THEORETICAL INVESTIGATION OF ACOUSTICAL PARAMETERS OF ELECTROLYTIC SOLUTION-AN ULTRASONIC STUDY

Bidyadhar Swain*, Rabindra N. Mishra, Upendra N. Dash

***Corresponding author: bidya.swain11@gmail.com**

Abstract: Ultrasonic wave propagation through liquid systems and solids is now well established as an effective means of examining certain physical properties of the materials. Ultrasonic technique has been employed extensively to investigate the acoustic parameters and predict the nature of molecular interactions in electrolytic solution. Various acoustical parameters, viz. acoustic impedance (Z), isentropic compressibility (K_s), intermolecular free length (L_f), solvation number (S_n), relative association (R_A), relaxation time (τ), Gibb's free energy change (ΔG), ultrasonic attenuation (α/f^2), free volume (V_f), internal pressure (π_i) and van der Walls constant (b) have been discussed along with working principle of interferometer. The qualitative intermolecular elastic forces between the solute and solvent molecules are explained in terms of compressibility. The structural arrangement of molecules in electrolyte solutions has been discussed on the basis of electrostatic field of ion.

Keywords: Ultrasonic interferometer, Acoustic impedance, Relative association, Isentropic compressibility, Hydration number.

1. Introduction

Because of high sensitivity to very low population densities at high energy states, ultrasonic methods have been preferred than the other techniques like dielectric relaxation, infrared spectroscopy, nuclear magnetic resonance, electron paramagnetic resonance, Raman effect etc. Ultrasonic method is a versatile non-destructive technique (NDT), which behaves like a powerful probe to assess the acoustic properties and predict the intermolecular interactions in binary and ternary mixtures [1-3] containing electrolytes. Since ultrasonic wave is a high frequency and low amplitude wave, due to its penetrating nature through liquid medium, it is of interest to study its interaction with matter to throw light into the molecular interaction and molecular kinetic properties of the materials. Ultrasonic energy is used in medicine, agriculture, engineering, defence and industry. In chemical industries it is very much useful in studying the chemical process and synthesis of chemical substances. The investigation of acoustic parameters of electrolytes in aqueous and mixed solvent systems has been the area of interest of many researchers [4, 5].

In the present study, we have investigated theoretically various acoustical parameters, such as acoustic impedance (Z), isentropic compressibility (K_s), intermolecular free length (L_f), relative association(R_A), solvation number (S_n), relaxation time (τ), Gibb's free energy change (ΔG), ultrasonic attenuation (α/f^2), internal pressure (π_i), free volume (V_f) and van der Walls constant (b) along with working principle of ultrasonic interferometer.

2. Measurement Techniques

2.1 Ultrasonic Interferometer

Ultrasonic velocity measurements in the electrolytic solutions were made by using a multi frequency ultrasonic interferometer (Model No-M84, Mittal enterprises, New Delhi, India) operating at a frequency of 2MHz at different temperatures. The temperature was maintained by a temperature controller device. Measurement of sound velocity was carried out by interferometric method which provides continuous wave method of ultrasonic velocity measurements and highly suitable for measurements in liquids in MHz region.

2.2 Description of Ultrasonic Interferometer

The ultrasonic interferometer consists of two parts

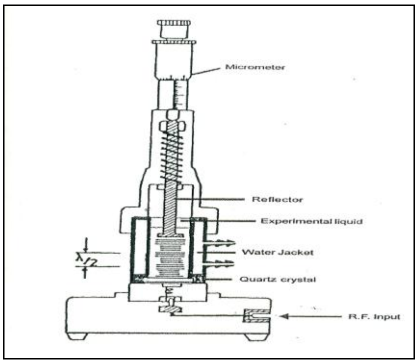
(A) High frequency generator

(B) Measuring cell

A. High frequency generator

It is a high frequency crystal controlled oscillator in the form of a modified pierce circult operating in the MHz region. It is designed to excite the transducer which is a quartz crystal at the bottom of the cell to produce ultrasonic frequency in the experimental liquid taken in the measuring cell. The generator is provided with a micro ammeter to observe the change in current. The generator is also provided with two controlling knobs. The knob marked 'Adj' is used to adjust the position of the needle on the ammeter. The knob marked 'Gain' is used to increase the sensitivity of the instrument for greater deflection. Two timer condensers on the back side of the generator are required for adjustment or tuning of the instrument when the deflection in the microammeter is insufficient for any particular liquid.

Ultrasonic Interferometer



Measuring Cell

B. Measuring Cell

It is a special designed double walled cell to hold the experimental liquid. It consists of three parts (i) Metal base (ii) container and (iii) reflector. A thermostatically regulated bath is connected to it to maintain the temperature of the liquid constant by circulating water in a double walled cell at any desired temperature. The reflector can be moved downward or upward by a micrometer screw system. The measuring cell is connected to the high frequency generator by a short co- axial cable.

2.3 Working principle of Ultrasonic Interferometer

The metal base of measuring cell is connected to the output terminal of the high frequency generator through a shielded co-axial cable. The container of the measuring cell is filled with the experimental liquid and then fitted with the reflector component. Then the measuring cell is connected to the metal base and the generator is switched on. The high frequency generator excites the quartz crystal that generates ultrasonic waves (produced by Piezo electric method). These waves travel through the experimental liquid medium and are reflected back by the movable metallic reflector kept parallel to the crystal inside the cell. The quartz crystal which first acts as generating transducer also acts as the detecting transducer. The incident and reflected ultrasonic waves are superimposed forming standing waves in the cells. As the reflecting plate is made to approach or proceed from the vibrating crystal. Cyclic changes of amplitude and phase of ultrasonic waves occur while the reflector passed through successive positions of maximum and minimum in the liquid medium. The acoustic propagation produces an electrical reaction on the oscillator of the quartz crystal. When the reflected wave returning to the crystal is 180^0 out of phase with the incident wave emanating from the crystal, the disturbance at the crystal will be reduced essentially to zero. This will cause a considerable rise in the plate current which is otherwise balanced at the output stage of a driving oscillator. The plate current will be maximum every time the reflector is moved half a wavelength.

2.4 Measurement of Ultrasonic Velocity

For carrying out the experiment the micrometer is slowly moved till the anode current on the ammeter in the high frequency generator shows the maximum. A number of maxima readings are observed and their number 'n' is noted. The total distance'd' moved by the reflecting plate thus can be known. The wavelength, λ and sound velocity, U can be calculated from relations.

$$\lambda = 2d/n \quad and \quad U = \lambda \times f$$

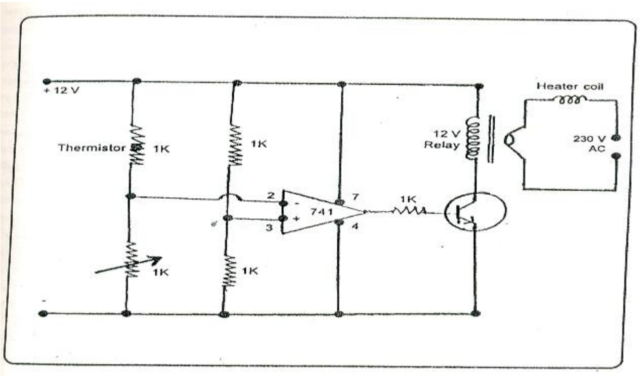
where, f is the frequency of ultrasonic waves in solution. Thus,

$$U = 2fd/n$$

The sound velocity of solution was measured at a frequency of 2MHz.

2.5 Principle of temperature controller device

In order to control temperature of the system, a system involving a thermistor is used as the sensor, an OP-amplifier as a comparator. A single power supply has been used to provide proper biasing to the OP-amplifier. The potential divider arangement have been used for biasing the Non-INV terminal of the OP-amplifier. The potential divider arrangement connected to INV terminal consists of a thermistor (NTC) and a variable resistor.



Temperature controller

The resistance of thermistor at room temperature and range of variable resistor being of the same order, provides a better adjustment of the variable resistor to control the temperature at different levels. The voltage on the INV terminal can swing on either side of this reference voltage allowing the output to swing between 0V and Vcc. The thermistor is immersed in water bath, which serves as a source for water to be circulated at controlled temperature. Water from this bath is circulated through a pump. Constant inflow and outflow of water from this bath stirs water in the bath. At the instant when the temperature of the bath equals room temperature, the resistance of the thermistor is high and the voltage on the INV terminal is lower than the Non-INV terminal. As a result of this the output of the OP-amplifier Vcc becomes positive, causing the thermistor to conduct. The relay is then activated and the heater turns on. As the temperature of the bath rises, the thermistor resistance starts decreasing. This increases the voltage at the INV terminal of the OP-amplifier. As the temperature rises slightly above the limit set by the potentiometer, the voltage at the inverting terminals becomes positive with respect to reference voltage at the Non—INV terminal. The output swing to '0' volt and the transistor is cut off. The relay is deactivated and the heater shuts' OFF'. Due to this, it starts cooling down. When the temperature of the bath approaches a value slightly less than the value, the thermistor resistance rises to such a value that the voltage on the INV terminal becomes negative with respect to the reference voltage. The output voltage Vcc becomes positive and the heater turns 'ON'. This process continues and the temperature is maintained within a certain range of the set value. As the gain of the OP- amplifier is very large, the range is quite small and the thermistor response time is also small. As the thermistor's temperature versus resistance characteristic is non linear, the calibration of potentiometer is also non-linear. So calibration of potentiometer at different temperature is necessary, which is done by attaching a dial to it. A thermometer is placed in the water bath, whose temperature is to be controlled. For different settings of the potentiometer the controlled temperature is recorded and appropriate markings are made on the potentiometer dial. Once it is calibrated, the potentiometer can be set at the desired setting and the temperature is suitably controlled. However, it is necessary to check the calibration at certain intervals as check against the deterioration in thermistor response.

3. Theory of Acoustic Parameters

a) Acoustic impedance (Z):

Acoustic impedance is the resistance of a medium which assess the absorption of sound wave in a medium. It is a function of elastic property of the medium (i.e. bulk modulus of elasticity). Acoustic impedance of a medium is a fundamental concept to understand the generation and propagation of ultrasonic waves. It depends upon the sound velocity (U) and density (d) of the medium, which is given as

$$Z = Ud \quad .. (1)$$

Acoustic impedance increases with increase in concentration of electrolytes [6]. This is well agreeing with the theoretical requirement as density and ultrasonic velocity increase with increase in the concentration of electrolytes. The increase in Z values with concentration of electrolytes at a given temperature may be attributed to the effective solute-solvent interactions.

b) Isentropic compressibility (K_s):

The ultrasonic velocity through a liquid medium depends on the density (d) and degree of compactness i.e., isentropic compressibility (K_s) of the medium using the Newton-Laplace equation as,

$$U = (K_s d)^{-1/2} \quad .. (2)$$

or, $K_s = 1/U^2 d = 1/ZU$

when an electrolyte (solute) dissolves in water (solvent) some of the surrounding solvent molecules are closely attached to the ions due to the influence of electrostatic field of the ions. Since the solvent molecules are oriented in the ionic field (electrostatic field), the solvent molecules are more compactly packed in the primary solvation shell as compared to the compactness in the absence of the ions. Thus, the electrostatic field of the ion causes compactness of the medium due to ion-solvent interaction giving rise to a phenomenon called electrostriction. The interstitial spaces in water are occupied by the solute molecules making the medium harder to compress, i.e., providing greater electrostriction. The medium does not respond to further application of pressure. Isentropic compressibility decreases as acoustic impedance increases with increase in concentrations. Hence, isentropic compressibility as well as internal pressure describes the molecular arrangement in the electrolyte solutions [6].

c) Intermolecular free length (L_f):

Jacobson (1952) suggested that the isentropic compressibility of a liquid can be understood in terms of the intermolecular free length which is the distance between the surfaces of the neighbouring molecules [7]. The intermolecular free length depends on the type of packing, and the extent of association in a given liquid and is given by the relation,

$$L_f = K_T \sqrt{K_s} \quad .. (3)$$

where $K_T = \{(93.875+0.375T) \times 10^{-8}\}$ is the temperature dependent Jacobson's constant.

The intermolecular free length (L_f) decreases with increase in concentration of solution at a given temperature i.e., $L_f \alpha \sqrt{K_S}$. It indicates that, there is a significant interaction between solute and solvent suggesting the structure promoting behaviour on addition of electrolytes [8].

d) Solvation number (S_n):

Solvation number is the no. of solvent molecules associated and taking part in the formation of primary shell with the central ion [9]. They can also be computed from compressibility method which is associated with ultrasonic velocity by the following relation,

$$S_n = n_1 n_2^{-1}\left(1 - K_s/K_s^0\right) \quad .. (4)$$

where n_1 and n_2 are the number of moles of solvent and solute, respectively and K_s^0 is the isentropic molar compressibility at infinite dilution.

In the case of aqueous solutions of electrolytes, the major effect of ion-solvent interaction is the phenomenon of hydration, and it involves the attachment of certain number of water molecules to the positive and negative ions. The first layer of firmly bound water molecules to the ions is almost incompressible, and they contribute towards the primary hydration of the ion. The second water layer beyond the primary hydration sheath, on which the ion has some orientation effect, is the secondary hydration. It is shown that the molecules of water which form the secondary hydration shells are compressed to the maximum extent possible due to the intense electric fields around the ions. The external pressure compressed the remainder of the solvent water molecules. Primary hydration number can be computed from entropies, apparent molal volume, and from mobility. The solvation number gives an idea about the compactness of the solution leads to structure making/breaking effect in the solutions.

e) Relative association (R_A):

Relative association is a parameter used to assess the association in any solution relative to the association existing in solvent. It is estimated using the following relation,

$$R_A = (d/d_0)(U_0/U)^{1/3} \quad .. (5)$$

where d_o and d are the densities of pure solvent and solution, respectively. U_0 and U are the velocities of pure solvent and solution, respectively.

The relative association (R_A) is one of the important properties [10] of the electrolyte solution which is a function of ultrasonic velocity. It is influenced by two factors: (i) breaking up of the associated solvent molecules on addition of the solute and (ii) the solvation of solute molecules. The former leads to a decrease and the latter to an increase in relative association. The increase values of R_A with increase in concentration suggesting the solvation of the solutes predominating over the breaking-up of the solvent structure.

f) Relaxation time (τ):

Relaxation time is the time taken for the excitation energy to appear as translational energy and it depends on temperature and on impurities. The dispersion of the ultrasonic velocity in binary mixture reveals information about the characteristic time of the relaxation process that causes dispersion. The relaxation time (τ) depends on the viscosity (η) can be calculated from the relation.

$$\tau = 4\eta/3U^2 d \qquad .. (6)$$

The relaxation time (τ) increases with increase in concentration of electrolytes suggesting the rearrangement of molecules due to co-operation process [11].

g) Gibb's free energy change (ΔG):

The relaxation time for a given transition is related to the activation free energy. The variation of τ with temperature can be expressed in the form of Eyring salt process theory.

$$\frac{1}{\tau} = \frac{k_B T}{h} \exp\left(\frac{-\Delta G}{k_B T} \right)$$

or, $\Delta G = -k_B T \ln\left(\frac{h}{k_B T \tau} \right)$

or, $\Delta G = k_B T \ln(\mathrm{k_B T} \tau/\mathrm{h})$ .. (7)

where $k_B = 1.38 \times 10^{-23}$ JK^{-1}molecule^{-1} is the Boltzmann's constant and $h = 6.626 \times 10^{-34}$ Js is Planck's constant.

Gibb's free energy change (ΔG) increases with increase in concentration of electrolytes at a given temperature suggests shorter time for rearrangement of molecules

h) Ultrasonic attenuation (α/f^2):

Ultrasonic attenuation is a measure of spatial rate of decrease in the intensity level of the ultrasonic wave and attenuation co-efficient (α) is characteristic of the medium which depends upon the external conditions like temperature, pressure and frequency of the measurement. It can also be computed from ultrasonic velocity by the following relation,

$$\alpha/f^2 = 4\pi^2 \tau/2U \qquad .. (8)$$

where f (= 2MHz) is the frequency of ultrasonic wave.

When a plane progressive wave passes through a system, each small volume in the system is subjected to a time dependent perturbation. The study of ultrasonic absorption is to understand how the system responds to the perturbation, and relaxes in fluid media.

i) Free volume (V_f):

According to Eyring and Kincaid [10], the free volume (V_f) is defined as the effective volume in which particular molecule of the liquid can move and obey perfect gas laws. Free volume in terms of ultrasonic velocity (U) and the viscosity of the liquid (η) is represented as,

$$V_f = (M_{eff} U / K\eta)^{3/2} \qquad .. (9)$$

Where $M_{eff} = \sum n_i m_i / \sum n_i$ is the effective molecular weight, n_i is the number of moles and m_i is the molecular mass of the ith component in the solution, $K = 4.281 \times 10^9$ is the dimensionless constant independent of temperature and nature of liquid.

Free volume is one of the significant factors in explaining the variations in the physico-chemical properties of liquids and liquid mixtures. The free space and its dependent properties have close connection with molecular structure and it may show interesting features about interactions, when two or more liquids are mixed together. This molecular interactions between like and unlike molecules are influenced by structural arrangements along with shape and size of the molecules. A liquid may be treated as if it were composed of individual molecules each moving in a volume V_f in an average potential due to its neighbours i.e., the molecules of a liquid are not quite closely packed and there are some free spaces between the molecules for movement and the volume V_f is called the free volume. The free volume (V_f) decreases with increase in concentration of electrolytes. Internal pressure (π_i) changes in a manner opposite to that of free volume at a given temperature. The decrease of V_f (or increase of π_i) indicates the formation of hard and/or tight solvation layer around the ion [12].

j) Internal pressure (π_i):

The internal pressure is the cohesive force, which is a resultant of force of attraction and repulsion between the molecules [13]. Cohesion creates a pressure of 10^3 to 10^4 atmospheres within the liquid. The internal pressure is an important parameter to study the thermodynamic properties of liquids and gives an idea of the solubility characteristics. Dissolved solutes exist under the internal pressure of the medium and their interactions with the solvent arise through hydrogen bonding, charge transfer, Columbic or van der Waal's interaction. The term a/v^2 in van der Waal's equation [14] being the measure of attractive force of the molecule is called the cohesive or internal pressure. The internal pressure varies due to all types of solute-solvent, solute-solute and solvent-solvent interactions.

The internal pressure based on the Maxwell's equation of thermodynamics is

$$P = T\left[\frac{\partial p}{\partial T}\right]_v - \left[\frac{\partial E}{\partial V}\right]_T \qquad ..\ (10)$$

On the basis of statistical thermodynamics, expression for the internal pressure by the help of free volume concept is given by

$$V_f = \frac{1}{V^2}\left[\frac{b'RT}{P+\left(\frac{\partial E}{\partial V}\right)_T}\right]^3 \qquad ..\ (11)$$

As $\left(\frac{\partial E}{\partial V}\right)_T$ is the internal pressure and neglecting P which is insignificantly small to π_i the above equation can be written as, $V_f = \frac{1}{V^2}\left[\frac{b'RT}{\pi_i}\right]^3$ .. (12)

The internal pressure can be obtained by combining and rearranging the equations (11) and (12) as,

$$\pi_i = b'RT\ (K\eta/U)^{1/2}(d^{2/3}/M_{eff}{}^{7/6}) \qquad (13)$$

where b' = 2 is the cubic packing factor for all liquids and R = 8.3143 $JK^{-1}mol^{-1}$ is the Universal gas constant.

k) Vander Waal's constant (b):

The van der Walls constant is also known as co-volume in the van der Walls equation [13] and is calculated from the relation,

$$b = \frac{M_{eff}}{d}\left[1-\left(\frac{RT}{M_{eff}U^2}\right)\left\{\left(1+\frac{M_{eff}U^2}{3RT}\right)^{1/2}-1\right\}\right] \qquad (14)$$

The increasing values of van der Walls constant with concentrations indicates, there exist a strong molecular interaction and binding forces between the solute and solvent molecules.

5. Conclusion

The acoustic parameters are investigated through ultrasonic technique, which provide qualitative information regarding solute-solvent and solvent-solvent interactions. The intermolecular elastic forces between the solute and solvent molecules are explained in terms of compressibility and the solvation number gives an idea about the compactness of the solution leads to structure making/breaking effect in the electrolytic solutions.

Acknowledgements

The authors thankfully acknowledge the support and facilities provided by DRIEMS, Tangi, Cuttack, India to carry out the research work in the institution.

References

[1] R. Uvarani and J. Sivapragasam, "Intermolecular interaction studies on ternary liquid mixtures at 303 K," J Chem Pharm Res, 4(1), pp.653–655, 2012.

[2] S.K. Pradhan, S.K. Dash , L. Moharana and B.B Swain, "Molecular interaction parameters of binary mixtures of diethyl ether and a polar solvents using ultrasonic probe," Indian J Pure Appl Phys, 50, pp.161–166, 2012.

[3] C. Shanmuga Priya, S. Nithya, G. Velraj, A.N. Kanappan, “Molecular interactions studies in liquid mixture using ultrasonic technique”. Int J Advan Sci Technol, 189, pp.59–73, 2010.
[4] S. Ravichandran and K. Ramanathan, “Ultrasonic investigations of $MnSO_4$, $NiSO_4$ and $CuSO_4$ aqueous in polyvinyl alcohol solution at 303K,” Rasayan J. Chem, 3, pp.375-384, 2010.
[5] V. Kannappan and R. Jaya Santhi, “Ultrasonic studies of isomeric butyl alcohol in aqueous solutions,” Indian J. Pure & Appl. Phys, 43, pp.167-171, 2005.
[6] D. Moharatha, M. Talukdar, G.S. Roy and U.N. Dash, “Evaluation of acoustic parameters of halides of alkali metals and Ammonium in aqueous and aqueous Dextran solutions at 298.15K,” Researcher, 3, pp.6-12, 2011.
[7] B. Jacobson, “Ultrsonic study in liquids and liquid mixtures,” Chem. Physics, 6, pp.927, 1952.
[8] S.R. Kanhekar, P. Pravina and K.B. Govind, “Thermodynamic properties of electrolytes in aqueous solutions of glycine at different temperatures,” Ind. J Pure & Appl. Phys., 48, pp.95-99, 2010.
[9] A.N. Kannappan and Y. Arumeyam Y, “Viscosity B-Coefficient and salvation number of sodium chloride , sodium formate and sodium acetate in DMF-Water mixtures,” Trans SAEST, 39, pp.51-53, 2004.
[10] H. Eyring and J.F. Kincaid, “Free volume and free angle ratio of molecules in liquid,” J. Chem. Phys, 6, pp.620, 1938.
[11] B.V. Jahagirdar, B.R. Arbad, A.A. Walvekar, A.G. Shankarwer and M. Lande,“Studies in partial molar volumes, partial molar compressibilities and viscosity B-coefficients of caffeine in water at four temperatures,” J. mol.liq, 85, pp.361-373, 2000.
[12] S. Singh, R. Singh, N. Prasan and S. Prakash, “Compressibility free length and molar and available volume in ternary liquid systems,” Ind. J. Pure & Appl. Phys, 3, pp.629,1977.
[13] J.D. Vanderwaals, “Essay on the continuity of the gaseous and liquid States,” London, 1873.
[14] S. Glasstone, “Thermodynamic for chemist,” D. van Mostrand Co., Inc., Newyork, 62, 1947.

Biographical Notes

Mr. B. Swain is working as an Assistant Professor in the Department of Engineering Physics of DRIEMS, Cuttack, Odisha since 2003 and having 22 years of UG teaching experience in Physics and Material Science. He is also a Ph.D scholar of Ravenshaw University and got five years of research experience. He has already published eight research articles in his field of research (Ultrasonics) in different national and international journals. He is working as a reviewer in the Journal of Pure and Applied Ultrasonics.

Dr. R.N. Mishra is working as an Associate Professor in the P.G Department of Physics of Ravenshaw University, Cuttack since 2010 and has 32 years of experience in teaching Physics to graduate and Postgraduate students. He had his Ph.D from Utkal University, Bhubaneswar in 2003 and got 19 years of research experience. He has published 32 research articles in the field of Solid state Physics, Liquid state Physics, Nuclear Physics and Astrophysics in different national and international journals. He is working as a reviewer in many reputed national and international journals.

Dr. U.N. Dash is a former professor and Head of P.G Department of Chemistry of Utkal University and retired in the year 2003 and presently working as visiting Professor in College of Engineering and Technology, Bhubaneswar, Odisha. He had his Ph.D from IIT, Kharagpur and D.Sc from Utkal University, Odisha. He had 49 years of teaching and research experience in Chemistry and Ultrasonic study. He has published 13 books and 205 research articles in the journal of national and international repute. There are 27 students have already been awarded Ph.D and 7 more students doing research under his guidance. He is also an editor-cum-treasurer of Journal of Teaching and Research in Chemistry (An international journal) since 1994 and working as a reviewer in many reputed national and international journals.