Mean Activity Coefficient from Cell Measurements

Verification of Debye-Huckel Limiting Law

Background

An electrochemical cell is constructed. The EMF of the cell for varying the concentrations of one participating electrolyte (HCl) will be measured. Such measurements are used to verify the Debye–Huckel limiting Law and to determine the mean activity coefficient of the electrolyte.

The procedure would generate the standard electrode potential difference of the electrochemical cell.

The Cell:

Pt | H_2Q(aq), Q(aq), HCl(aq,c) | AgCl(s) | Ag(s)

The LHS electrode (reduction) reaction for the quinhydrone (equimolecular mixture of quinone(Q) and hydroquinone (H_2Q)) electrode ;

Q(aq) + $2H^+$(aq) + 2e = H_2Q(aq)

Electrode potential, LHS;

$$E_{LHS} = E^o_{Q/H_2Q} - \frac{RT}{2F}\mathbf{ln}\,\frac{a_{H_2Q}}{a_Q a^2_{H^+}}$$

The RHS electrode (reduction) reaction;

AgCl(s) + e = Ag(s) + Cl^- (aq, a_{Cl^-})

Electrode potential, RHS;

$$E_{RHS} = E^o_{AgCl/Ag} - \frac{RT}{F}\mathbf{ln}\,a_{Cl^-}$$

Cell Potential;

$$E_{cell} = E_{RHS} - E_{LHS} = \left[E^o_{AgCl/Ag} - \frac{RT}{F}\mathbf{ln}\,a_{Cl^-}\right] - \left[E^o_{Q/H_2Q} - \frac{RT}{2F}\mathbf{ln}\,\frac{a_{H_2Q}}{a_Q a^2_{H^+}}\right]$$

$$E_{cell} = \left(E^o_{AgCl/Ag} - E^o_{Q/H_2Q}\right) - \frac{RT}{2F}\mathbf{ln}\,a^2_{Cl^-} + \frac{RT}{2F}\mathbf{ln}\,\frac{a_{H_2Q}}{a_Q a^2_{H^+}}$$

$$= E^o_{cell} - \frac{RT}{2F}\mathbf{ln}\,a^2_{H^+}a^2_{Cl^-} \qquad \because a_{H_2Q} = a_Q \text{(equimolecular mixture)}$$

$$E_{cell} = E^o_{cell} - \frac{RT}{F}\mathbf{ln}\,a_{H^+}a_{Cl^-} \qquad \text{and using } a_i = \yen_i c_i$$

$$E_{cell} = E^o_{cell} - \frac{RT}{F}\mathbf{ln}\,\yen_+ c_{H^+}\yen_- c_{Cl^-} = E^o_{cell} - \frac{RT}{F}\mathbf{ln}\,\yen^2_\pm c^2$$

by definition $\yen^2_\pm = \yen_+\yen_-$ (1:1 electrolyte)

$$E_{cell} = E^o_{cell} - \frac{RT}{F}\mathbf{ln}\,\yen^2_\pm c^2$$

$$E_{cell} = E^o_{cell} - \frac{RT}{F}\mathbf{ln}\,c^2 - \frac{RT}{F}\mathbf{ln}\,\yen^2_\pm$$

$$E_{cell} = E^o_{cell} - \frac{2.303RT}{F}\mathbf{log}\,c^2 - \frac{2.303RT}{F}\mathbf{log}\,\yen^2_\pm$$

$$\mathbf{log}\,\yen_\pm = -A\sqrt{I} = -0.509\sqrt{c}$$

Debye-Huckel limiting law (1:1 electrolyte)

$$E_{cell} = E^o_{cell} - 2\frac{2.303RT}{F}\mathbf{log}\,c - 2\frac{2.303RT}{F}\mathbf{log}\,\yen_\pm$$

$$E_{cell} = E^o_{cell} - 2\frac{2.303RT}{F}\mathbf{log}\,c - 2\frac{2.303RT}{F}(-A)\sqrt{c}$$

$$E_{cell} = E^o_{cell} - 2\times 0.0592\,\mathbf{log}\,c + 2\times 0.0592A\sqrt{c} \qquad @25^0C$$

$E_{cell} = D + E\,\mathbf{log}\,c + F\sqrt{c}$ rewriting the 'coefficients' as $D,\ E,\ F$.

$$E_{cell} = E^{o}_{cell} - 2\frac{2.303RT}{F}\mathbf{log}\,c - 2\frac{2.303RT}{F}\mathbf{log}\,\text{¥}_{\pm}$$

$$E_{cell} = E^{o}_{cell} - 2\times 0.0592\,\mathbf{log}\,c + 2\times 0.0592\,A\sqrt{c} \qquad @25^{0}C$$

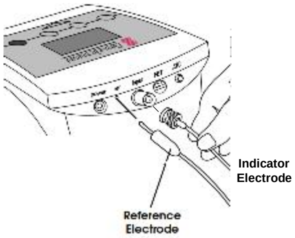
$E_{cell} = D + E\,\mathbf{log}\,c + F\sqrt{c}$ rewriting the 'coefficients' as $D,\ E,\ F$.

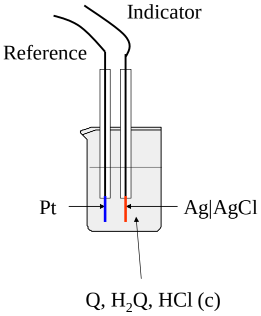
$0.1184A = F$ Evaluate A

$\mathbf{log}\,\text{¥}_{\pm} = -A\sqrt{c}$

$\text{¥}_{\pm} = 10^{-A\sqrt{c}}$ Tabulate $\text{¥}_{\pm}$ values for all c

1. Find the E_{cell} for a series of cells for a series cells of HCl solutions of concentrations c;
2. Plot E_{cell} vs c.
3. By a suitable curve fitting procedure determine *E, F, G* and *verify* the value of
   i. *A* of the DHE
   ii. *E^o* of the cell and
   iii. the experimental value of (*2.303RT/F*)
4 Generate a table showing the variation of *the mean activity coefficients,* $\text{¥}_{ï}$ for HCl in the concentration range studied assuming the DHE used above is valid in that range.





Procedure (in brief)

1. Prepare a 0.100 M HCl solution. Make a few more solutions (0.05M, 0.025M, 0.0125M and 0.00625 M) by serial dilution.
2. Connect the electrodes to the appropriate slots of a pH meter (high impedance voltmeter).
3. Wash the electrode pair with the HCl solution.
4. Immerse the electrode pair in the above mentioned solution.
5. Measure the voltage (EMF) of the electrochemical cell.
6. Repeat 3, 4, 5 for all HCl solutions.