EFFECT OF AMMONIUM IONS ON THE POLAROGRAPHIC BEHAVIOR OF NITRILES AND AMIDES OF SOME PYRIDINECARBOXYLIC ACIDS

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The character of the polarographic reduction of picolinonitrile, nicotinonitrile, isonicotinonitrile, isocinchomeronic acid dinitrile, picolinamide, and nicotinamide on a dropping mercury electrode with a buffer-solution base electrolyte in the presence of ammonium ions depends on the concentration of the ammonium ions, which interact with the ring nitrogen.

In a study of the polarographic behavior of cyanopyridines [1] in the presence of various base electrolytes it was noted that nicotinonitrile (I) in ammonium hydroxide solution (in contrast to alkalis) gives polarograms with not one but two one-electron diffusion waves, the heights of which depend in different manners on the NH_4OH concentration. A similar pattern is also observed in other electrolytes that contain the ammonium ion [2]. We were unable to find information in the literature regarding the action (other than hydrolytic) of ammonia solutions on cyanopyridines. In this connection, it seemed expedient to make a systematic study of the effect of ammonium ions on the polarographic reduction of cyanopyridines and some other pyridine derivatives.

The polarograms of the cyanopyridines, which were recorded in an Izmailov–Pivneva buffer-solution base electrolyte (base electrolyte A) with pH 8.0, demonstrated that in the absence of ammonium ions I gives two waves, the half-wave potentials of which are −1.50 and −1.96 V, and the limiting currents are 0.3 and 2.0 μA. The addition of ammonia to the indicated solution has a substantial effect on the electrode reactions, since the limiting current of the second wave is reduced to 1.0 μA (Fig. 1a, curve 2), while the first wave, which characterizes the reduction of the protonated molecules (curve 1), increases, and its potential is shifted to the negative side. It should be noted that the effect of ammonium ions is displayed most sharply when they are introduced into the electrolyte in amounts that do not exceed the equimolar

TABLE 1. Polarographic Characteristics of Cyanopyridines (c $4 \cdot 10^{-4}$ M) in Ammonium-Salt Base Electrolytes

Compound	0,1 N NH_4Cl				0,1 N $(NH_4)_2SO_4$				0,1 N $(NH_4)_2C_2O_4$			
	$-E_{1/2}$, V	i, μA	slope	αn_α	$-E_{1/2}$, V	i, μA	slope	αn_α	$-E_{1/2}$, V	i, μA	slope	αn_α
Picolinonitrile	1,36	3,2	0,060	0,97	1,31	0,36	0,076	0,76	1,31	3,1	0,074	0,78
Nicotinonitrile	1,53	2,4	0,050	1,18*	1,47	1,85	0,053	1,10	1,48	1,85	0,053	1,10
	1,81	2,0	0,057	1,03*	1,74	1,56	0,056	1,05	1,74	2,0	0,056	1,05
Isonicotinonitrile	1,18	4,1	0,059	1,00	1,14	4,0	0,059	1,00	1,18	4,1	0,057	0,97
	1,83	6,0	0,071	0,83	1,82	9,1	0,075	0,79	1,87	8,8	0,059	1,00

* The n values, which were found by microcoulometry, are 1.06 and 1.04, respectively.

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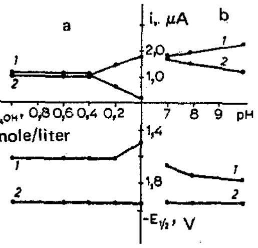

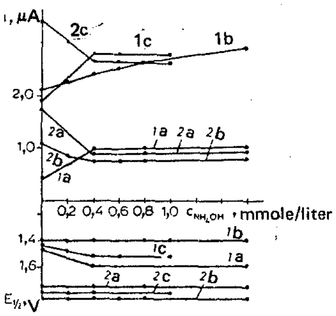

Fig. 2

Fig. 1. Dependence of the limiting current and the half-wave potentials of 3-cyanopyridine (I, c $4 \cdot 10^{-4}$ M) on the concentration of added ammonium hydroxide (base electrolyte A, pH 8) and on the pH of the ammonium hydroxide solution (base electrolyte B, c_{NH_4OH} $1\text{-}6 \cdot 10^{-2}$ M): 1) for the first half-wave; 2) for the second half-wave.

Fig. 2. Dependence of the current and half-wave potentials of nicotinamide (a), picolinamide (b), and picolinonitrile (c) on the concentration of added ammonium hydroxide in base electrolyte A (pH 7.0, c_{dep} $4 \cdot 10^{-4}$ M): 1) for the first half-wave; 2) for the second half-wave.

quantity with respect to I. When the ammonium-ion concentration is further increased, the half-wave potential and the current retain constant values. The limiting current in this case is limited by diffusion.

An investigation of the polarographic behavior of I as a function of the pH of a universal buffer solution for c_{NH_4OH} $1\text{-}6 \cdot 10^{-2}$ M (base electrolyte B) demonstrated that two electrode processes are realized simultaneously (Fig. 1b) in alkaline media (pH 8-10). One proceeds with participation of hydrogen ions (wave 1, $\Delta E_{1/2}/\Delta pH = -33$ mV/pH unit) [3], while hydrogen ions do not participate in the other process (wave 2). Both of these processes are one-electron processes. The sum of the currents of both reduction waves is constant, but the magnitude of the current of each of them depends on the pH of the medium. It should be noted that when ammonium ions are absent, wave 1 is practically absent in base electrolyte A at pH > 8 [1].

Picolinonitrile, the amides of picolinic and nicotinic acids (Fig. 2), 4-cyanopyridine (II, $E_{1/2} = -1.30$ V*), and 2,5-dicyanopyridine (III, $E_{1/2} = -1.22$ V*) are reduced like I in ammonia solutions on a dropping mercury electrode. However, the changes in the current and half-wave potentials are less significant in the case of II and III.

The results of the investigation of the polarographic behavior of nitriles of pyridinecarboxylic acids in ammonium-salt base electrolytes are presented in Table 1. In this case, two waves with half-wave potentials of ~ −1.5 and −1.8 V are observed on the polarograms of I. The first wave has a well expressed limiting current. Measurement of the current of the second wave is hindered because of reduction of ammonium ions. As in the ammonium hydroxide base electrolyte, both waves correspond to reversible one-electron reduction. It is characteristic that I is reduced in one step in K^+, Na^+, and Li^+ salt base electrolytes. It is necessary to note that the investigated starting materials do not undergo hydrolytic transformations under the described conditions.

Thus the results of the experiments showed that processes that indicate the interaction of ammonium ions with the depolarizer occur during the reduction of nitriles and amides of pyridinecarboxylic acids on a dropping mercury electrode in buffer solutions in the presence of ammonium hydroxide. The structure of the substituent attached to the pyridine ring apparently does not have a decisive effect on this reaction, since the action of ammonium ions both on cyanopyridines and on the corresponding amides is by and large

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* Base electrolyte A, pH 7.0.

similar. In both cases, the greatest effect from the presence of ammonium ions is manifested for an equimolar ratio of ammonium ions and the investigated substance. It should be noted that when the pH increases due to ammonium hydroxide, the dependence of the magnitude of the current of the nitriles and amides of pyridine-2-carboxylic acid and pyridine-3-carboxylic acid on the pH is the same as in the case of an increase in the concentration of hydrogen ions [1]. Moreover, when ammonia is present, new waves do not appear on the polarograms of these pyridine derivatives, and one observes only that the waves of the reduction of the protonated molecules increase, and the waves corresponding to the electrode processes in which hydrogen ions do not participate decrease. Considering this, the nature of this phenomenon can be explained by interaction of the ammonium ions, which are proton donors [4], with the nitrogen atom of the pyridine ring. The reaction is completed by transfer of a proton to molecules of the reduced pyridine derivatives. When $c_{NH_4OH} < c_{dep}$, the addition of NH_4^+ to the ring nitrogen is apparently realized in the near-electrode space, while when $c_{NH_4OH} > c_{dep}$ it is realized in the depths of the solution, since the height of wave 1 depends on c_{NH_4OH} in the first case but is independent of it in the second case. The second step of the above-indicated reaction (addition of an electron and formation of an H−N bond) proceeds on the electrode surface.

The elucidated regularities make it possible to conclude that the quantitative determination of pyridine derivatives in the presence of ammonium ions should be carried out when $c_{NH_4OH} > c_{dep}$.

EXPERIMENTAL

The polarograms were recorded with a PÉ-312 electronic polarograph in a thermostatted cell at 25 ± 0.2°. The oxygen was removed from the solutions with a jet of argon saturated with water vapors. The half-wave potentials were determined from graphs of the dependence of $\log [i/(i_{lim}-i)]$ on E and were corrected with allowance for the cell resistance. The comparison electrode was an external calomel half cell. The pH values of the solutions were measured with a pH meter. The capillary had the following characteristics (for $E=0$ and $h=40.4$ cm): $m=3.1$ mg/sec, $t=1.3$ sec, $m^{2/3}t^{1/6}=2.04$ mg$^{2/3}$sec$^{-1/2}$. The base electrolytes used were the Izmailov−Pivneva aqueous buffer solution [5] with lithium hydroxide (base electrolyte A) and universal buffer solutions prepared from phosphoric, boric, and acetic acids [6], the pH of which was brought up to 8-10 with aqueous ammonium hydroxide (base electrolyte B).

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