

STUDY OF ACOUSTICAL PROPERTIES OF ELECTROLYTIC SOLUTION – A THEORETICAL APPROACH

R.VELAVAN¹, MYVIZHIP²,

¹Professor, ²Assistant Professor, Dept. of Physics, ²Department of Bioinformatics,

¹BIST, BIHER, Bharath university, Chennai-73,

velavan.phy@bharathuniv.ac.in

Abstract

Ultrasonic is a sound energy produced from the vibrating body in the form of waves whose frequency is greater than 20K Hz, above the human hearing range. Ultrasound can be produced in research laboratories by means of simple and compact ultrasonic interferometer at a cost effective way. This article explains the working principle of interferometer.

Introduction

Ultrasonic measurements provide qualitative information regarding the elastic forces acting between molecules on the basis of compressibility and other related data. The present work is to study the behavior of electrolytes in aqueous medium[1-9].

Adiabatic Compressibility

Compressibility measurements yield interesting information. They are also highly accurate. Here we assume that the bound water molecules are highly compressed by the intense field of the ion and that further compression affects only the unbound water. The decrease in volume accompanying further compression is proportional to the amount of unbound water and hence can provide information to estimate the quantity of bound water. This leads to a total hydration number[10-19].

The adiabatic compressibility [1] is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. If there is no heat flow, the entropy is unchanged in a reversible process, is one at constant entropy[20-29]. Adiabatic compressibility is expressed as

$$\beta = (1/V)[\partial V/\partial P]_S \quad \text{-----}(1)$$

It can be determined with the measurement of density and ultrasonic velocity U as

$$\beta = (1/u^2 p) \text{ cm}^2/\text{dyne} \quad \text{-----}(2)$$

When a solute is dissolved in solvent, the compressibility can be lowered by the influence of electrostatic field of the ions present on the surrounding solvent molecules[30-35]. The

$$P = \beta_s^\circ - \beta_s = d\beta_s = \left[\frac{Z_i^2 e^4}{2D^2 KT} \right] \sum n_i \sum z_i^2 \quad \text{-----}(3)$$

lowering of compressibility due to the electrostatic pressure P between two charges particles is given by [36-41]

Where β_s° is the compressibility of the solvent

β_s is the compressibility of the solution at a given temperature,

K is the Boltzman's constant

e the electronic charge, D the dielectric constant, Z_i the valiancy and n_i the number of ions of the i^{th} kind per mole.

From the relation between U and β the variation of sound velocity with concentration can be expressed as,

$$\frac{du}{dc} = -\left(\frac{u}{2}\right) \left[\left(\frac{1}{\rho}\right) \frac{d\rho}{dc} + \left(\frac{1}{\beta}\right) \frac{d\beta}{dc} \right] \quad \text{-----(4)}$$

If both $(1/\rho)$ ($d\rho/dc$) and $(1/\beta)$ ($d\beta/dc$) are positive, then will decrease with increase in concentration. On the other hand, if $(1/\beta)$ ($d\beta/dc$) is negative and of greater magnitude than $(1/\rho)$ ($d\rho/dc$) then $d\rho/dc$ is positive and hence the velocity will increase with the concentration.

Intermolecular Free Length (L_f)

The intermolecular free length is one of the characteristic features of the liquid systems which determine the distance between the surfaces of neighboring molecules [2]. In the sense [42-49], the actual distance covered by the acoustic waves between the nearby molecules in the liquid systems. Jacobson's empirical relation is expressed as

$$UL_f = \rho^{1/2} = k \quad \text{-----(5)}$$

Where k is the Jacobson's constant is made use of in the determination of L_f as,

$$L_f = \left(\frac{K}{U_p^{1/2}} \right) = K(\beta_{ad})^{1/2} A^\circ \quad \text{-----(6)}$$

Previously, TMD, TSVM and TACM behaviors are justified on the basis of mixture hypothesis. Added solutes leverage the concomitant of the regions of bonded bulkiness and broken hydrogen bonded or unbonded denseness in the relative proportions. The structural equilibrium exists between the water clusters of bonded bulkiness and broken bonded denseness. If it deviates from the equilibrium and favours unbonded denseness, then structure breaking effect is dominant. In reverse, the equilibrium is shifted towards the bonded bulkiness, then structure-making effect dominant [50].

Adiabatic compressibility of solution is related to specific acoustic impedance (Z) of the solution via the relation

$$\beta = \rho/Z^2$$

Where ρ is the density of the solution.

At the low concentration of the organic liquids, there is no significant change in the temperature dependence of acoustic impedance of aqueous solutions when compared to pure water.

Relaxation Time (T)

Relaxation time depends on the viscosity of liquid [3]. It gives the orientation of the molecules in a particular direction. The relaxation time decreases with the increase in temperature for Glycine.

Eyring's indicates that the variations of sound velocity in the liquid can be determined based on the intermolecular free length between the adjacent molecules.

$$\text{Relaxation time } \tau = \frac{4\eta}{3\rho U^2} \quad \text{-----(7)}$$

Where

η -Viscosity of liquid, ρ - Density of liquid, U -Velocity of Ultrasonic

Specific Acoustic Impedance

The acoustic parameter, specifies acoustic impedance Z is calculated as,

$$Z = (\rho u) \text{ Rayl} \quad \text{----- (8)}$$

The general behavior of specific acoustic impedance is to have a linear increase in its value with concentration at a given temperature[3].

To understand the structural interactions in dilute aqueous solutions specific acoustic impedance is highly reasonable tool with good precision.

The maximum density at 39°C, the maximum sound velocity at 74°C, and the maximum adiabatic compressibility at 64°C are the unique properties of liquid water. These properties are stabilized due to thermal expansion and structural changes of water in liquid systems. It is well known that shifts in the temperature of maximum density (TMD), the temperature of sound velocity maximum (TSVM) and the temperature of adiabatic compressibility minimum (TACM) are caused by added solutes. These effects attribute to the solute ions in the structure of water. Similarly it is noticed that the temperature of specific acoustic impedance maximum (TSAIM) is also unique to water structure. But the effect of added solutes on the (TSAIM) has not been carried out properly so far. Both the "uniformity" and "mixtures" models support the unique properties of liquid water, which always leads to controversy.

Ultrasonic Attenuation (α)

Ultrasonic attenuation or absorption co-efficient is a unique property of the liquid medium. Several factors like temperature, pressure, and frequency play vital role in the calculation of ultrasonic attenuation. Thus, it is calculated as below equation [4].

$$\omega^2 \tau$$

$$\text{Ultrasonic Attenuation } \alpha = \frac{\omega^2 \tau}{2U} \text{-----(9)}$$

Where τ –Relaxation Time, $\omega = 2\pi f$, $f = 3\text{MHz}$.

Free Volume

The concept of free volume is an extension of the idea that its neighbours enclose each molecule [5,6]. The free volume is defined as the average volume available for the molecules to move inside the hypothetical cell generated due to the repulsion of the proximal molecules.

Eyring et al have given a relation for the calculation of free volumes of liquids from the velocity of sound in liquid U and that in vapour v_g as

$$V_g = (\gamma RT/M)^{3/2}$$

Where v_g is the ratio of the two principal specific heats and, R is the gas constant, T and M are the temperature and molecular weight respectively.

Suryanarayana and Kuppaswamy based on dimensional analysis, obtained a relation for free volume in terms of ultrasonic velocity and viscosity of liquid as,

$$V_f = (MU/K)^{3/2}$$

Where, M is the molecular weight, U is the ultrasonic velocity and K is a constant equal to 4.28×10^{13} which is independent of temperature for all liquids.

The Surface Tension of Solutions

In 1878 J. Willard Gibbs showed surface activity to be due to uneven distribution of a solute molecule between the surface and the body of a solution. By a purely thermodynamic argument he deduced that, if a solute distributes itself so that the surface contains q moles of solute per 1 cm^2 of area in excess of that present in the body of the solution, then for dilute solutions q at equilibrium should be given

$$q = - \frac{C}{RT} \frac{d\gamma}{dC} \text{-----(10)}$$

Where C is the solution concentration, T the absolute temperature, R the gas constant, and $d\gamma/dC$ is the rate of change of the surface tension of solution with respect to concentration. When $d\gamma/dC$ is positive, then the surface tension of a solution increases with concentration, q must be negative, and the body of the solution is richer in the solute than the surface, as is the case with many electrolytes. However, when $d\gamma/dC$ is negative, then the surface tension of solution decreases with concentration, q is positive, and the surface contains a higher concentration of solute than the solution.

The surface tension is determined using the formula,

$$\text{S.T.} = \rho V^{3/2} \cdot 6.3 \times 10^{-4}$$

Rao's Constant

Rao's rule or Rao's constant extrapolates the relationship between molecular weight, density and ultrasonic velocity of liquids as,

$$R = \frac{M}{\rho} \cdot u^{1/3} \quad \text{-----} (11)$$

It is also known as the molar sound velocity. Several authors have provided theoretical explanation of Rao's formula on the basis of phase rule and kinetic theory of liquids.

Rao's constant has a tendency to increase with the concentration of the solution.

Wada's Constant

Wada's analyzed the variation of molar compressibility with concentration for many liquid systems and has derived the empirical relation,

$$B = \left[\frac{M}{\rho} \right] (\beta_{ad})^{-1/7} \quad \text{-----} (12)$$

This also usually increases with the concentration of the solution.

Conclusion:

The ultrasonic velocity, density, viscosity are theoretically calculated. These theoretical results are used to calculate experimental data.

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