

Experiment # °**Title of experiment:**

Determination of Activity Coefficients by electrochemical method

Aim:

Determination of Activity Coefficients of Hydrochloric Acid Solutions

Introduction:

The activity coefficient γ , based upon molality (m) is defined as:

$$a = m \gamma \quad (1)$$

where a is the activity, γ is activity coefficients

An ideal solution is defined as one for which γ is unity, but for a non-ideal solution it differs from unity. However, even for non-ideal solutions, in the limit of zero ionic strength, the activities of ions are equal to their concentrations. The activity coefficients, thus, become unity in the limit of zero ionic strength. The ionic strength I is defined by the expression;

$$I = \frac{1}{2} \sum C_i Z_i^2 \quad (2)$$

where C is the concentration and Z is the charge of the ions of type i . The Debye-Hückel "limiting law" predicts the mean ion activity coefficient (γ_{\pm}) by the equation:

$$\log(\gamma)_{\pm} = -A |Z_+ Z_-| * \sqrt{I} \quad (3)$$

where Z_+ , Z_- are the charges of anion and cation respectively. The constant A has the value 0.509 at 25 °C for aqueous solutions. For 1:1 (uni-univalent) electrolytes the ionic strength equals the concentration, $I = C$. For high concentrated solutions, the following equation may be used.

$$\log(\gamma)_{\pm} = -A |Z_+ Z_-| \sqrt{I} + C I \quad (4)$$

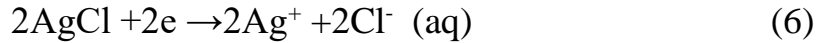
Where C is a constant.

There are several methods for the determination of activity coefficients. The measurement of electromotive force of a cell is one of the most convenient methods.

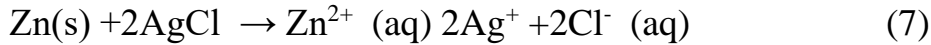
Consider the following cell:



The reactions in anode and cathode are :



The net reaction is:



The electromotive force of this cell (E.M.F) is

$$E = E_{\text{Ag}/\text{AgCl}} - E_{\text{Zn}/\text{Zn}^{2+}} \quad (8)$$

For the two electrodes, the potential is:

$$E_{\text{cathod}} = E_{\text{Ag}/\text{AgCl}} = E^{\circ}_{\text{Ag}/\text{AgCl}} - \frac{RT}{2F} \ln a_{\text{Ag}^+}^2 a_{\text{Cl}^-}^2 \quad (9)$$

$$E_{\text{anode}} = E_{\text{Zn}} = E^{\circ}_{\text{Zn}} - \frac{RT}{2F} \ln \frac{a_+}{a_m} \quad (10)$$

where $(a_-)^2$ is the activity of Cl^- , a_+ is the activity of Zn^{2+} and a_m is the activity of zinc metal and the activity of silver metal is constant

$$E = E_{\text{C}} - E_{\text{a}} = E_{\text{Ag}/\text{AgCl}} - E_{\text{Zn}/\text{Zn}^{2+}} \quad (11)$$

$$E = (E^{\circ}_{\text{AgCl}} - E^{\circ}_{\text{Zn}}) - \left[\frac{RT}{2F} \ln a_m^2 a_-^2 \right] - \left[\frac{RT}{2F} \ln \frac{a_+}{a_m} \right] \quad (12)$$

Rearranging the equation and adding a_m to E° we get a new constant \bar{E} instead

$$E = \bar{E} - \frac{RT}{2F} \ln a_-^2 - \frac{RT}{2F} \ln a_+ \quad (13)$$

$$E = \bar{E} - \frac{RT}{2F} \ln a_-^2 a_+ \quad (14)$$

Since we can only measure the mean Ionic Activity (a_{\pm})

$$(a_{\pm})^v = (a_+)^{v^+} \times (a_-)^{v^-} \quad (15)$$

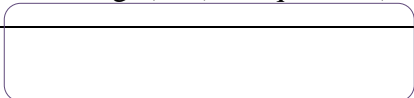
For an electrolyte of v_+ cation and v_- anion we can find:

$$v = v^+ + v^-$$

For ZnCl_2 :

$$(a_{\pm})^3 = (a_+)^1 \times (a_-)^2 \quad (16)$$

Substituting (a_{\pm}) in equation (14)



$$E = \bar{E} - \frac{RT}{2F} \ln (a_{\pm})^3 \quad (17)$$



$$E = \bar{E} - \frac{3RT}{2F} \ln((a_{\pm})) \quad (18)$$

Mean Ionic Activity is related to mean molality (m_{\pm}) and mean activity coefficient (γ_{\pm}) as

$$a_{\pm} = m_{\pm} \gamma_{\pm} \quad (19)$$

Equation (20) is used to calculate mean activity coefficient (γ_{\pm}) mathematically

$$E = \bar{E} - \frac{3RT}{2F} \times \ln(m_{\pm} \times \gamma_{\pm}) \quad (20)$$

However we need to calculate the value of \bar{E} graphically after rearranging eq.(20)

$$E + \frac{3RT}{2F} \times \ln(\gamma_{\pm}) = \bar{E} - \frac{3RT}{2F} \times \ln(m_{\pm})$$

Changing ln into log gives:

$$E + \frac{6.909RT}{2F} \times \log(\gamma_{\pm}) = \bar{E} - \frac{2.303RT}{2F} \times \log(m_{\pm})^3 \quad (21)$$

The mean activity coefficient (γ_{\pm}) for $ZnCl_2$ is related to ionic strength as:

$$\log(\gamma)_{\pm} = -0.5 |Z_+Z_-| \sqrt{I} + CI$$

$$\log(\gamma)_{\pm} = -\sqrt{I} + CI \quad (22)$$

Substituting in equation (21)

$$E - \frac{6.909RT}{2F} \sqrt{I} + \frac{6.909RT}{2F} \times CI = \bar{E} - \frac{2.303RT}{2F} \times \log(m_{\pm})^3$$

For $ZnCl_2$ $m_+ = m$, $m_- = 2m$

$$(m_{\pm})^3 = (m)^1 \times (2m)^2 = 4m^3$$

$$I = \frac{1}{2} \sum C_i Z_i^2$$

$$I = 3M$$

Since we use dilute solutions, **m=molarity**

$$E - \frac{6.909RT}{2F} \times \sqrt{3m} + \frac{6.909RT}{2F} \times 3Cm = \bar{E} - \frac{2.303RT}{2F} \times \log(m_{\pm})^3$$

$$E - \frac{6.909RT}{2F} * \sqrt{3m} + \frac{6.909RT}{2F} \times 3Cm = \bar{E} - \frac{2.303RT}{2F} \times \log(m_{\pm})^3$$

Note that $(m_{\pm})^3 = 4m^3$

and $\frac{2.303RT}{2F} \times \log(m_{\pm})^3$ is moved to the left side of this equation.

$$E - \frac{6.909RT}{2F} \sqrt{3m} + \frac{2.303RT}{2F} \times \log 4(4m^3) = \bar{E} - \frac{6.909RT}{2F} \times 3Cm \quad (23)$$

From eq. (23) E is the potential value from the Voltmeter of each concentration. The left side of equation 23 is drawn as (Y) with the independent variable **molarity (x)**. We draw the equation to get the value of \bar{E} which is the intercept

Materials:

Ag rod, Zn electrode or sheet, Sand paper, pH meter, two connection leads with Alligator clips.

Different concentration of ZnCl₂ 0.0005, 0.001, 0.003, 0.005, 0.008 M

AgNO₃ (0.01 M), Saturated KCl solution. Lugen tube with side arm. 50 mL beaker.

Procedure:

1. Clean the Ag rod and Zn electrode by the sand paper then wash with tap water followed with distilled water and dry.
2. Start with the lowest concentration of ZnCl₂, add 50 mL of 0.0005M into the beaker, hold Zn electrode with Alligator clips then immerse the Zn electrode from the top.

3. Close the tip of the Lugin tube with filter paper and be sure that no solution is dripping. In a nother test tube fill the tube with saturated KCl solution. Add a few drops of AgNO₃ until a white ppt of AgCl is formed. Transfer the white solution to the lugin tube. Be sure no bubbles are present. Hold the Ag with the Alligator clips then immerse the Ag electrode and be sure that it touches the white ppt of AgCl. You can add 2 drops of AgNO₃ .Immerse the tip of the lugin tube in the Zn solution.
4. Turn on the Voltmeter, choose the potential mode and put on stand -by. Connect the Zn electrode to the anode and Ag electrode to the cathode.
5. Turn on the Voltmeter on potential mode, wait for 5 seconds then record reading.
6. Turn the Voltmeter to stand-by mode and change the ZnCl₂ into 0.001M.
7. Repeat the previous steps until you record the potential of all solutions.

Results:

Fill up the following table

ZnCl ₂ (M)	Potential reading from Voltmeter	Left side of eq. 23
0.0005		
0.001		
0.003		
0.005		
0.008		

Report:

1. Plot Left side of eq. 23 versus m of ZnCl₂
2. Find \bar{E} from the intercept of the straight line.
3. Calculate γ_{\pm} for each concentration of ZnCl₂ from eq. 21 and from the simple Debye Huckel equaion

$$\log(\gamma)_{\pm} = -0.5 |Z_+Z_-| \sqrt{I}$$

4. Discuss the relation of γ_{\pm} with concentration from your data.

