SURFACE CATALYTIC HYDROGEN EVOLUTION IN POLAROGRAPHY OF NONBUFFER PYRIDINE SOLUTIONS*

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Original article submitted February 26, 1963

In polarography of pyridine solutions with electrodes having a very short dropping period, t, and at quite high concentrations of the indifferent electrolyte, i.e., under conditions unfavorable to pyridine adsorption on the mercury drop electrode, the catalytic hydrogen waves are of a purely volume nature [1-3]. However, if the concentration of the indifferent electrolyte is reduced, or the cations in it, having appreciable superequivalent adsorption [4], are replaced by less adsorbable cations (for example, on going along the series from Cs⁺ to Li⁺ salts), pyridine solutions show an appreciable additional surface catalytic current [3], due to the pyridine protonation reaction taking place in the adsorbed state.

In the present paper, making use of the existing data on pyridine adsorption on a mercury electrode from solutions of different KCl concentrations [5], we have attempted to find the pyridine protonation rate constants, when the pyridine is in the adsorbed state. To this end, we have made a study of the catalytic waves produced by pyridine in concentrations from 1 to 50 mM in nonbuffer solutions on a background of 0.05, 0.10, 0.25, and 0.50 N KCl at 25°C. The choice of nonbuffer solutions is due to the fact that they are considerably less likely than buffer solutions to form a surface active polymeric pyridine reduction product [2], which distorts the catalytic wave. In order to find solely the surface component of the total observed limiting catalytic current, we have made use of the fact that the volume and surface components of the current depend in different ways on the time during the lifetime of the drop [6]. The catalytic current as a function of time (i-t curves) were taken on an OP-1 oscillographic polarograph (built by TsLA Energochernet), provided with a device for taking i-t curves on the first drop, keeping its potential constant with respect to the auxiliary removable saturated calomel electrode. Figure 1 gives samples of such i-t curves, taken on the first (1) and second (2) drops.

Consider catalytic hydrogen evolution on the basis of the reaction layer idea of Brdicka, Wiesner, and Hanus [7, 8] and the mechanism proposed previously for the formation of the waves [9]. The limiting volume catalytic current is determined by the pyridine protonation rate within the reaction layer, the thickness of which, μ₁, is a function of the current strength [9] in nonbuffer solutions as a result of the formation of hydroxyl ions which retard the process, thus

\[ \tau_0 = k_0' [H_2O] \cdot s \cdot F \cdot \mu_1, \]

\[ \mu_1 = \sqrt{\frac{D}{k_0' [OH^-]}} = \sqrt{\frac{D \cdot \kappa_{OH^-}}{k_0' \cdot \tau_{lim}}}, \]

where \( k_0' \) is the protonation rate constant in the volume reaction layer, \( D \) is the diffusion coefficient of the catalyst, \( \kappa_{OH^-} = 706 \, m^2/s^{1/6} \) is the proportionality constant in Il'kovich's equation for the instantaneous hydroxyl ion * This paper is published on the basis of a resolution of a meeting of the principal editors of the journals of the Academy of Sciences, USSR, held July 12, 1962, as the dissertation work of L. D Klyukina.
Diffusion current (it is assumed that the distance from the electrode surface of the OH\(^{-}\) ions formed on it obeys Il'kovtch's equation [9]), \( k_0 \) is the interaction rate constant between the electrochemically active cation form of the catalyst and the hydroxyl ions in the volume of the solution, \( s \) is the surface of the drop electrode at the instant of time \( t \) after the drop is formed (\( s = 0.85 \text{ m}^2/\text{g}^{1/3} \)), \( m \) is the rate at which mercury flows out of the capillary in the drop electrode, and \( i_{\text{lim}} \) is the total (volume and surface) instantaneous limiting catalytic current. The value of \( i_{\text{lim}} \) is taken in (2) rather than \( i_0 \), since hydroxyl ions are formed in both the volume and the surface reactions. It follows from (1) and (2) that

\[
i_0 = 0.85 \cdot k_0' \cdot [\text{H}_2\text{O}] \cdot F \cdot m^{1/3} \cdot t^{1/3} \cdot \sqrt{\\frac{D x_{\text{OH}^-}}{k_0' \cdot i_{\text{lim}}}}.
\]

If the surface current fraction is very small, \( i_{\text{lim}} \approx i_0 \), and, as follows from (3), \( i_0 = k t^{1/2} \), i.e., the current increases proportional to the square root of the drop lifetime.

The surface component of the limiting catalytic current, \( i_{\text{surf}} \), is independent of the concentration of the hydroxyl ions formed; \( i_{\text{surf}} \) is determined solely by the amount of adsorbed catalyst, \( \Gamma \), at a given potential at a given instant of time, and the protonation rate of the adsorbed catalyst by water, \( k_{\text{surf}}' \) [10], is

\[
i_{\text{surf}} = S \cdot F \cdot k_{\text{surf}}' \cdot [\text{H}_2\text{O}] \cdot \Gamma.
\]

Pyridine adsorption on the negatively charged surface of the mercury is described by Frumkin's [5] S-shaped adsorption isotherm. However, at very low coatings of the electrode surface by the adsorbed material, as occurs in pyridine solutions at potentials of \(-1.8-(-1.9)\) V, the Frumkin isotherm is practically coincident with the Langmuir or Henry isotherm. Reaching adsorptive equilibrium requires a time which, under the conditions existing in polarography, can reach tens of seconds and even several minutes [11]. The value of \( \Gamma \) differs from the equilibrium value, \( \Gamma_0 \), for any given solution. Thus, \( \Gamma = \gamma \Gamma_0 \), where \( \gamma \leq 1 \) is the degree to which adsorptive equilibrium has been set up. If the adsorption follows the Langmuir isotherm, then, as Delahay and Pike [11] have shown, the value of \( \gamma \) increases at the very start of adsorption approximately proportional to the square root of the adsorption time

\[
\gamma = a t^{1/2},
\]

\[
\Gamma = a t' \cdot \Gamma_0.
\]

It follows from (4) and (5) that \( i_{\text{surf}} \) varies proportional to \( t^{7/6} \). We have found the value of \( i_{\text{surf}} \) from the difference between the total limiting current and its volume component, \( i_0 \). The value of \( i_0 \) was calculated from (3) by substituting in it the known values of \( k_0 \) and \( k_0' \) from [3], \( x_{\text{OH}^-} \) from [12] (table), and the experimental values of the total limiting current, \( i_{\text{lim}} \). As an example, Fig. 2 gives logarithmic graphs of \( i_{\text{surf}} \) vs. \( t \) for 50, 10, and 5 mM of pyridine on a background of 0.1 N KCl. As may be seen from Fig. 2, the points lie on curves, the slope of which is nearly \( 7/6 \), as required by the theory.

<table>
<thead>
<tr>
<th>KCl, Conc., M</th>
<th>( B_0 )</th>
<th>( B )</th>
<th>( \Gamma_0 ) 10^{11} M/cm^2</th>
<th>( \gamma' ) 10^{10}, M/cm^2</th>
<th>( k_{\text{surf}}' ) 1/M-sec</th>
<th>( k_{\text{surf}}' ) 1/M-sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>26</td>
<td>0.097</td>
<td>3.68</td>
<td>0.72</td>
<td>1.4</td>
<td>4.37</td>
</tr>
<tr>
<td>0.10</td>
<td>25</td>
<td>0.074</td>
<td>2.81</td>
<td>0.55</td>
<td>1.3</td>
<td>4.66</td>
</tr>
<tr>
<td>0.25</td>
<td>22</td>
<td>0.044</td>
<td>1.67</td>
<td>0.33</td>
<td>1.2</td>
<td>4.96</td>
</tr>
<tr>
<td>0.50</td>
<td>20</td>
<td>0.034</td>
<td>1.3</td>
<td>0.26</td>
<td>1.0</td>
<td>4.66</td>
</tr>
</tbody>
</table>

In calculating the surface protonation rate constant from (4), we need to know the values of \( \Gamma \) These values were calculated from the pyridine adsorption isotherms, starting with the values of \( \Gamma_0 \) in the adsorption indices \( B \) using Frumkin's equation [13], with the correction for the completeness of setting up adsorptive equilibrium on the drop electrode as given by Delahay and Pike [11]. It was assumed in the calculations that the value of \( \Gamma_0 \) is independent of KCl concentration, and at 25°C is equal to 8.06 \times 10^{-10} M/cm^2 [5]. To find the values of \( \Gamma \) at the potentials for the limiting catalytic current [\(-1.80 - (-1.85)\) V] use was made of the value of the index, \( B_0 \), at the electrocapillary zero potential. The values of \( B \) and \( B_0 \) are taken from [5] (see table). The diffusion coefficient of pyridine was taken equal to the value for N-methylpyridinium ions (\( D = 1.05 \times 10^{-5} \text{ cm}^2/\text{sec} \)). The rate constants for pyridine protonation by water, \( k_{\text{surf}}' \), are given in the table for four KCl concentrations. For comparison, the same table gives the rate constants for volume pyridine protonation, \( k_0' \).