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Chapter

A New Method for Determination of Molecular Weight of Compounds Soluble in Protic Solvents by Electrochemical Impedance Spectroscopy

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Abstract

This chapter deals with a new method for determining the molecular weight of chemical substances soluble in protic solvents. One of the well-known methods for the determination of molecular weight of a substance, based on one of the colligative properties, is Ostwald and Walker’s method, which depends on relative lowering of vapor pressure of solvent. In this paper we proposed a new method for determining the molecular mass of the substances that are soluble in protic solvents such as water, methanol and ethanol employing electrochemical impedance spectroscopy (EIS) technique and Raoult’s law. The moisture and vapor pressure dependent proton conductivity of some organic compounds and metal-organic frame works (MOFs) can be utilized to find the molecular mass of solutes soluble in protic solvents. This property is considered as key for determination of molecular weight of chemical substances using EIS and is simpler than Ostwald and Walker’s method. This method is a non-destructive and also useful to determine the molecular weight of polymers and proteins soluble in protic solvents.

Keywords: impedance, molecular weight, vapor pressure, Raoult’s law

1. Introduction

Electrochemical impedance spectroscopy (EIS) finds a special place among the various electrochemical techniques. It is a powerful tool for analyzing the interfaces formed in the heterogeneous systems. EIS supplies a large amount of informations, though it may not provide all the answers. EIS uses tools developed in electrical engineering and describes the behavior of the systems under study in terms of an equivalent circuit consisting of the circuit elements resistors, capacitors, Warburg impedance etc. The mathematical foundations of EIS were dealt by Heariside [1], through which it is possible to solve the integrodifferential equations appearing in the
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solutions of electrical circuits by converting them into a system of algebraic equations. The main advantage of EIS is the fact that it is based on the linear time invariant (LTI) theory and validity of the data may be verified using Kramers-Kronig integral transforms. Nernst was the first person who described the chemical applications of impedance spectroscopy through his work [2], followed by many others including those applications to the distribution of relaxation time constants by Cole and Cole [3] and Davidson and Cole [4]. The impedance of mass transfer was explained by Warburg using so called Warburg impedance, which extended EIS to apply for redox reactions [5]. With further development in the understanding of EIS, the structure of double layer in the absence and presence of adsorbed species was studied initially at dropping mercury electrode and then at solid electrodes using AC bridge. The analysis of electrochemical reactions using the electro analog circuit was introduced by Dolin and Ershler [6] and Randles [7, 8], where the age of electrical analog began [9] and continues up till now. The fundamental aspects of EIS give the idea to validate the data and to model the processes limited by diffusion, electrode kinetics and adsorption on different types of electrode geometries. The availability of modern instrumentation to obtain impedance data as well as computer programs to interpret the results have made this technique popular. Now a days, EIS finds applications in corrosion, biosensors, battery development, fuel cell development, drug cell membrane interaction [10], paint characterization, sensor development, polymers etc.

The development of organic proton conducting materials to substitute the per fluorinated polymers such as nafion is an important area of research in the field of fuel cell technologies [11–15]. Recent research in this field emerged some coordination polymers and metal-organic frame works (MOFs) for their proton transport capabilities, though the literature on these materials in other domains such as magnetism, catalysis, inclusion phenomenon and in supramolecular chemistry are quite extensive [16–23]. Under high humidity conditions or with water channels, MOFs show high degree of proton conductivities, comparable to nafion [24–28]. The proton conducting ability of these materials primarily depend on the existence of charge carrying molecular or ionic species such as $H_3O^+$, $OH^-$, or $NH_4^+$ Lewis acidic moieties. These molecular or ionic species with the complex network of hydrogen bonds or their arrangements with the water molecules play a vital role for proton conductivity. These characteristics are considered to be the important structural requirements of the proton conducting polymers and MOFs [29–33]. With the above-mentioned features, several new MOFs that exhibit Nafion-like proton conducting characters, under humidified and ambient temperature conditions have been reported [34]. The proton conducting ability of these materials was evaluated using EIS [34–36] which depends on humidity levels of the surroundings.

In this chapter, through an innovative approach we would like to propose a new method for the determination of molecular weight of compounds which are soluble in water and other protic solvents, using proton conducting ability of organic compounds or MOFs by EIS technique.

2. Electrochemical impedance spectroscopy—a tool to evaluate the proton conductivity of solid materials theory and discussion

Now a days proton conducting solid state electrolytes gained a considerable attention owing to their application in fuel cells1, electrochromic devices [37], humidity
sensors [38] and gas separators [39]. Nafion, a perfluorinated polymer with sulphonic acid is used as solid-state proton conductor under hydrated conditions [40]. This polymer has many disadvantages, under high temperature (>80°C) the water clusters are lost in the pores of Nafion. At low humidity levels water clusters in the Nafion pores are low. Both factors reduce the conductivity of Nafion [40]. In addition to these drawbacks, high cost, high fuel cross over, non eco-friendly synthesis and variation of conductivity with degree of sulphonation limit its applications. These limitations made the researchers to look for alternate solid state proton conducting materials. Many coordination compounds and MOFs having proton conducting ability were not explored for their proton conductivities. Recent reports on proton conducting nature of MOFs promise their enhanced proton conductivity at high temperature and low fuel cross over.

It was reported that the organic compounds with heteroatoms incorporated within the pores of MOFs as guests with controlled loading. The amphoteric heterocyclic moiety has shown electrolytic conductance through proton. This system has shown an improved proton conductance even at higher temperatures and precisely the theoretical open circuit potential of hydrogen-oxygen fuel cell. Only few compounds have been studied for their proton conductivities. Their proton conducting properties can further be extended to calculate the molecular weight of solutes dissolved in the protic solvents and the vapor pressure of the protic solvents at any temperature knowing the normal boiling point. Conversely, this property can also be used for the calculation of molar enthalpy of vaporization of protic solvents. These applications have not been verified for these compounds. This method could be an alternate for Ostwald and Walker Method for determining molecular weight of substances and a useful technique for knowing the molecular weight of polymers soluble and an unknown substance in protic solvent. The proposed method is based on EIS technique.

EIS is a routine method for characterization of various electrical properties of different types of materials and the interfaces formed by the materials with electronically conducting materials. EIS is a simple non-destroying technique, where a system study is perturbed by an AC sinusoidally varying potential to the system under study and measuring the current through the system. The response to the applied sinusoidally varying potential at a frequency is a sinusoidally varying current at the same frequency with shift in phase. The ratio of

\[ R = \frac{E}{I} \] (1)

Similar to resistance, the term impedance measures the ability of a material to resist the flow of charges in definite direction. However, impedance differs from resistance in two main aspects. First, it is associated with alternating current (AC); second, it is usually mentioned at a particular frequency.

Measurement of impedance is done by applying a sinusoidally varying an AC potential to the system under study and measuring the current through the system. The response to the applied sinusoidally varying potential at a frequency is a sinusoidally varying current at the same frequency with shift in phase. The ratio of
applied sinusoidally varying potential to the resulting sinusoidally varying current at the same frequency is called impedance, using which the information on conductivity of the system can be obtained.

The input or excitation signal, i.e. sinusoidally varying potential at a frequency can be expressed as a function of time as follows:

\[ E(t) = E_0 \sin(\omega t) \]  

Where, 

\[ E(t) \] refers to the potential at time \( t \), \( E_0 \) is the amplitude of the applied AC potential and \( \omega \) is the angular frequency given by the expression \( \omega = 2\pi f \) (\( f \) = applied frequency in Hz)

In a linear system the excitation of voltage at a frequency \( \omega' \) provides a current \( I' \) at the same frequency. This generated current is different in amplitude and phase from voltage as given below:

\[ I(t) = I_0 \sin(\omega t + \phi) \]  

In a non-linear system \( I-V \) relation gives a distorted response which is not purely sinusoidal, but it is still periodic [41].

An analogous expression to Ohm’s law allows us to calculate the impedance of the system as:

\[ Z = \frac{E(t)}{I(t)} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = \frac{Z_0 \sin(\omega t)}{\sin(\omega t + \phi)} \]  

The impedance is therefore expressed in terms of a magnitude, \( Z_0 \), and a phase shift \( \phi \). Using Euler’s relationship, the impedance is then represented as a complex number

\[ Z = \frac{E(t)}{I(t)} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 (\cos \phi + j \sin \phi) \]  

Accordingly, the impedance is a vector quantity since it has a magnitude, \( Z_0 \), and direction given by phase shift, \( \phi \).

When we apply the above concepts to a pure resistor, for which the phase angle \( \phi \) is zero,

\[ E(t) = E_0 \sin(\omega t) \]  
\[ I(t) = I_0 \sin(\omega t) \]  
\[ R = \frac{E(t)}{I(t)} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t)} = \frac{E_0}{I_0} \]  

When the concept is applied for a capacitor, where, \( \phi = \frac{\pi}{2} \)

Charge in the capacitor,

\[ q = CE \]
Current,

\[ I = \frac{dq}{dt} = C \frac{dE}{dt} \]  \hspace{1cm} (10)

\[ I = C E_0 \omega \cos (\omega t) \]  \hspace{1cm} (11)

\[ I = \frac{E_0}{X_C} \sin \left( \omega t + \frac{\pi}{2} \right) \]  \hspace{1cm} (12)

Where \( X_C \) is capacitive reactance, i.e. the resistance offered by a pure capacitor for the alternate current flows across it. Its value depends on frequency of AC excitation voltage and is given as:

\[ X_C = \frac{1}{\omega C} \]  \hspace{1cm} (13)

Where, ‘\( C \)’ is capacitance of the pure capacitor (in F).

Since the current leads the voltage by a phase angle of \( \frac{\pi}{2} \), the capacitive reactance is taken along the ordinate (Y-axis) and is given as imaginary component.

\[ i.e. \quad -iX_C = \frac{-i}{\omega C} = \frac{E(t)}{I(t)} \]  \hspace{1cm} (14)

Where, \( i = \sqrt{-1} \), an imaginary number.

When a capacitor and a resistor are in series connection, the excitation voltage is given as,

\[ E = E_R + E_C \]  \hspace{1cm} (15)

\[ E = IR - iX_CI \]  \hspace{1cm} (16)

\[ \frac{E}{I} = R - iX_C \]  \hspace{1cm} (17)

Since the value of \( X_C \) depends on frequency, the total resistance in this series depends on the frequency of excitation voltage and is called impedance (\( Z \)).

\[ Z = R - iX_C \]  \hspace{1cm} (18)

In general, the impedance can be represented as,

\[ Z(\omega) = Z_{Re} - iZ_{Im} \]  \hspace{1cm} (19)

Where, \( Z_{Re} = \) real part of impedance,

\( Z_{Im} = \) imaginary part of impedance.

The magnitude of impedance is given as,

\[ |Z| = \sqrt{(Z_{Re})^2 + (Z_{Im})^2} \]  \hspace{1cm} (20)

\[ |Z| = \sqrt{R^2 + \frac{1}{\omega^2 C^2}} \]  \hspace{1cm} (21)
The phase angle $\varphi$ is given as,

$$\varphi = \tan^{-1}(Z_{im}/Z_{re}) \quad (22)$$

$$\varphi = \tan^{-1}(X_C/R) \quad (23)$$

$$\varphi = \tan^{-1}(1/\omega CR) \quad (24)$$

It is well known that impedance is a specific form of the transfer function of the system [41]. If $I(s)$ and $E(s)$ are the Laplace transforms of the sinusoidal current and voltage respectively, the transfer function [41] is given as,

$$TF(s) \approx \frac{E(s)}{I(s)} \approx \frac{E_0}{I_0} \left( \cos \varphi + \frac{s}{\omega} \sin \varphi \right) \quad (25)$$

Were, $s$ is the Laplace complex variable or frequency,

$$s = i\omega \quad (26)$$

Now solutions to the Eq. (26) are confined to the frequency domain.

$$Z \approx TF(i\omega) = \frac{E_0}{I_0} \left( \cos \varphi + i \sin \varphi \right) \quad (27)$$

### 2.2 Variation of frequency

When we consider a homogeneous system, it is represented by a conductance ($G$) or resistor ($R$) in parallel connection with a capacitor ($C$) as shown in **Figure 1.**

The corresponding Nyquist and Bode (phase and impedance) plots for the above equivalent circuit are presented in the **Figures 2 and 3** respectively.

By rule the net impedance of this homogeneous system, from the above equivalent circuit, is given as,

$$\frac{1}{Z} = \frac{1}{R} - \frac{1}{iX_C} \quad (28)$$

$$\frac{1}{Z} = \frac{1}{R} + i\frac{1}{X_C} \quad (29)$$

$$\frac{1}{Z} = G + i\omega C \quad (30)$$

![Figure 1. An equivalent circuit for a homogeneous system.](image)
Conductance \(G\) and capacitance \(C\) of the homogeneous material describe its ability to conduct and store electric charge respectively. If the homogeneous material is considered as a slab of cross-sectional area \(A\) and thickness \(l\), these properties are given by the following expressions,

\[
G = \sigma \frac{A}{l} \tag{32}
\]

\[
C = \varepsilon \frac{A}{l} \tag{33}
\]

Where \(\sigma\) and \(\varepsilon\) are conductivity and permittivity of the homogeneous system respectively.

From Eqs. (27) and (31),
Therefore,

\[ G = \frac{1}{|Z|} \cos \varphi \]  

\[ C = -\frac{1}{|Z| \omega} \sin \varphi \]  

Using the above equations, we can measure the thickness of the homogeneous material.

Inspection of the above equation reveals that the impedance of the homogeneous material is dispersed with frequency and the dispersion is more pronounced for the frequencies greater than \( G/C \),

\[ \omega = \frac{G}{C} \]  

Giving the condition at which, the impedance measurement provides the most accurate estimates of both properties. This characteristic frequency of the homogeneous system is called ‘natural frequency’ of the system.

A heterogeneous system can be considered to consist of a number of different materials or slabs sandwiched together. The total impedance of such a system is given as,

\[ Z_N(\omega) = \sum_{n=1}^{N} \frac{1}{G_n + i\omega C_n} \]  

Each slab in the heterogeneous system has its own natural frequency defined by the expression \( \omega = \frac{G}{C} \). If the magnitudes of impedance of corresponding \( N \) slabs are sufficiently different, then these slabs can be easily identified within the combined dispersions immediately.

For example, using the last expression, the total impedance of a heterogeneous system consisting of two different materials or slabs (P and M), the impedance dispersion can be written as,

\[ Z_N(\omega) = \frac{1}{G_P + i\omega C_P} + \frac{1}{G_M + i\omega C_M} \]  

Dispersion of conductance (\( G \)) and capacitance (\( C \)) with frequency are obtained by simplifying this equation as,
The solid-state proton conducting electrolytes can be synthesized by simple solution crystallization method. The Nyquist plots recorded will not be straightforward to give the electrical properties of solid-state proton conductors. Equivalent circuits are used to derive the electrical properties of solid-state electrolytes. The equivalent circuit that fits well with the Nyquist plots will also provide the nature of arrangement of different dielectric slabs inside the solid-state protonic conductor. The mechanism for proton conduction could be derived from the temperature studies.

3. Determination of molecular mass using the electrochemical impedance spectra of solid-state proton conductors

Vapor pressure is a characteristic property of a substance in the condensed phase at constant temperature. It is the pressure exerted by the vapor molecules of a substance on the surface of the condensed phase of the same substance, when the vapor molecules are in equilibrium with its condensed phase at constant temperature. The vapor pressure of a liquid at constant temperature is constant and increases with temperature. At one temperature the vapor pressure of the liquid becomes equal to atmospheric pressure at which the liquid boils and temperature is called boiling point of the liquid. At the same temperature the vapor pressure of a liquid decreases when a non-volatile solute is dissolved in it which is called lowering of vapor pressure of the solvent. The proton conducting ability of coordination polymers and MOFs depends on the humidity levels or water vapor level in an environment. Greater the humidity level greater will be the proton conductivity. The proton conductivity of a coordination polymer or MOF is measured from the charge transfer resistance \( R_{ct} \) value obtained from EIS [34–36]. The charge transfer resistance measured using EIS is inversely proportional to proton conducting of the CPs or MOFs, which in turn directly proportional to humidity level or moisture level in the atmosphere.

Therefore, the charge transfer resistance \( R_{ct} \) of CPs or MOFs in the presence of known volume of pure water or protic solvents, measured in a closed container,

\[
R_{ct} \propto \frac{1}{P^0} \tag{44}
\]

Where \( P^0 \) is vapor pressure of pure protic solvent.

The charge transfer resistance measured after dissolving a known weight of solute in the same volume of water or protic solvents in the closed container at same temperature,

\[
R'_{ct} \propto \frac{1}{P} \tag{45}
\]
Where $P$ is vapor pressure of solvent in solution.

From Raoult’s law

$$P = P^0 X_1$$  \hspace{1cm} (46)

or

$$X_1 = \frac{P}{P^0}$$  \hspace{1cm} (47)

Where $X_1$ is mole fraction of protic solvent.

Therefore

$$X_1 = \frac{R_{ct}}{R_{ct}}$$  \hspace{1cm} (48)

$$\frac{n_1}{n_1 + n_2} = \frac{R_{ct}}{R_{ct}}$$  \hspace{1cm} (49)

Where $n_1$ and $n_2$ are number of moles of solvent and solute respectively.

Using Eq. (50) the molecular weight of the solute can be calculated.

This method is also applicable for determining molecular weight of the substances which are insoluble in water but soluble in methanol or ethanol, since some CPs or MOFs showing reversible proton conductivity in CH$_3$CH$_2$OH are also reported [35, 36].

### 4. Conclusion

The measurement of vapor pressure of solvents in pure form and in solutions is a tedious one in Ostwald and Walker’s method of determining molecular mass from relative lowering of vapor pressure, the proposed method is easy with simple experimental setup and can be used to determine the molecular weight of substances and polymers soluble in protic solvents.

### Abbreviations

EIS  
metal organic framework  
R  
resistance  
C  
capacitance  
E  
voltage  
I  
current
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