EXPERIMENT 6 - CONDUCTANCE OF ELECTROLYTES

THEORY

We all know that the solutions of electrolytes conduct an electric current by the motion of the cations towards the cathode, and anions towards the anode. Metallic conductors are known to obey Ohm’s Law:

\[ I = \frac{\Delta \Phi}{R} \]  

(1)

where \( I \) is the current in amperes, \( \Delta \Phi \) is the difference in the electric potential between the terminals of the conductor in volts, and \( R \) is the resistance in ohms. \( R \) depends upon the dimensions of the conductor:

\[ R = \frac{1}{\rho \ A} \]  

(2)

where \( l \) is length, \( A \) is the cross-sectional area and \( \rho \) is the special resistance, i.e. resistivity, in \( \Omega \cdot m \). Reciprocal resistance, \( 1/R \), is known as conductance, and reciprocal resistivity, \( 1/\rho \), as conductivity. Conductivity is given by the symbol \( \kappa \) and has units \( \Omega^{-1} m^{-1} \) or \( S = \Omega^{-1} \). Hence,

\[ \kappa = \frac{1}{RA} \]  

(3)

Conductivity depends upon the number of charge carriers (i.e. ions) present in the solution. It is therefore, reasonable to express it in terms of molar conductivity:

\[ \Lambda_m = \kappa/c \]  

(4)

where \( c \) is the molar concentration of the electrolyte. We can classify electrolytes as a) strong electrolytes, and b) weak electrolytes. The strong electrolytes have high molar conductivities, and their conductivities change very little if the solution is diluted down. In the case of weak electrolytes, however, there is little conductivity in concentrated solutions. The conductivity increases upon increasing dilution. The value of \( \Lambda_m \) extrapolated to zero concentration (i.e. theoretical infinite dilution) is known as \( \Lambda_{m0} \), the molar conductivity at infinite dilution when ion interaction is assumed to be zero. It is also known as the limiting molar conductivity.

Kohlrausch’s Law:

\[ \Lambda_m = \Lambda_{m0} - K c^{1/2} \]  

(5)

where \( K \) is an experimental constant. One can obtain the value of \( \Lambda_{m0} \) from the intercept of the slope of the \( \Lambda_m \) versus \( c^{1/2} \) plot.

Since each ion is assumed to be migrating independently, the value of \( \Lambda_{m0} \) can also be obtained from the addition of individual conductivities of ions:

\[ \Lambda_m = \Lambda_{m+}^{0} + \Lambda_{m-}^{0} \]  

(6)

or

\[ \Lambda_m = \nu_+ \lambda_+ + \nu_- \lambda_- \]  

(7)

where \( \nu_+ \) and \( \nu_- \) are the numbers of cations and anions per formula unit of the electrolyte, and \( \lambda_+ \) and \( \lambda_- \) are the limiting ionic conductivities. For a dilute, weak electrolyte

\[ \Lambda = \alpha \Lambda_m^{0} \]  

(8)

where \( \alpha \) is the degree of ionization as in the dissociation for acetic acid HAc given below:

\[ \text{HAc} + \text{H}_2\text{O} \rightarrow \text{Ac}^- + \text{H}_3\text{O}^+ \]  

(1-\( \alpha \))c \( \alpha c \)  

\( \alpha c \)
where \( c \) is the molar concentration. For this acid dissociation constant \( K_a \) can be given by

\[
K_a = \frac{[\text{Ac}][\text{H}_3\text{O}^+]}{[\text{HAc}]} = \frac{\alpha^2 c}{1 - \alpha}
\]

(10)

PROCEDURE
1. Read the cell constant, \( x \), for the cell used in your experiments from the conductometer. \( x = \kappa R \) (11)
where \( \kappa \) is the conductivity and \( R \) is the resistance, as previously.
2. Calibrate the conductometer by immersing the conductivity cell into a beaker, filled with deionized (distilled) water. Set the knob to red line and adjust the scale.
3. Rinse the conductivity cell with 0.02 M KCl, then fill a beaker with 100 ml of this solution and immerse the conductivity cell.
4. Keep the conductivity cell steady in the solution and adjust the knob to “conductance”. Read and record the value from the upper scale (in units of \( \mu \text{mhos} \)).
5. Take 25 ml of the 0.02 M KCl solution into a beaker add 75 ml distilled water. Repeat steps 2-4 with this solution.
6. Prepare 0.02 M KCl solutions at 1/16 and 1/64 dilutions in the same way explained in step 5 and repeat steps 2-4 with these solutions. Serial dilutions are strongly encouraged.
7. Repeat steps 5-6 with solutions of 0.02 M KAc, 0.02 M HCl and 0.05 M HAc.

CALCULATIONS
1. Determine the \( \Lambda_m \) values using equation (4). Make sure that you obtain the correct units. \( \Lambda_m = \text{Sm}^2/\text{mol} \)
2. Tabulate the \( R \), \( \kappa \), and \( \Lambda_m \) values for all the solutions.
3. Using equation (5), plot \( \Lambda_m \) versus \( c^{1/2} \) for each solution to determine the \( \Lambda_{m0} \) values.
4. Using the Kohlrausch Law, determine the \( \Lambda_{m0} \) for acetic acid:
   \[
   \Lambda_{m0}(\text{HAc}) = \Lambda_{m0}(\text{HCl}) + \Lambda_{m0}(\text{KAc}) - \Lambda_{m0}(\text{KCl})
   \]
(12)
5. Using equation (8), determine \( \alpha \) for each HAc concentration used, and calculate \( K_a \) (again for each case) using equation (10).
6. Determine the average \( K_a \) value for all the experiments.
7. Alternatively, determine \( K_a \) by extrapolation to “zero concentration” on a \( K_a \) versus \( (\alpha c)^{1/2} \) plot.
8. Compare the results obtained in steps 6 and 7.

DATA SHEET:

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