POLAROGRAPHIC BEHAVIOUR OF METALS IN ETHANOLAMINES

Part I. Iron

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INTRODUCTION

Wolfson and Jessop have mentioned that iron gives a polarographic wave in alkaline triethanolamine solutions, but no detailed investigations have been reported. In the present work mono-, di-, and triethanolamines have been employed as cationic complexing agents to study the polarographic behaviour of the ferric iron.

EXPERIMENTAL

Monoethanolamine (B.D.H. reagent grade) and pure di- and triethanolamine (Fisher Scientific Co.) are employed in the base solution. Acetic acid and sodium hydroxide solutions have been used to regulate the pH of the base solutions. No maximum suppressor is used in base solutions containing triethanolamine but in solutions containing mono- and diethanolamines 0.005% gelatin is used.

Details of procedure for running and evaluating the polarograms have been described previously. The values of m for the dropping mercury electrodes used are 1.370, 1.227, 1.120 and 1.150 mg. per second, while the droptime has been adjusted to 5 seconds a drop in 1 N potassium chloride.

RESULTS

(A) Base Solutions Containing Triethanolamine

1. Effect of pH.

In these experiments acetic acid and sodium hydroxide are employed to adjust the pH of the solutions. In solutions of pH less than 11, the concentration of sodium ion is maintained at 0.2 M. The colour of the solutions below pH 9 is yellow, while above this value it is colourless. The results are given in Table I from which it is clear that above pH 9.8, the polarograms exhibit two waves at about —0.9 V and —1.5 V vs. S.C.E. corresponding
to the reduction of iron (III) to iron (II), and iron (II) to metallic iron respectively. Below pH 9.8, the second wave has a tendency to get merged with the final current rise. The height of the second wave is double that of the first wave between pH 9.8 and 11, and not at higher values. The half-wave potential becomes less negative with a diminution in pH. The values of \( E_2 - E_1 \) indicate that the second wave is irreversible at all pH values, while the first wave is irreversible only between pH 8 and 11.

### Table I

**Effect of pH on the polarographic behaviour of iron in triethanolamine**

<table>
<thead>
<tr>
<th>pH</th>
<th>( (E_1)_1 ) vs. S.C.E.</th>
<th>( (E_1)_2 ) vs. S.C.E.</th>
<th>( (E_2 - E_1)_1 ) (Volt)</th>
<th>( (E_2 - E_1)_2 ) (Volt)</th>
<th>Heights of the waves in terms of divisions of the graph (S/70)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.50</td>
<td>-1.072</td>
<td>-1.675</td>
<td>0.060</td>
<td>0.050</td>
<td>11.0 9.8</td>
</tr>
<tr>
<td>12.70</td>
<td>-1.034</td>
<td>-1.593</td>
<td>0.060</td>
<td>0.060</td>
<td>12.6 15.9</td>
</tr>
<tr>
<td>11.00</td>
<td>-0.870</td>
<td>-1.470</td>
<td>0.083</td>
<td>0.085</td>
<td>12.0 24.0</td>
</tr>
<tr>
<td>9.80</td>
<td>-0.695</td>
<td>-1.370</td>
<td>0.085</td>
<td>0.080</td>
<td>12.0 24.0</td>
</tr>
<tr>
<td>8.30</td>
<td>-0.422</td>
<td>No wave</td>
<td>0.086</td>
<td>No wave</td>
<td>11.8 No wave</td>
</tr>
<tr>
<td>8.05</td>
<td>-0.396</td>
<td>&quot;</td>
<td>0.089</td>
<td>&quot;</td>
<td>12.0 &quot;</td>
</tr>
<tr>
<td>7.10</td>
<td>-0.363</td>
<td>&quot;</td>
<td>0.061</td>
<td>&quot;</td>
<td>7.3 &quot;</td>
</tr>
<tr>
<td>6.85</td>
<td>-0.316</td>
<td>&quot;</td>
<td>0.057</td>
<td>&quot;</td>
<td>6.9 &quot;</td>
</tr>
<tr>
<td>6.40</td>
<td>-0.256</td>
<td>&quot;</td>
<td>0.054</td>
<td>&quot;</td>
<td>7.3 &quot;</td>
</tr>
<tr>
<td>5.80</td>
<td>-0.189</td>
<td>&quot;</td>
<td>0.045</td>
<td>&quot;</td>
<td>8.0 &quot;</td>
</tr>
<tr>
<td>3.70</td>
<td>Very close to</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.60</td>
<td>+0.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* In this table \( E_1 \) represents the half-wave potential and the subscripts 1 and 2 refer to the first and the second waves respectively.

It has been noticed that interesting data regarding complex formation and polarographic waves of good analytical value are obtained in the alkaline region. Hence a detailed study employing sodium hydroxide, sodium carbonate, acetate, and ammonium chloride—ammonium hydroxide has been made and the results are given below.

2. **Effect of sodium hydroxide, sodium carbonate and ammonium chloride—ammonium hydroxide on the ratio of the heights of the two steps, the half-wave potential and the reversibility of polarographic waves in presence of triethanolamine.**

(a) **Sodium hydroxide.**—Some of the polarograms showing the effect of sodium hydroxide at different concentrations of triethanolamine are given
in Fig. 1. The average value of the results of analysis of the waves are given in Table II. The results indicate that for a given concentration of triethanolamine, the half-wave potential of the first wave increases in the beginning and then tends to remain constant, as the concentration of sodium hydroxide is increased. When the concentration of sodium hydroxide is kept constant (below 1.0 molar) the half-wave potential of the first wave practically remains constant for low concentrations of triethanolamine (below 0.1 molar) and becomes more positive with an increase in the concentration of sodium hydroxide. In a good number of cases, these values could not be determined on account of the interference of the final steep current rise. It is interesting to note that in most cases the values of $(i_d)_2/(i_d)_1$ is less than 2.

### TABLE II

*Effect of sodium hydroxide on the polarographic waves of iron (III) in presence of triethanolamine*

Conc. of iron (III) 1.182 millimolar

<table>
<thead>
<tr>
<th>Conc. of sodium hydroxide (Molar)</th>
<th>Conc. of triethanolamine (Molar)</th>
<th>Half-wave potential 1st wave $(E_1)$ vs. S.C.E. (Volt)</th>
<th>Half-wave potential 2nd wave (Volt)</th>
<th>Slope of log plot* $(i_d)_2/(i_d)_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.002</td>
<td>-1.029</td>
<td>-1.530</td>
<td>0.070</td>
</tr>
<tr>
<td>0.10</td>
<td>0.020</td>
<td>-1.030</td>
<td>-1.616</td>
<td>0.131</td>
</tr>
<tr>
<td>0.10</td>
<td>0.100</td>
<td>-1.034</td>
<td>-1.593</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>0.300</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>0.002</td>
<td>-1.069</td>
<td>-1.579</td>
<td>0.035</td>
</tr>
<tr>
<td>1.00</td>
<td>0.020</td>
<td>-1.074</td>
<td>-1.641</td>
<td>0.045</td>
</tr>
<tr>
<td>1.00</td>
<td>0.100</td>
<td>-1.072</td>
<td>-1.675</td>
<td>0.045</td>
</tr>
<tr>
<td>1.00</td>
<td>1.000</td>
<td>-1.058</td>
<td>-1.733</td>
<td></td>
</tr>
<tr>
<td>5.00</td>
<td>0.002</td>
<td>-1.072</td>
<td>-1.414</td>
<td>0.045</td>
</tr>
<tr>
<td>5.00</td>
<td>0.020</td>
<td>-1.079</td>
<td>-1.450</td>
<td>0.038</td>
</tr>
<tr>
<td>5.00</td>
<td>1.000</td>
<td>-1.076</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Slope of the log plot of the first wave is about 0.060 Volt. Some log plots are given in Fig. 2.
† Waves not well formed.

(b) Sodium carbonate.—The results are summarized in Table III. The two reduction waves are very well developed and the ratio of the heights is
1: 2 in contrast to the behaviour noticed in base solutions containing sodium hydroxide. The half-wave potential shifts to less negative values with an
increase in the concentration of iron. At a constant concentration of ferric iron, the half-wave potentials of the first and the second waves progressively increase with an increase in the concentration of triethanolamine. The values of $E_1 - E_2$ indicate that at low concentrations of triethanolamine (0.02 M), the first wave is reversible while at higher concentrations of triethanolamine it is irreversible. The second wave, however, is practically irreversible. It is surprising that a reversible value (0.029 V) should have been obtained with 0.1 M triethanolamine and 0.1 M sodium carbonate, when the concentration of iron is 1.5 millimolar. In fact there was a progressive diminution in the value of $E_1 - E_2$ when the concentration of iron (III) was increased from 0.3 to 1.5 millimolar.

**Table III**

**Effect of sodium carbonate on the polarographic behaviour of iron (III) in presence of triethanolamine**

<table>
<thead>
<tr>
<th>Conc. of Triethanolamine (Molar)</th>
<th>Conc. of Sodium Carbonate (Molar)</th>
<th>Conc. of Iron (Molar)</th>
<th>$(E_{1})_1^*$ vs. S.C.E. (Volt)</th>
<th>$(E_{2})_2^*$ vs. S.C.E. (Volt)</th>
<th>$(E_1 - E_2)_1$ (Volt)</th>
<th>$(E_1 - E_2)_2$ (Volt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>1.00</td>
<td>1.182</td>
<td>-0.843</td>
<td>-1.531</td>
<td>0.061</td>
<td>0.076</td>
</tr>
<tr>
<td>0.02</td>
<td>1.00</td>
<td>3.546</td>
<td>-0.799</td>
<td>-1.540</td>
<td>0.064</td>
<td>0.074</td>
</tr>
<tr>
<td>0.10</td>
<td>1.00</td>
<td>1.182</td>
<td>-0.867</td>
<td>-1.557</td>
<td>0.066</td>
<td>0.077</td>
</tr>
<tr>
<td>0.10</td>
<td>1.00</td>
<td>5.910</td>
<td>-0.813</td>
<td>-1.546</td>
<td>0.068</td>
<td>0.079</td>
</tr>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>1.182</td>
<td>-0.774</td>
<td>-1.504</td>
<td>0.072</td>
<td>0.075</td>
</tr>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>5.910</td>
<td>-0.760</td>
<td>-1.553</td>
<td>0.070</td>
<td>0.079</td>
</tr>
<tr>
<td>1.00</td>
<td>1.00</td>
<td>1.182</td>
<td>-0.906</td>
<td>-1.637</td>
<td>0.067</td>
<td>0.070</td>
</tr>
<tr>
<td>1.00</td>
<td>1.00</td>
<td>5.910</td>
<td>-0.874</td>
<td>-1.637</td>
<td>0.072</td>
<td>0.075</td>
</tr>
<tr>
<td>1.00</td>
<td>0.10</td>
<td>1.182</td>
<td>-0.820</td>
<td>-1.635</td>
<td>0.078</td>
<td>0.068</td>
</tr>
<tr>
<td>1.00</td>
<td>0.10</td>
<td>5.910</td>
<td>-0.785</td>
<td>-1.649</td>
<td>0.092</td>
<td>0.100</td>
</tr>
</tbody>
</table>

* $E_1$ represents the half-wave potential and the subscripts 1 and 2 refer to the first and the second waves respectively.

In 0.02 M triethanolamine with an increase in the concentration of iron, the first wave is divided into two poorly separated waves, the second one being much smaller than the first (Fig. 3). The complexity of the wave, however, does not affect the constancy of the value of the diffusion current constant.

(c) Ammonium chloride (1 M)—ammonium hydroxide (1 M).—Some of the polarograms showing the effect of concentration of triethanolamine are given in Fig. 4. The results are summarized in Table IV. It is clear
that the half-wave potentials progressively increase with increasing concentration of triethanolamine and finally attain a constant value. The first wave is reversible while the second wave is irreversible. It has been noticed that the height of the second wave is double the first in all the cases.

**TABLE IV**

*Effect of ammonium chloride (1 M)—ammonium hydroxide (1 M) on polarographic waves of iron (III) in presence of triethanolamine*

<table>
<thead>
<tr>
<th>Conc. of iron 1·182 millimolar</th>
<th>Conc. of triethanol amine (Molar)</th>
<th>1st wave Half-wave potential (E1)1 vs. S.C.E. (Volt)</th>
<th>(E1−E1)1 (Volt)</th>
<th>2nd wave Half-wave potential (E2)2 vs. S.C.E. (Volt)</th>
<th>(E2−E2)2 (Volt)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0·02</td>
<td>−0·449</td>
<td>0·058</td>
<td>−1·436</td>
<td>0·051</td>
</tr>
<tr>
<td></td>
<td>0·10</td>
<td>−0·491</td>
<td>0·056</td>
<td>−1·463</td>
<td>0·043</td>
</tr>
<tr>
<td></td>
<td>0·30</td>
<td>−0·519</td>
<td>0·062</td>
<td>−1·468</td>
<td>0·043</td>
</tr>
<tr>
<td></td>
<td>0·50</td>
<td>−0·528</td>
<td>0·057</td>
<td>−1·476</td>
<td>0·040</td>
</tr>
<tr>
<td></td>
<td>0·70</td>
<td>−0·535</td>
<td>0·062</td>
<td>−1·483</td>
<td>0·043</td>
</tr>
<tr>
<td></td>
<td>1·00</td>
<td>−1·532</td>
<td>0·056</td>
<td>−1·480</td>
<td>0·038</td>
</tr>
</tbody>
</table>

3. *Effect of concentration of iron (III) on the diffusion current in base solutions containing triethanolamine*

Table V shows the effect of concentration of iron on the diffusion current constant under varying conditions. The diffusion current constant only for the first wave has been given, since the second wave is not suitable for analytical purposes. The results indicate that in base solutions containing sodium carbonate the diffusion current constant decreases with an increase in the concentration of iron except in solutions containing 0·02 M triethanolamine + 1 M sodium carbonate. In these solutions the solubility of iron is limited. Hence the presence of sodium carbonate is not of any advantage in the polarographic estimation of iron. The most suitable base solutions for the estimation of iron contain 0·1 M triethanolamine + 0·1 to 1·0 molar sodium hydroxide but in presence of ammonium chloride-ammonium hydroxide, the concentration of triethanolamine has to be 1·0 molar due to the low solubility of the complex.
### TABLE V

Effects of concentration of iron (III) on the diffusion current constant

The values $i_d$ in mg$^-1$ sec$^-1$ has been given at -1.4 V, -1.1 V and -0.85 V vs. S.C.E., in solutions containing sodium hydroxide, sodium carbonate and ammonium chloride-ammonium hydroxide respectively. In this table B.S., X, and Trien represent base solution, $m^1$ $t^1$, and triethanolamine respectively.

<table>
<thead>
<tr>
<th>Conc. of ferric iron (Millimolar)</th>
<th>Diffusion current constant</th>
<th>Conc. of ferric iron (Millimolar)</th>
<th>Diffusion current constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$i_d$</td>
<td></td>
<td>$i_d$</td>
</tr>
<tr>
<td></td>
<td>$Cm^1 t^1$</td>
<td></td>
<td>$Cm^1 t^1$</td>
</tr>
<tr>
<td>(1) B.S.: 0.02M Trien + 0.1M NaOH</td>
<td></td>
<td>(6) B.S.: 0.002M Trien + 1.00M NaOH</td>
<td></td>
</tr>
<tr>
<td>$X = 1.361$</td>
<td>0.296</td>
<td>$X = 1.361$</td>
<td>0.448</td>
</tr>
<tr>
<td></td>
<td>1.95</td>
<td></td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>0.591</td>
<td></td>
<td>1.120</td>
</tr>
<tr>
<td></td>
<td>1.85</td>
<td></td>
<td>2.240</td>
</tr>
<tr>
<td></td>
<td>2.364</td>
<td></td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>1.84</td>
<td></td>
<td>2.40</td>
</tr>
<tr>
<td></td>
<td>4.728</td>
<td></td>
<td>1.07</td>
</tr>
<tr>
<td>(2) B.S.: 0.1M Trien + 0.1M NaOH</td>
<td></td>
<td>(7) B.S.: 0.02M Trien + 5.00M NaOH</td>
<td></td>
</tr>
<tr>
<td>$X = 1.361$</td>
<td>0.296</td>
<td>$X = 1.579$</td>
<td>2.240</td>
</tr>
<tr>
<td></td>
<td>1.86</td>
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<tr>
<td></td>
<td>0.591</td>
<td></td>
<td>5.600</td>
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<tr>
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<td>1.85</td>
<td></td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>2.360</td>
<td></td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>1.87</td>
<td></td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>4.720</td>
<td></td>
<td>2.240</td>
</tr>
<tr>
<td></td>
<td>1.86</td>
<td></td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>7.080</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3) B.S.: 1.00M Trien + 0.10M NaOH</td>
<td></td>
<td>(8) B.S.: 0.10M Trien + 5.00M NaOH</td>
<td></td>
</tr>
<tr>
<td>$X = 1.379$</td>
<td>0.296</td>
<td>$X = 1.577$</td>
<td>5.600</td>
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<tr>
<td></td>
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<td></td>
<td>0.97</td>
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<td>1.84</td>
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</tr>
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</tr>
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<td>8.274</td>
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</tr>
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<tr>
<td></td>
<td>16.548</td>
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</tr>
<tr>
<td></td>
<td>1.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4) B.S.: 0.02M Trien + 1.00M NaOH</td>
<td></td>
<td>(9) B.S.: 0.02M Trien + 1.00M Na$_2$CO$_3$</td>
<td></td>
</tr>
<tr>
<td>$X = 1.589$</td>
<td>0.380</td>
<td>$X = 1.415$</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td>1.75</td>
<td></td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>1.520</td>
<td></td>
<td>5.910</td>
</tr>
<tr>
<td></td>
<td>1.72</td>
<td></td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>7.980</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5) B.S.: 0.10M Trien + 1.00M NaOH</td>
<td></td>
<td>(10) B.S.: 0.10M Trien + 1.00M Na$_2$CO$_3$</td>
<td></td>
</tr>
<tr>
<td>$X = 1.382$</td>
<td>0.296</td>
<td>$X = 1.391$</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td>1.94</td>
<td></td>
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<td>1.184</td>
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<td>1.71</td>
<td></td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>5.920</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>1.69</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>11.840</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.70</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The use of 5 M sodium hydroxide decreases the diffusion current constant and the solution becomes viscous without any obvious advantage. It may also be pointed out that in most cases the value of the diffusion current constant is slightly higher at lower concentrations of iron (below 0.3 millimolar).

4. Use of sodium acetate

In these experiments 0.2 M sodium ions have been included to eliminate the migration current. The second wave is too very close to the final current rise. At pH 8.3 the half-wave potentials for the first wave of iron are $-0.413 \text{ V}$, $-0.422 \text{ V}$, $-0.440 \text{ V}$, and $-0.453 \text{ V}$, vs. S.C.E., when the base solutions contain 0.02, 0.10, 0.50, and 1.00 molar triethanolamine respectively. The values of $E_1 - E_t$ are 0.080 V, 0.086 V, 0.060 V, and 0.060 V indicating that the wave is reversible at higher concentrations of triethanolamine. Due to solubility difficulties the effect of concentration of iron on the diffusion current has been tried employing 0.5 M triethanolamine solution. These solutions have an yellow colour at higher concentrations of iron, perhaps due to the formation of colloidal hydrous ferric oxide. The diffusion current constant decreases by about 18% when the concentration of iron is changed from 1 to 5 millimolar at pH 8.3 and also at pH 7.

(B) Base Solutions Containing Diethanolamine

The behaviour of diethanolamine complexes of iron resemble closely the triethanolamine complexes but the solubility of the complex is very much
less in diethanolamine solutions. Table VI gives the results obtained with sodium hydroxide and sodium carbonate. The other base solutions employed in the case of triethanolamine have not been used due to the low solubility of the complex. The half-wave potential of the first wave is very nearly constant at different concentrations of the amine while that of the second wave increases with an increase in the concentration of the amine. The \( E_2 - E_1 \) value of the second wave varies with the variation in the concentration of the amine reaching almost a constant value at higher concentrations of the amine. In these base solutions the solubility of the diethanolamine complex is quite low for the method to be of practical value in estimating iron.

**Table VI**

Effect of sodium hydroxide and sodium carbonate on the polarographic waves of iron (III) in presence of diethanolamine

<table>
<thead>
<tr>
<th>Composition of the base solution</th>
<th>( (E_4)_1 ) vs. S.C.E. (Volt)</th>
<th>( (E_4 - E_4)_1 ) (Volt)</th>
<th>( (E_4)_2 ) vs. S.C.E. (Volt)</th>
<th>( (E_4 - E_4)_2 ) (Volt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 0.10M NaOH + 0.30M Dien</td>
<td>-1.026</td>
<td>0.075</td>
<td>-1.576</td>
<td>0.064</td>
</tr>
<tr>
<td>(2)</td>
<td>+ 0.65M</td>
<td>-0.938</td>
<td>0.078</td>
<td>-1.611</td>
</tr>
<tr>
<td>(3)</td>
<td>+ 1.00M</td>
<td>-0.928</td>
<td>0.069</td>
<td>-1.624</td>
</tr>
<tr>
<td>(4) 1.00M NaOH + 0.30M Dien</td>
<td>-1.005</td>
<td>0.075</td>
<td>-1.637</td>
<td>0.048</td>
</tr>
<tr>
<td>(5)</td>
<td>+ 0.65M</td>
<td>-0.995</td>
<td>0.065</td>
<td>-1.675</td>
</tr>
<tr>
<td>(6)</td>
<td>+ 1.00M</td>
<td>-0.994</td>
<td>0.062</td>
<td>-1.709</td>
</tr>
<tr>
<td>(7) 5.00M NaOH + 0.30M Dien</td>
<td>-1.047</td>
<td>0.069</td>
<td>-1.639</td>
<td>0.035</td>
</tr>
<tr>
<td>(8)</td>
<td>+ 1.00M</td>
<td>-1.040</td>
<td>0.059</td>
<td>-1.681</td>
</tr>
<tr>
<td>(9) 0.10 M Na₂CO₃ + 0.30 Dien</td>
<td>-0.821</td>
<td>0.086</td>
<td>-1.466</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>+ 0.005% gelatin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10)</td>
<td>+ 0.65M Dien</td>
<td>-0.834</td>
<td>0.064</td>
<td>-1.493</td>
</tr>
<tr>
<td></td>
<td>+ 0.005% gelatin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(11)</td>
<td>+ 1.00M Dien</td>
<td>-0.830</td>
<td>0.064</td>
<td>-1.512</td>
</tr>
<tr>
<td></td>
<td>+ 0.005% gelatin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(12) 1.00M Na₂CO₃ + 0.30M Dien</td>
<td>-0.816</td>
<td>0.074</td>
<td>-1.519</td>
<td>0.062</td>
</tr>
<tr>
<td></td>
<td>+ 0.005% gelatin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(13)</td>
<td>+ 0.65M Dien</td>
<td>-0.833</td>
<td>0.068</td>
<td>-1.535</td>
</tr>
<tr>
<td></td>
<td>+ 0.005% gelatin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(14)</td>
<td>+ 1.00M Dien</td>
<td>-0.837</td>
<td>0.060</td>
<td>-1.550</td>
</tr>
</tbody>
</table>

It has also been noticed in the present investigation that at high concentrations, the ratio of the height of the second to the first wave decreases with increasing concentrations of the amine. The effect, however, is not
so prominent as in the case of triethanolamine solutions. In base solutions containing 0.10 M sodium hydroxide the ratio changes from 1.9 to 1.6 when the concentration of diethanolamine is changed from 0.3 to 1.0 M.

(C) Base Solutions Containing Monoethanolamine

The solubility of the monoethanolamine complexes of iron is very low in all the base solutions that have been used in the present work. Hence no detailed studies have been made.

DISCUSSION

(A) Base solutions Containing Triethanolamine

1. Effect of pH on the half-wave potential

Fig. 5 indicates the variation of half-wave potential with pH. The values of $E_1 - E_f$ given in Table I indicate that the ferric to ferrous reduction is irreversible between pH 11 and 8. The dotted line indicates the reversible half-wave potential calculated by employing Eyring's method and it can be seen that the form of the curve remains the same. It can therefore be concluded that the different slopes are due to changes in the nature of the complexes that are being reduced at the dropping mercury electrode. The region AB corresponds to the complex of triethanolammonium ion with ferric iron. The low value of the slope at BC is perhaps due to a comparatively slow change in the ratio ion/amine around the pK value of the triethanolamine. The high value of the slope of the curve CD indicates that ferric-triethanolamine complex is getting formed. The change of the slope at DE is indicative of partial modification of the complex by the entry of hydroxyl group. Meites has also suggested that the hydroxyl group gets into the complex at high pH values. When the strength of the alkali is increased considerably, the introduction of the hydroxyl group into the molecule probably ceases and the hydroxo-triethanol complex remains unaltered with the result that in the region EF there is very little change in the half-wave potential.

2. Effect of pH on the ratio of heights of the two waves

It has been noticed (Tables I and II) that at high concentrations of the alkali, the ratio of the heights of the second to the first wave is not equal to two but varies from nearly 2 to 0.2. Since the second wave is a two electron process and the first a one electron process it is reasonable to expect (according to Ilkovic Equation) the ratio to be equal to two. Similar low values for the ratio have also been obtained by Komarek in alkaline mannitol solutions of iron (III). The above remarkable fact can be explained by assuming the existence of two types of ferrous complexes, the half-wave
potential of one being more positive than the other and the equilibrium between the two complexes being slow at the dropping mercury electrode. The first wave is due to the complex getting discharged at a less negative potential. The wave having a more negative potential does not appear as it gets masked with the final rise of current due to sodium discharge.

3. Nature of complex formation

In the case of reversible reduction to the metallic state, the half-wave potential of the complex metal ion is related to the excess concentration of the complexing ion according to the equation: 

\[ E = E^* + \frac{RT}{nF} \log K_c \]

\[ E = E^* + \frac{RT}{nF} \log [L] \]

**VARIATION OF HALF-WAVE POTENTIAL WITH pH**

**Fig. 5**

- A, B, C, D, E, F

\[ \text{pH Variation of Half-Wave Potential} \]
where \( q \) is the number of ligands attached to the complex metal ion, \( n \) the number of electrons involved in the reduction process, \( C_x \) the excess concentration of the complexing agent, and \( \Delta E_1 \) the shift in the half-wave potential.

In the case of reduction from one oxidation state to another, the above equation can be modified as

\[
\frac{\Delta E_1}{\Delta \log C_x} = - (p - q) (0.06014/a)
\]

where \( p \) is the number of ligands attached to the oxidised complex, \( q \) the number of ligands attached to the reduced complex, and \( a \) the number of electrons involved in the reduction process.

For irreversible reductions the following equations can be written based on the treatment given by Tamanushi and Tanaka.\(^{11}\)

\[
\frac{\Delta E_1}{\Delta \log C_x} = - q \left( \frac{0.06014}{an} \right)
\]

where \( a = \) the fraction of the total applied potential that favours the forward reaction.

The value of \( a \) is obtained from the following expression:—

\[
E_1 - E_i = - \left( \frac{0.0574}{na} \right)
\]

In the case of reduction from one oxidation state to another, equation 2 can be modified as

\[
\frac{\Delta E_1}{\Delta \log C_x} = - p \left( \frac{0.06014}{an} \right)
\]

It is interesting to note that in irreversible reductions from one oxidation state to another the number of ligands attached to the reduction complex does not enter the equation. The application of equations 1 and 3 for the reduction of ferrous ion to metal seems to be justifiable since freshly deposited iron is in the form of amalgam.\(^{12}\)

The application of the above equations to obtain the formulae of the complexes formed is beset with many difficulties: (1) the waves show varying degrees of irreversibility with a change in the concentration of the complexing agent and the equations for the irreversible wave can be applied only when the value for the irreversibility is constant; (2) the ratio of the second
to the first wave of iron complexes in sodium hydroxide solutions is much less than two; (3) in sodium carbonate solutions, when 1·00 M triethanolamine is present, the half-wave potential of the second wave does not change when the concentration of sodium carbonate is changed from 0·10 to 1·00 M; a definite shift however, is noticed when 0·1 M triethanolamine is present; the half-wave potential of the first wave is susceptible to changes in the concentration of iron; further, the irreversibility of the first wave is not sufficiently high to warrant the elimination of q in p — q of the reversible wave equation.

(a) Base solutions containing sodium hydroxide and triethanolamine.—Ref. to Table II indicates that (E2), is practically constant at low concentrations of triethanolamine and the wave is reversible. Hence it has to be concluded that p = q under these conditions. Equality of p and q is also established for all concentrations of triethanolamine when the base solution has large amounts (5 M) of sodium hydroxide. With higher concentrations of triethanolamine, the half-wave potential of the complex diminishes. This is rather surprising since it is usual to find an increase in the value of the half-wave potential. Similar behaviour has also been noticed by Meites in systems containing copper-ammonia-citrate complex but a suitable explanation is not forthcoming at present to explain such exceptions.

(b) Base solutions containing sodium carbonate and triethanolamine.—At a given pH the half-wave potentials in sodium carbonate base solutions have been found to be 0·1 V more positive than in base solutions containing sodium acetate, indicating the formation of new type of complex (the carbonato-ethanol complex). It is difficult to get the formula of the ferric complex. Applying equations 3 and 4 the formula of the ferrous complex can be written as follows:—

\[
\text{Fe (II) (Trien)} \quad \text{(CO}_3\text{)}_\text{2}.
\]

(c) Base solutions containing ammonia-ammonium chloride and triethanolamine.—In this base solution the first wave is reversible while the second wave is slightly irreversible. At high concentrations of triethanolamine (above 0·7 molar) the half-wave potential of the first wave is almost a constant indicating that \( p = q \). Applying equations 2, 3 and 4 for the concentration range of triethanolamine between 0·1 and 0·7 molar one gets \( p - q = 1 \) and \( q = 1 \). The following formulæ can be written for the complexes:

\[
[\text{Fe (III) (Trien)}_\text{2} (\text{NH}_3)]^{+++}; \quad [\text{Fe (II) (Trien)}_\text{1} (\text{NH}_3)]^{++}
\]
(B) Base Solution Containing Diethanolamine and Sodium Carbonate

In this base solution the first wave is reversible at higher concentrations of diethanolamine. The second wave, however, is irreversible and the irreversibility reaches a constant value at higher concentrations of the amine. Applying equations 2, 3 and 4 the following formulæ can be written for the complexes formed:

\[ \text{[Fe (III) (Dien)₂ (CO₃)₁]}^+ \text{ and [Fe (II) (Dien)₂ (CO₃)₁]} \]

**Summary**

1. Employing ethanolamines as the complexing agents a systematic study on the polarographic behaviour of iron has been carried out at various pH values and in the presence of the following electrolytes: (a) sodium hydroxide, (b) sodium carbonate, (c) acetate, and (d) ammonium chloride-ammonium hydroxide.

2. In triethanolamine solutions containing sodium hydroxide, sodium carbonate, and ammonium chloride-ammonium hydroxide, the polarograms consist of two waves corresponding to the reduction of ferric to ferrous and ferrous to iron. The ratio of the heights between the second and the first wave is less than two in the case of sodium hydroxide while in the other two cases it equal to two. The variation of half-wave potential with pH has indicated the formation of complexes involving triethanolammonium ion, triethanolamine, and hydroxyl group.

3. The suitability of using triethanolamine in base solutions for polarographic estimation of iron has been discussed.

4. Experiments conducted with mono- and diethanolamines show that the solubility of the complexes is very much lower in the base solutions which makes the study very difficult.

5. The formation of the following complexes have been indicated from the polarographic measurements:

(1) \[ \text{[Fe (III) (Dien)₂ (CO₃)₁]}^+ \]
(2) \[ \text{[Fe (II) (Dien)₂ (CO₃)₁]} \]
(3) \[ \text{[Fe (II) (Trien)₁ (CO₃)₁]} \]
(4) \[ \text{[Fe (III) (Trien)₂ (NH₃)₂]}^{4+} \]
(5) \[ \text{[Fe (II) (Trien)₁ (NH₃)₃]}^{2+} \]

**Acknowledgement**

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Polarographic Behaviour of Metals in Ethanolamines—I

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Effect of sodium hydroxide (0.1M) on the polarographic behaviour of iron (1.182 millimolar) in presence of triethanolamine.

Curves 1, 2, 3 and 4 have been taken using 0.002, 0.02, 0.10 and 1.00 M triethanolamine.

Sensitivity: s/30, s/50, s/50, s/50 respectively.

The voltage line just before the beginning of the polarogram corresponds to -0.573 V vs. S.C.E.

Effect of sodium carbonate (1 M) and triethanolamine (0.02 M) on the polarographic behaviour of iron.

Curves 1 and 2 have been obtained with 1.182 and 3.546 millimolar iron at s/50 and s/150.

Curves 3 and 4 are the blanks at s/50 and s/150.

The voltage line just before the beginning of the polarogram corresponds to -0.473 V vs. S.C.E.
Effect of ammonium chloride (1 M) and ammonium hydroxide (1 M) on the polarographic behaviour of iron (1.182 millimol.) in presence of triethanolamine.

Curves 1, 2, 3 and 4 have been taken with 0.02, 0.10, 0.30 and 0.50 M triethanolamine at 6/30, 6/50, 7.50 and 8.50 respectively. There has been slight precipitation under the conditions at which curve 1 is recorded.

The voltage line just before the beginning of the polarogram corresponds to −0.273 V vs. S.C.E.