressions for P and Q into equation (1), we obtain the final formula for determining the number of electrons:

$$n = \frac{S_i \cdot a \cdot b \cdot M}{F(C_o V_o - C_\kappa V_\kappa)}$$

(4)

The values of S_i, a, b, C_o, V_o, C_k, V_k and the numbers of electrons found from them during the oxidation of DEAMHO in the studied protolytic medium are presented in table 1.

Thus, it was established [1-4] that the number of electrons released during the oxidation of one DEAMHO molecule on a platinum electrode in CH_3COOH and the background electrolytes studied is close to one (Table 1).

To determine the number of electrons participating in the electrode reaction during the electrooxidation of DEAMHO on a platinum microanode and to prove the reversibility or irreversibility of this process, a logarithmic analysis of its current-voltage curves in different acid-base properties of the background electrolytes and non-aqueous protolytic medium — acetic acid was used. For each such curve, the magnitude of the dependence $y = lg \frac{I}{I_d - I}$ was calculated for 10–15 equidistant values of potentials in the region of the DEAMHO wave, and then a graph was plotted using the obtained values. In all cases, these dependences were almost rectilinear. However, the slopes of the lines to the potential axis, as a rule, were always much smaller than could be expected for a reversible process with the number of electrons participating in it equal to 1, which indicates a poor reversibility (irreversibility) of the corresponding electrode process.

Table 1

The results of determining the number of electrons participating in the oxidation of one DEAMHO molecule on a platinum microdisk anode in acetic acid and background electrolytes of different nature
(V_o = 80.0 ml, V_k = 250 ml, a = 12.5 s / mm, b = 0.047 mA / mm)

Solvent	Nature and concentration of background electrolyte, mol/l	S_i, mm^2	E, V	C_o, mol/l	$C_к$, 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

The equations of all the straight lines y = a + bE we have obtained are given 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:

$$a = \frac{\sum x_i^2 \cdot \sum y_i - \sum x_i \cdot \sum x_i y_i}{P \sum x_i^2 - \left(\sum x_i\right)^2} \qquad (5)$$

and $$b = \frac{P \sum x_i y_i - \sum x_i \cdot \sum y_i}{P \sum x_i^2 - \left(\sum x_i\right)^2}, \qquad (6)$$

where P is the number used to calculate the values;

$$x_i = -E \quad \text{and} \quad y = \lg \frac{I}{I_d - I} \qquad (7)$$

Using these values of the parameters "a" and "b", the most probable values of the potentials of the half-waves $E_{1/2}$ and the product "αn" we the transport coefficient and n is the number of electrons participating in the process.

The re calculated, where α is calculations were carried out according to the formulas:

$$E_{1/2} = -\frac{a}{b} \qquad (8)$$

and $$\alpha n = 0,0584 \cdot b \qquad (9)$$

Table 2

The results of a logarithmic analysis of the voltamograms of the DEAMHO oxidation on a platinum microanode in acetic acid media

. Solvent	Nature and concentration of background, mol/l	Electrode rotation speed, rpm	P	y=a+bE $x_i = -E$; $y = \lg \frac{I}{I_d - I}$	$E_{1/2}$, V	αn
CH$_3$COOH	0,25 CH$_3$COOK	1085	12	y=-4,9831+3,2461·x	1,10	0,16
	0,25 CH$_3$COONa		13	y=-3,5302+3,0173·x	1,19	0,17
	0,15 LiNO$_3$		13	y=-2,7165+2,1732·x	1,23	0,12
	0,15 LiCl		11	y=-3,8882+2,8562·x	1,40	0,18

0,20 LiClO$_4$		12	y=-5,0600+3,5391·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 less than the true number (1) obtained by the coulometric method, which once again indicates the irreversibility of the process of electro-oxidation of DEAMHO in the acetic acid media studied.

The reason for the slow course of the electrochemical reaction, apparently, is the slow transformation of the depolarizer into its more active form, capable of exchanging electrons, which is associated with the expenditure of a certain activation energy. In such cases, the limiting oxidation current of the reagent, as a rule, has a diffusion character.

Establishment of the nature of the anode currents at different speeds of rotation of the microdisk electrode and 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 studied extremely insufficiently. Meanwhile, the study of such processes would allow us to more fully establish the laws and anomalies of electrochemical kinetics.

To determine the nature of the anode current of DEAMHO oxidation, first of all, it was necessary to identify the dependencies of the magnitude of the depolarizer current limit on the number of revolutions of the disk microanode. The study conducted at 24°C and various electrode speeds (380, 725, 1085, 1400 rpm), showed that the magnitude of the reagent oxidation current limit is directly proportional to the number of revolutions of the disk microanode (Fig. 3.).
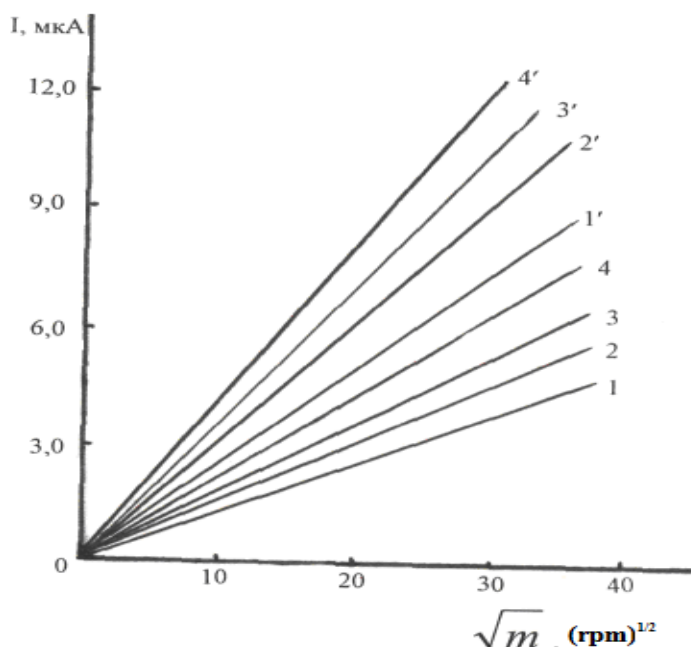

Fig.3. Dependence of the limiting oxidation current of DEAMHO on $\sqrt{m}$ (rpm)$^{1/2}$ in CH$_3$COOH. Background concentration, mol/l: 1, 1 '- 0.20 MLiNO$_3$; 2, 2 '- 0.25 M CH$_3$COOK; 3, 3 '- 0.20 MLiClO$_4$; 4, 4 '- 0.15 MLiCl. Concentration of DEAMHO, mol/l: 1,2, 3, 4, - 2·10^{-4}; 1 ', 2', 3 ', 4' - 4·10^{-4}.

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

As can be seen from the figure and data table. 3, all four experimental points corresponding to different electrode rotation speeds fit well onto a straight line passing through the origin of coordinates, which indicates the diffusion nature of the DEAMHO electro-oxidation current limit on a platinum disk microanode.

The detected limitation of the anode current of DEAMHO oxidation by the mass transfer rate was established for all studied background electrolytes and the used protolytic solvent - CH_3COOH. This conclusion is also confirmed by the found average value of the temperature coefficient of the electrochemical oxidation current of DEAMHO, which is found in the temperature range of 24-40 ° C and is equal to 3.5 - 4.5% per degree (Table 4). The experiments were not conducted in wider temperature ranges of the solution, since the backgrounds used in the studied protolytic media were below 24 ° C due to their limited solubility partially precipitated, and above the 40 ° C there was a dissolution of the agar-agar gel of the connecting bridge.

Table 3

Results and dependences of the strength of the limit current of electrooxidation of one DEAMHO molecule on a platinum microdisk anode in an acetic acid medium in the presence of background electrolytes of different nature on the square root of the number of electrode rotation per minute.

Nature and concentration of background, mol/l	Electrode rotation speed, rpm	$\sqrt{m}$, (rpm)$^{1/2}$	Value of the limiting current, µA	
			$2 \cdot 10^{-4}$ M	$4 \cdot 10^{-4}$ M
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
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

Table 4

The results of the dependence of the magnitude of the limiting oxidation current of one DEAMHO molecule on a platinum microdisk anode on the temperature of the studied non-aqueous acetic acid solutions

Nature and concentration of the background, mol/l	Temperature coefficient of the limiting current	Temperature of the test solution, ^{0}C	Value of the limiting current, μA	
			$2 \cdot 10^{-4}$M	$4 \cdot 10^{-4}$M
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		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		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		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$_3$		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$_4$		40,0	13,46	26,87

Based on the research, it was established that during electrooxidation of one DEAMHO molecule on a platinum microdisc anode in protolytic non-aqueous media, depending on the nature of the background and the medium, the half-wave potential ($E_{1/2}$) of the oxidation of the reagent shifts to a more positive potential acidic backgrounds. It was shown that a direct proportional relationship between the magnitude of the limiting current and the concentration of the reagent used for all studied non-aqueous solutions and background electrolytes is fairly well observed in the concentration range $2 \cdot 10^{-2} - 2 \cdot 10^{-5}$ mol/l.

CONCLUSIONS

In conclusion, the diffusion nature of the reagent electro-oxidation current was established in all studied backgrounds and non-aqueous solutions on the basis of the polarization oxidation curves of

DEAMHO taken at different solution temperatures and rotational speeds of the platinum disk microanode, and its irreversible nature was determined 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 electro-oxidation of DEAMHO on a platinum disk microanode in all studied environments is irreversible and is accompanied by the recoil of one electron.

The obtained data suggested that DEAMHO 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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