HCl $\rightarrow$ S values deviate from those obtained by different methods (Table 3). Such deviation may be attributed to difference in surface solvent interaction on membrane interface at various solvent compositions [since HCl activity is the same on both sides of the membrane in cell (A)].

This deviation may be explained on the basis of the membrane potential model based on the rate theory as proposed by Nagasawa and Kobatake. Accordingly, the membrane potential $\Delta E^o$ can be expressed by Eq. (2).

$$\Delta E^o = \frac{RT}{F} \left[ \alpha \ln \frac{C_2}{C_1} - \alpha \ln \left( \frac{C_1^+ + \beta}{C_1^+ + \alpha} \right) + \frac{I_+}{I_+ + I_-} \ln \left( \frac{C_1^+ + \beta}{C_1^+ + \alpha} \right) \right]$$  \hspace{1cm} (2)

where $\alpha = \frac{k_1(l_+ - l_-) + k_2 l_+}{k_2(l_+ + l_-) + k_2 l_+}$ and $\beta = \frac{k_1 l_+ + k_2}{k_1 l_+ + k_2}$

and $I_+$ = mobility of cation and $I_-$ = mobility of anion.

Through the membrane matrix $k_1$, $k_2$ and $k_3$ are complex functions involving the radius of the pores in the membrane, electrical potential due to the fixed charge and the fixed charge on the membrane respectively. On analogy $\theta$ one can consider $\alpha$ as membrane selectivity towards a particular ion and $\beta$ as the measured effect of adsorption of ions on membrane surface.

Eq. (2) can be expressed as Eq. (3) if one assumes $\alpha \approx 1$ and $\Delta E^o \neq 1$, i.e., $\beta$ values are different in different interphases. In Eq. (3) the concentration terms have been replaced by activity terms.

$$\Delta E^o = \frac{RT}{F} \left[ -\ln \left( \frac{a_1^+ + \beta^*}{a_1^+ + \alpha^*} \right) + \left( \frac{I_+}{I_+ + I_-} \right) \ln \left( \frac{a_1^+ + \beta^*}{a_1^+ + \alpha^*} \right) \right] \hspace{1cm} (3)$$

Since diffusion studies across clay membranes have revealed that no anion migrates across cation selective membrane, one can ignored anion transport through membrane.

Hence, $\frac{I_+}{I_+ + I_-}$ term representing the difference in mobilities between cation and anion through the membrane, may now be regarded as the relative mobilities of cation in two different solvents only Eq. (3) may then be written as Eq. (4).

$$\Delta E^o = \frac{RT}{F} \left[ -\ln \left( \frac{a_1^+ + \beta^*}{a_1^+ + \alpha^*} \right) + \frac{I_+}{I_+ + I_-} \ln \left( \frac{a_1^+ + \beta^*}{a_1^+ + \alpha^*} \right) \right] \hspace{1cm} (4)$$

where $\frac{I_+}{I_+ + I_-}$ = transport number of migrating cation when it moves from one solvent to another.

On rearranging of Eq. (4), and assuming $\beta^* \ll \alpha$ and $\beta^* \rightarrow 0$ as $\alpha \rightarrow 1$ (ref. 1), we get

$$\Delta E^o = \frac{RT}{F} \left( \frac{I_+}{I_+ + I_-} \right) \Delta \beta$$  \hspace{1cm} (5)

A study of membrane potential measurements involving aqueous solution of HCl by Adhikari and Ghosh$^9$ have revealed that even a minute value of fixed charge cannot explain membrane potential and, therefore, $\Delta E^o$ depends primarily on $\Delta \beta$ for a particular set of solvent composition.

### Table 3 — E.M.F. Values Observed Presently and Those Determined from Conventional Methods

<table>
<thead>
<tr>
<th>Methanol Membrane used</th>
<th>$E^o$ (mmV)</th>
<th>$E^o$ (mmV)</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ref. 6 at 30°C</td>
<td>work present (mmV)</td>
<td>$E^o$</td>
</tr>
<tr>
<td>Jabalpur clay</td>
<td>13-29</td>
<td>12-5</td>
<td>0-79</td>
</tr>
<tr>
<td>Zeokarb</td>
<td>225</td>
<td>do</td>
<td>16-0</td>
</tr>
<tr>
<td>IRC-120</td>
<td>do</td>
<td>16-25</td>
<td>2-96</td>
</tr>
<tr>
<td>IRC-50</td>
<td>do</td>
<td>15-25</td>
<td>1-96</td>
</tr>
<tr>
<td>Jabalpur clay</td>
<td>19-92</td>
<td>23-5</td>
<td>3-58</td>
</tr>
<tr>
<td>Zeokarb</td>
<td>do</td>
<td>25-95</td>
<td>6-03</td>
</tr>
<tr>
<td>IRC-120</td>
<td>do</td>
<td>24-70</td>
<td>4-78</td>
</tr>
<tr>
<td>IRC-50</td>
<td>do</td>
<td>24-10</td>
<td>4-18</td>
</tr>
</tbody>
</table>

Authors acknowledge suggestions received from Prof. C. E. Marshall, University of Missouri, USA and Prof. M. N. Das of Jadavpur University, Calcutta, in preparing the manuscript.

### References


### Potential Oscillations Under Galvanostatic Conditions of Formaldehyde Oxidation

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Received 8 June 1977; accepted 30 August 1977

Potential oscillations are registered during galvanostatic steady state polarization of formaldehyde in acid-chloride medium. The likely cause of this phenomenon is explained.

**During the investigation of the electro-oxidation of formaldehyde under the conditions of galvanostatic steady state polarization,$^4$ there was an accidental observation of the periodic potential oscillations in acid-chloride medium. However, such an observation was not recorded in acid-sulphate solutions. Both in acid-chloride and acid-sulphate solutions no such phenomenon occurred in either methanol or ethanol solutions. The likely cause of the occurrence of oscillation is explained in this note.**

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Initially the adsorbate was introduced at a potential of about 400 mV with respect to reversible hydrogen electrode (RHE) at 25° into the experimental electrolyte (0-1 M HCl). The formaldehyde concentration was 0-1 M. The potential oscillations (between about +670 mV to about +90 mV) were registered during the galvanostatic steady state polarization at 1 x 10^{-4} amp/geom. cm^2 with a 2 x 1 x 0-1 cm^3 sheet platinized-platinum electrode of about 970 cm^2 true surface area.

The above phenomenon concerning the oscillations could be explained on the basis of the following experimental facts:

(a) The open circuit chemisorption of formaldehyde results in the chemisorbed layer consisting of mostly CHO and H on the platinized-platinum electrode in acid-chloride solutions.

(b) During the galvanostatic steady state oxidation of the organic fuel the plausible reactions occurring are represented by Eqs. (1-4).

\[
\begin{align*}
\text{H} & \rightarrow \text{H}^+ + \text{e}^- \quad \ldots (1) \\
\text{CHO} + \text{OH} & \rightarrow \text{HO}-\text{CHO} \rightarrow \text{O} + \text{H}_2\text{O} \quad \ldots (2) \\
\text{C} & \rightarrow \text{C} + \text{OH} \rightarrow \text{HO}-\text{C} \quad \ldots (3) \\
\text{COOH} + \text{OH} & \rightarrow \text{OC(OH)}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \ldots (4)
\end{align*}
\]

Of these only reaction (1) occurs in the low potential regions.

(c) Some portion of the platinum sites are to be denuded before the open circuit dehydrogenative chemisorption could get initiated on these bare sites. Such a requirement has been shown to exist with chemisorption of ethanol also in the lower potential regions. The existence of bare sites facilitates the anchorage of the adsorbate.

(d) The dehydrogenative chemisorption reaction occurs many times faster than the steady state oxidation of the chemisorbed residue.

The dehydrogenative chemisorption in the case of formaldehyde is very much faster than that in the case of methanol or ethanol as revealed by their open circuit potential decay patterns. In the case of formaldehyde the potential decay is many times faster than the other two adsorbates.

From the facts cited above it is clear that during the steady state electro-oxidation of formaldehyde initially hydrogen ionization (reaction 1) occurs up to about 300 mV and above this potential the organic residue gets oxidized and the reaction could proceed and get arrested at any stage in the scheme of reactions (2) to (4). In other words either CHO or CO or COOH or all of them or any two of them could remain as the surface residue at any stage of the steady state oxidation of formaldehyde. During this oxidation process many platinum sites are denuded and at a certain surface bareness value the avalanche dehydrogenative chemisorption of formaldehyde occurs at a larger rate (> 10^{-4} amp/geom. cm^2). Hence the potential spontaneously decays and reaches a lower value in the hydrogen region (about +90 mV RHE) in about 1 min. As the potential reaches a lower value and the coverage of organic reaches a higher value, the dehydrogenative chemisorption rate becomes insignificant (< 10^{-4} amp/geom. cm^2) and hence the potential rises due to steady state oxidation under the galvanostatic conditions. This oxidation occurs for some time (about 6 min) until certain surface bareness (about 0-25) is created. It is then that the dehydrogenative chemisorption sets in and the potential once again abruptly decays. As this cycle of reactions repeats many times the oscillatory pattern obtains. Such an oscillatory pattern was not registered in systems like methanol and ethanol because these adsorbates dehydrogenatively chemisorb relatively reluctantly as revealed by their slow potential decay under open circuit conditions. This is testified by the fastest attainment of the lowest potential in the potential decay curves at identical temperature (26°) and concentration of the adsorbates (0-1 M).

Elsewhere we have identified the formation of formaldehyde during the electro-oxidation of ethanol. Apparently we should anticipate the existence of the oscillatory pattern with ethanol too. However, such oscillations were not generated by ethanol since only 10^{-5} M formaldehyde alone was identified when 0-1 M ethanol was electrolysed.

It is very interesting to note that these oscillations obtain only in acid-chloride and not in acid-sulphate solutions. This could be explained by considering all the components of mixed adsorption. For any multicomponent system \( \Sigma_0 = 1 \) and for acid-sulphate and acid-chloride solutions we have respectively the Eqs. (5) and (6)

\[
\begin{align*}
(1-\theta_{\text{org,sot}}) & = \theta_{\text{OH,ss}} + \theta_{\text{sot}} + \theta_{\text{B,sot}} \quad \ldots (5) \\
(1-\theta_{\text{org,cl-}}) & = \theta_{\text{OH,ss}} + \theta_{\text{cl-}} + \theta_{\text{B,cl-}} \quad \ldots (6)
\end{align*}
\]

where \( \theta_{\text{OH,ss}} \) is the steady state hydroxyl coverage and is practically small. The terms on the left hand side of Eqs. (5) and (6) are almost same at the beginning of the oxidation of the organic residue. The bare surface with sulphate solutions (\( \theta_{\text{B,sot}} \)) is larger at this potential in comparison with the bare surface with chloride solutions (\( \theta_{\text{B,cl-}} \)). Furthermore, \( \theta_{\text{sot}} \) is small and not much potential-dependent. The chloride coverage \( \theta_{\text{cl-}} \) increases with potential and remains significantly larger at higher potential. In acid-chloride solutions, chloride coverage at higher potential being high, bare surface availability is small and some initial oxidation of the organic has to take place prior to the fast chemisorption of the organic absorbate. This cycle of slow oxidation followed by fast chemisorption repeats and results in the oscillatory pattern in the case of acid-chloride solutions.

The author is thankful to Prof. Hira Lal for his interest and to the Director, Indian Institute of Technology, Bombay, for the facilities.

References