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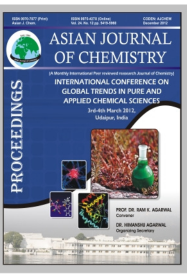

Studies of Properties of Liquids by Ultrasonic Method†

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Ultrasonic study and transport properties of pure and mixed liquids are useful to study interactions in solutions. The thermodynamic parameters such as density, viscosity, adiabatic compressibility, acoustic impedance, intermolecular free length, relative association and hydration number have been discussed. These parameters are further used to study molecular interactions in solution.

Key Words: Molecular interactions, Density, Viscosity, Adiabatic compressibility, Acoustic impedance, Intermolecular free length, Relative association, Hydration number.

INTRODUCTION

Every material substance can be characterized by a large number of properties like shape, texture, colour, mass, melting point, boiling point, reactivity, *etc*. Almost everything what we see appears to fit into the three states of matter: solid, liquid and gas[1]. The physical properties of solids and gases such as electric, dielectric, thermal, elastic are studied on the basis of crystal lattice theory and kinetic theory respectively, but there is no unique model to study the properties of liquid state. A solid is rigid substance occupying definite volume and possess definite shape. A gas is a compressible substance in which the molecules prefer a random motion. But in the liquid state molecules are in continuous action and move rather freely throughout the liquid. However, the particles are much closer than those in a gas. Thus, the state in which a substance exists is the result of the competition between intermolecular force between the molecules and heat energy, which gives the motion to the molecule. The intermolecular forces tend to bring order to the movement of molecules while heat energy points in the direction of randomness or chaos.

Dependence of intermolecular forces: To study the nature of the liquid state one has to consider dependence of the intermolecular forces. The intermolecular forces depend on the nature of the substance, the distance that separates the two molecules, the time the molecules spend in close proximity and the pressure and temperature of a given liquid system. The intermolecular forces responsible for the molecular interactions can be classified as long range forces and short range forces. The long range forces are the electrostatic induction and dispersion forces arise when the molecules come close enough together causing a significant overlap of electron clouds and are often highly directional. Though spectroscopic methods play a major role in the molecular interaction studies, the non-spectral studies such as calorimetric, magnetic and viscosity measurements have also been widely used in the elucidation of the formation of complexes.

Various techniques to study the properties of liquids: The study of molecular interactions in liquids provides valuable information regarding internal structure, molecular association, complex formation, internal pressure, *etc*. For such a study different experimental techniques like NMR, microwave absorption, IR spectroscopy and ultrasonic method have been used. NMR techniques basically reflect the effect on proton bearing molecules, while microwave absorption study provides useful information through the dielectric constant when energies of interactions are large. Spectroscopic methods provide information about intermolecular interactions. But to detect weak interactions in liquids ultrasonic techniques are best techniques due to useful wavelength range. Moreover ultrasonic parameters are directly related to large number of molecular and thermodynamic properties. Since various liquids state theories are based upon thermodynamic considerations, therefore ultrasonic velocity measurement and absorption provides a powerful tool to study them. But the properties of liquids cannot be explained using experimental values of

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density, viscosity and ultrasonic velocity of the liquids only because these parameters do not provide the enough information about the nature and relative strength of various types of interactions between the components of the liquid system and moreover some properties of liquids are independent of concentration, pressure, *etc*. Hence some derived parameters such as adiabatic compressibility (β_a), specific acoustic impedance (z), intermolecular free length (L_f), relative association (R_A), hydration number (S_n) and others are helpful to obtain information about their volume, elastic properties, complex formation in liquid mixtures and changes in the liquid properties. Not only the derived parameters but the excess parameters provide the information about the nature of the liquid state also.

Sound waves are separated in to three types *e.g.*, sonic waves, ultrasonic waves and infrasonic waves. The upper limit of frequency range of ultrasonic waves for liquids is 500 MHz. Ultrasonic velocity measurement has wide range of application but the important field is solution chemistry and drug industry. The advantages of ultrasonic waves are as follows:

1) At higher frequency the high absorption coefficient values are easily measurable; 2) Shorter wavelength occurs at higher frequency. So that the plain wave condition are more easily realized, which is especially important for the smaller specimens; 3) Frequency associated with relaxation phenomena after fall with ultrasonic range and they can be easily focused.

All waves of frequency more than 20 kHz are ultrasonic waves. The upper limit of ultra sound does not depend upon any intrinsic physical property of ultrasonic but on the technical difficulty of producing such waves. Almost any material that has elasticity, can prorogate ultrasonic waves. Numbers of workers have reported the study of liquids with ultrasonic method[3-7].

Different acoustic parameters: The molecular interactions in pure liquids and mixed liquids can be understood by the measurement of viscosity, density and ultrasonic velocity and the thermodynamic properties derived from these such as adiabatic compressibility (β), specific acoustic impedance(z), intermolecular free length(L_f), solvation number (S_n), internal pressure (π_i), relaxation strength (r), absorption coefficient (α/f^2) available volume (V_a), Rao's constant (R), Wada's constant (W) *etc*., are excellent tools to detect solute-solute and solute-solvent interaction. The sign and magnitude of excess parameters have been used to investigate the interact ions between the components of a system. Moreover the excess parameters also been used to explain the structure making and structure breaking properties of the liquid mixture. The presence of dispersion forces makes a positive contribution to the excess values[8-10]. Similarly a dipole-dipole, dipole-induced dipole, charge transfer and H-bonding interaction make a negative contribution by following parameters as u^E, η^E, β^E, L_f^E, V_f^E make positive contribution by z^E indicating presence a strong interaction between components. On the other hand the excess parameters with negative z^E are attributed to weak interactions. Following are some examples of liquids in which different acoustical parameters along with molecular interactions are discussed on the basis of ultrasonic velocity measurement methods.

Ultrasonic study of sugar solution: Saccharides are the typical non-electrolytes with several hydroxyl groups. Fructose is one of the examples of saccharides known as ketohexose with molecular formula $C_6H_{12}O_6$. Fructose has the highest solubility among all sugars. The hydration behaviour of saccharides has been found to be related to the number or configurations of OH groups. The hydration of fructose depends upon number of hydroxyl groups and the potential of H bonding sites[11]. In a study, the calculation of relative association for D-fructose in ionic solutions such as aqueous NaCl and aqueous $MgCl_2$ is shown in Table-1. As Mg is divalent, the aqueous $MgCl_2$ is more ionic than aqueous NaCl; the values of relative association are larger in case of $MgCl_2$ than in case of NaCl. This suggests the molecular interaction between fructose with $MgCl_2$ is strong than NaCl[12].

TABLE-1
VALUES OF RELATIVE ASSOCIATION OF FRUCTOSE AT DIFFERENT CONCENTRATIONS (c) AT 30 °C IN (AQUEOUS $MgCl_2$ AND AQUEOUS NaCl AT 2 MHz

Concentration (c) (mol/Kg)	Values of relative association (R_A)	
	Aqueous NaCl	Aqueous $MgCl_2$
0.0555	0.9915	0.9881
0.1110	1.0020	1.0103
0.1665	1.0139	1.0619
0.2220	1.0177	1.0039
0.2775	1.0275	0.9944

Ultrasonic study of ternary mixtures: In a recent study the calculation of apparent molar volume (ϕ_v) for a ternary system like ($HgCl_2$ + KCl + $MgSO_4$) shows negative values. This predicts ion-solvent interactions in the system. The variations in apparent molal volume can be further used to find the strength of molecular interactions in the systems[13].

Ultrasonic study of liquid metals: In mono-atomic fluids, a simple two state model is assumed. According to this model, two structures are present near melting point having different coordination numbers, corresponding, respectively, to order of packing respectively in the solid state and to a hard sphere like packing in the liquid state.

The energy required by an atom to jump from one state to another is known as the activation energy and is equal to the difference in the free energy Δf of the two states. The equilibrium would be established again after a lapse of finite time called relaxation time. Ultrasonic attenuation in the liquid metals is due to structural relaxation process. It is seen that lower is the melting point of metal higher is its attenuation coefficient. Here liquid mercury shows high ultrasonic attenuation[14]. This is mainly due to its viscosity and thermal conductivity.

TABLE-2
DIFFERENT ACOUSTIC PARAMETERS FOR LIQUID METALS

Liquid metal	Adiabatic compare compressibility (m^2N^{-1})	Ultrasonic velocity (U) m/s	α/f^2
Hg (298K)	3.419×10^{-12}	1470	5.71 ± 0.1
Zn (723K)	1.856×10^{-12}	2790	3.7 ± 0.6
Ga (303K)	1.992×10^{-12}	2870	1.58 ± 0.03

Ultrasonic study of aldehydes and amines: The complexation between aldehydes and amines can be detected by ultrasonic method. The aromatic aldehyde *e.g.* benzaldehyde that is electron deficient carbonyl carbon atom when mixed with and amine like benzylamine (electron donor) forms stable

TABLE-4
ULTRASONIC VELOCITY AND OTHER PARAMETERS FOR IONIC LIQUIDS

Concentration (x) mol	In aqueous NaCl			In aqueous KCl		
	Sound velocity (u) m/s	Intermolecular free length (L_f) A^0	Wada's constant $B \times 10^{-3}$	Sound velocity (u) m/s	Intermolecular free length (L_f) A^0	Wada's constant $B \times 10^{-3}$
0.2	1521	0.4137	5.146	1517	0.4149	4.270
0.4	1535	0.4092	5.178	1526	0.4113	4.333
0.6	1549	0.4047	5.217	1541	0.4065	4.370

charge transfer complex. Such complex can be detected by ultrasonic method. The free energy calculation for such mixture is found to be negative, indicating that donor-acceptor complex formation between aldehydes and amines are thermodynamically stable[15].

Ultrasonic study of aqueous solutions of transient and inner transition metal ions: Ultrasonic investigation for transition and inner transition metal ions in aqueous solutions is used to detect the presence of strong ion-dipole interactions. The strength of interaction depends on size, concentration, nature of solvent and charge distribution of ions. A recent study[16] reports that ultrasonic velocity measurements can be used to investigate the primary and secondary sheath of solvation. The solvent molecules are attached to the ion by strong coordinate bond in primary sheath of solvation and there are weak forces of attraction between solute and solvent species in secondary sheath. The solvation number in the primary sheath corresponds to coordination number and it is concentration in, while the solvation number in the secondary sheath is concentration dependent. The decrease in solvation number shows primary solvation. The solvation numbers for Mn, Co, Ni, Zn and Cu ions, in aqueous solution is given in Table-3.

TABLE-3
VALUES OF SOLVATION NUMBERS OF AQUEOUS SOLUTIONS OF TRANSITION AND INNER TRANSITION METAL IONS AT VARIOUS CONCENTRATIONS AND AT 303 K

Conc. (M)	Mn^{2+}	Co^{2+}	Ni^{2+}	Zn^{2+}	Cu^{2+}
0.001	242.6	231.8	517.1	343.7	53.4
0.002	77.9	51.6	165.2	425.8	302.2
0.004	131.9	80.8	74.2	151.3	146.8

Ultrasonic study of amino acids: The transfer volume of amino acids from aqueous to ionic solution can be explained on co sphere volume model in terms of solute-co solute interactions. According to this model ion-ion interactions contribute positive values to partial molar volumes (ΔV_ϕ^0). The positive and negative changes explains the predominant interactions in the solutions[17].

Ultrasonic study of ionic liquids: Water is highly polar in nature. The water molecules are attached to the ions strongly by electrostatic forces which introduce a greater cohesion in the solution. The ionic radii of sodium, potassium and chlorine are 0.95 Å, 1.33 Å and 1.81 Å[18]. It is observed that the ultrasonic velocity in aqueous solution contains Na^+ with ionic radius of 0.95Å are found to be larger than in solutions containing potassium or magnesium ions as shown in Table-4. This suggests that the compressibility of aqueous solution with sodium ions has more compressibility compared to other solutions. Higher compressibility value of a liquid indicates small change in its volume. Hence greater is its opposition for motion of energy, then there is loss of energy. Therefore ultrasonic velocity values are small in aqueous KCl.

Excess parameters for citric acid in ionic solutions: The sign of L_f^E play vital role in assessing compactness due to molecular arrangement and the extent of molecular interactions in the liquid mixtures through change transfer, dipole-induced dipole and dipole-dipole interactions. Negative (L_f^E) in the solutions is an indication of strong interactions in the liquid mixtures at low volume fractions of citric acid. As the volume fraction X increases L_f becomes more positive showing weak interaction between solute and solvent particles, as well as small interstitial accommodation of citric acid molecules in sodium chloride and magnesium chloride solution. This trend suggests that hetero association and homo association of molecular decreases. The excess value of (L_f) being negative at low temperature and at lower volume fraction (x) suggests weak interaction of citric acid with electrolytes. However the excess in free length shows positive values at higher temperature and volume fraction, but the changes are very small.

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