Cyclic Voltammetry of Eu(III) in Presence of Chlorides & Perchlorate

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The cyclic voltammograms of Eu(III) recorded in perchloric acid, sodium chloride and potassium chloride solutions show that reduction of Eu(III) is quasireversible at the hanging mercury drop electrode. The difference between the anodic and cathodic peak potentials in each supporting electrolyte is much larger than what would be expected for a one-electron reduction process. The cathodic peak is sharp but the anodic peak is rounded and diffuse. Heterogeneous rate constants of the electron-transfer process occurring in different media have been calculated.

A number of reports are available in the literature on the reduction of Eu(III) at dropping mercury electrode (d.m.e.) in the presence of different base electrolytes and the reduction process has been reported to be totally irreversible. The reversible reduction of Eu(III) at d.m.e. in the presence of EDTA and in formate buffer has also been reported.

We present herein our results of cyclic voltammetric study of Eu(III) in 0.1 M perchloric acid, 0.1 M potassium chloride and 0.1 M sodium chloride media using hanging mercury drop electrode (HMDE) as the indicator electrode and the platinum spiral as the auxiliary. From a study of the reduction of Eu(III) in chloride and perchlorate media, necessary parameters have been calculated.

Cyclic voltamogram CV-I (Bioanalytical System Inc, USA) in combination with an X-Y recorder (Digilog) was used to record the cyclic voltammograms. The scan rate was varied from 20 mV/s to 100 mV/s. The starting and returning potentials were 0 and −1.0 V respectively.

All potentials were measured against saturated calomel electrode (SCE) which was connected to the test solution through a sodium nitrate bridge. A special cell having three-electrode assembly was used. All experiments were carried out at 25 ± 0.1°C by immersing the cell and the reference electrode in a cryostat type MK-70 (VEB)MLW-PRUFERATEWERK, GDR).

The working concentration of Eu(III) and supporting electrolytes in all the experiments were 4 × 10⁻⁴ M and 0.1 M respectively.

Three typical cyclic voltammograms of Eu(III) solution in different supporting electrolytes at a scan rate of 30 mV/s are presented in Fig. 1. The cathodic peaks in all the cases are sharp but the anodic peaks appear rounded and diffuse.

It is clear from Table I that the separation of peak potential, \( \Delta E_p \) (\( = E_{pa} - E_{pc} \)) at different scan rates is large in all the supporting electrolytes, and that it increases with increase in sweep rate. Further, the ratio \( (I_{pa}/I_{pc}) \) of peak anodic current to peak cathodic current at different scan rates is less than unity in all the

<table>
<thead>
<tr>
<th>Scan rate (V/s)</th>
<th>( \Delta E_p ) (V)</th>
<th>( I_{pa}/I_{pc} )</th>
<th>( \Delta E_p ) (V)</th>
<th>( I_{pa}/I_{pc} )</th>
<th>( \Delta E_p ) (V)</th>
<th>( I_{pa}/I_{pc} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.17</td>
<td>0.74</td>
<td>0.12</td>
<td>0.75</td>
<td>0.16</td>
<td>0.77</td>
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<td>0.03</td>
<td>0.23</td>
<td>0.69</td>
<td>0.16</td>
<td>0.79</td>
<td>0.22</td>
<td>0.71</td>
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<tr>
<td>0.04</td>
<td>0.25</td>
<td>0.66</td>
<td>0.22</td>
<td>0.64</td>
<td>0.24</td>
<td>0.69</td>
</tr>
<tr>
<td>0.05</td>
<td>0.31</td>
<td>0.60</td>
<td>0.25</td>
<td>0.60</td>
<td>0.28</td>
<td>0.67</td>
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<td>0.06</td>
<td>0.36</td>
<td>0.57</td>
<td>0.28</td>
<td>0.58</td>
<td>0.30</td>
<td>0.62</td>
</tr>
<tr>
<td>0.07</td>
<td>0.39</td>
<td>0.63</td>
<td>0.32</td>
<td>0.57</td>
<td>0.31</td>
<td>0.66</td>
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<tr>
<td>0.08</td>
<td>0.41</td>
<td>0.60</td>
<td>0.33</td>
<td>0.60</td>
<td>0.33</td>
<td>0.65</td>
</tr>
<tr>
<td>0.09</td>
<td>0.46</td>
<td>0.61</td>
<td>0.34</td>
<td>0.59</td>
<td>0.33</td>
<td>0.64</td>
</tr>
<tr>
<td>0.10</td>
<td>0.49</td>
<td>0.61</td>
<td>0.37</td>
<td>0.59</td>
<td>0.33</td>
<td>0.72</td>
</tr>
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</table>
three supporting electrolytes (Table 1). It also decreases continuously on increasing the scan rates. The plots of $I_{pc}/V^{1/2}$ versus scan rates in different electrolytes are shown in Fig. 2. The values of $K_s$ calculated at scan rates of 20, 30 and 40 mV/s are given in Table 2.

From the data it can be concluded that the reduction of Eu(III) at the mercury electrode is diffusion-controlled (Fig. 2). However, the separation in peak potentials ($\Delta E_p$) in all cases is much higher than that for a one-electron reversible process and its value increases on increasing the scan rates (Table 1). The heterogeneous rate constants in all cases are of the order of $10^{-3}$ cm s$^{-1}$.

The above observations lead one to conclude that the reduction of Eu(III) at HMDE is quasi-reversible. The low values of $I_{ps}/I_{pc}$ (Table 1) appear to be due to the fact that the product species, Eu(II), is liable to partly diffuse into the solution so that the current observed during the returning cycle is less than the current that would have resulted if the reduced species had stayed at the mercury surface.

**References**