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Study of Intermolecular interactions in binary, ternary and quaternary mixtures

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Abstract:

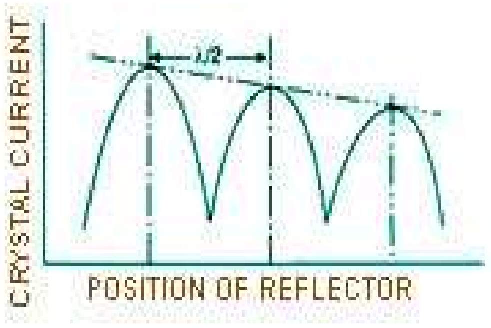
The basic parameters like velocity (U), density .(ρ) and viscosity (η) can be measured by ultrasonic Interferometer. From these parameters various thermodynamical and acoustical parameters such as adiabatic compressibility(β), specific acoustic impedance(Z), Solvation number (S_n), intermolecular free length(Lf), excess energy of activation, excess internal pressure have been estimated. The ion-solvent and solvent -solvent interactions are studied on the basis of increase or decrease in ultrasonic velocity, density, viscosity and other derived acoustical parameters in terms of structure making and structure breaking tendencies of various ions.

Keywords: Ultrasonic velocity, ion-solvent, solvent–solvent, adiabatic compressibility and free length

Introduction: The study of molecular interactions in the liquid mixtures is of considerable importance in the elucidation of the structural properties of the molecules. A theoretical attempt has been made to describe binary as well as ternary solutions containing electrolytes. **Aashees Awasthi and J P Shukla** studied the intermolecular interaction through hydrogen bonding in ternary liquid mixtures. Thermodynamic properties of non electrolytic solutions have proven to be a very useful tool in elucidating the structural interactions among the components. **Manish Gupta and Isht Vibhu** have studied excess properties of binary mixture of tetrahydrofuran with 1-propanol and 2-propanol .The interaction between **THF** and1-p/2-p is such that the basic network of intermolecular association in 1-p/2-p is disrupted. Various acoustical properties such as isentropic compressibility, intermolecular free length and relative association are very useful in understanding the molecular interaction between unlike molecules in liquid mixtures. **Lagemann and Dunbar** were the first to point out the velocity approach for qualitative determination of the degree of association in liquids. Recent developments have made it possible to use ultrasonic energy in medicine, engineering, agriculture and other industrial applications. **Ozawa and Minimisava** have observed concentrations of ultrasonic velocity invariant with respect to temperature in alcohol-water mixtures. **Hanel** has measured sound velocity and thickness of thin samples by time resolved acoustic microscopy. **Bae and Yun** have studied the ultrasonic velocity in binary solutions of silicon dioxide and water. **Wong and zhu** have studied the speed of sound in seawater as a function of salinity, temperature and pressure. **Skumiel and labowski** have given a theoretical analysis of the effect of an external constant magnetic field on the propagation of ultrasonic waves in electrically conducting liquids as well as the results of measurements carried out in mercury. **Aminabhavi and Gopala Krishna** have studied the density, viscosity, refractive index and speed of sound of aqueous acetonitrile system at T = 298.15 K. **Sandhu et al** reported excess molar volumes for binary mixtures containing acetonitrile and n-alkanol systems at T = 308.15 K where as **Saha et al** studied viscosities of acetonitrile and methanol binary liquid mixtures at various temperatures. **Nikam et al** utilized the density and viscosity data of acetonitrile and various primary and secondary alcohols at different temperatures to explain the molecular interactions while **Ku and Tu** that of acetonitrile and1-chlorobutane.**Krishnaiah et al** studied the speed of sound for chlorobenzene and acetonitrile mixtures while **Bakshi et al** reported various thermodynamic properties for the liquid binary solvent mixtures of acetonitrile with dimethyl acetamide, dimethyl sulphoxide, nitrobenzene and methanol at T = 298.15 K. Grolier et al studied the excess molar volumes and excess molar heat capacities for acetonitrile with dipolar solvents at T =298.15K while **Garcla** and **Ortega** reported viscosity, excess volume and excess free energy of activation at various temperatures for the systems of acetonitrile and alkyl benzoates. Recently B.R.Shinde and S.S.Jadhav have studied various acoustical parameters such as acoustical impedance (Z), adiabatic compressibility (β), Intermolecular free length (Lf),and solvation number (Sn)with the help of experimentally calculated parameters viz. ultrasonic velocity, density, and viscosity for $MgSO_4$ + water system for wide range of concentrations and at varying temperatures to study ion solvent interactions of Mg^{++} ions and water molecules.

Methodology: The ultrasonic velocity of the liquid can be measured with the help of Ultrasonic Interferometer. The principle used in the measurement of velocity (U) is based on the accurate determination of the wavelength (λ) in the medium. Ultrasonic waves of known frequency (f) are produced by a quartz crystal fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal. If the separation between these two plates is exactly a whole multiple of the sound wavelength ,standing waves are formed in the medium. The acoustic resonance give rise to an electrical reaction on the generator driving the quartz crystal and the anode current of the generator becomes a maximum.

(Ultrasonic Interferometer)



If the distance is now increased or decreased, and the variation is exactly one-half wavelength (***λ /2***), or multiple of it, anode current becomes maximum. From the knowledge of wavelength (λ) the velocity (v) can be obtained by the relation:

Velocity=Wavelength x frequency

$v=\lambda x \boldsymbol{f}$

The Ultrasonic Interferometer consists of the following parts:

High frequency generator: Single and Multi frequency

Measuring cell:

Max displacement of the reflector: 20 mm
Required quantity of liquid : 10 c.c.
Least count of micrometer: 0.01mm/ 0.001mm

iii) Shielded cable : 50 O

If the variation in the velocity with temperature is to be studied, water at various desired constant temperatures is made to circulate through the double walled jacket of the cell with external circulating water bath.

Sample calculations:

Sample: Water

Frequency f = 2MHz

Average $\lambda/2$ = 0.375

Ultrasonic velocity in sample, $v = \lambda x \boldsymbol{f}$ **=1480m/sec**

density of liquid (ρ)= 996.458 kg/m^3

Compressibility $\beta=1/U^2\rho = 1/996.458x(1480)^2$

$= 4.58x10^{-10}$ N/m^2

A number of parameters related to ultrasonic velocity are: Compressibility, Effective Debye Temperature, Excess enthalpy, Hydrogen bonding, Intermolecular free length, Solvation Number, Vanderwaal's constant, Rao's constant, Wada constant, Molecular Interaction, Proton Relaxation Rate, Relative association, Relaxation time and Relaxation strength, Acoustic Impedance, Stacking constant, Space filling factor, cohesive energy barrier, Latent heat of vaporization Specific heat ratio, Miscibility and compatibility of blends and many more.

Ultrasonic velocity for the solutions was measured using a single crystal ultrasonic interferometer of 2 MHz frequency (Model F-81) supplied by Mittal enterprises, New Delhi with an accuracy of ± 0.25 m/sec at 278 K. The temp was kept constant by constant temperature water bath with an accuracy of ± 0.1 K. The temp of the circulating water near the cell was measured by using PT-100 sensor and was found to be accurate to 273.23 K. The densities of various concentrations have been measured using 25 ml capacity specific gravity bottle and digital balance (Shinko, model HTR-220E, made in Japan) with an accuracy of 0.0001 gm.

The density of liquid is often approximated by measuring its specific gravity. The specific gravity of a substance is the ratio of the substance to the density of pure water. If equal volumes are considered, the specific gravity becomes simply the ratio of two masses. Numerically, the specific gravity has no units, while density is expressed as pounds per gallon, grams per millimeter etc. In this portion of the experiment, instead of graduated cylinder a Gay-Lussac specific gravity bottle is used called Pycnometer(pick-nah-mih-ter). A Pycnometer is a precision piece of glassware that consists of two portions: a bottle and a stopper. The bottom portion is a small bottle with a volume which may be accurately determined from the mass of water it holds at a particular temperature. The stopper is a capillary tube with a ground glass (frosted)bottom that fits snugly into ground glass neck of the bottle. For example, if the pycnometer holds 5.02 g of the water, then its volume must be about 5.02 ml because 1 gm of the water occupies about 1 ml. Since the volume of the container may be accurately determined using the density of water, the entire

25 ml specific gravity bottle (pycnometer)

experiment involves only the determination of the weights of the empty dry pycnometer, the pycnometer full of unknown liquid and finally the pycnometer full of water.

Procedure: 1 Obtain a dry pycnometer for the accurate determination of its mass. It is important that the stoppers are not exchanged from bottle to bottle, since each stopper is ground to fit one bottle and no other. 2.Weigh the clean dry bottle and stopper to the nearest 0.001 g on the top loading balance and record the mass. 3. Now obtain approximately 15 ml of unknown liquid in 25 ml graduated cylinder and record its identifying number. Use a disposable pipette to file the specific gravity bottle until the bottle is completely full. Insert the stopper so the ground glass end is in the bottle. Note that the liquid should completely fill the capillary tube in the stopper. Dry the outside of the bottle with a tissue paper. Be sure to remove any liquid which collects at either the mouth of the bottle or the top of the stopper by lightly touching the areas with the tissue. 4. In the case that the top does not fit tightly into the bottle, the capillary level may slowly drop to the level of the mouth of the bottle. If this should happen allow the level of the liquid in the capillary to fall to the same point for the unknown liquid and the water in the next step to insure that equal volumes are used. 5.Weigh the bottle containing your unknown liquid to the nearest 0.001 g and record the mass.6.Pour the liquid down the sink and rinse the bottle several times with distilled water. Fill the bottle with distilled water and dry the outside as before. Weigh the bottle and water to the nearest 0.001 g and record the mass.

7. Rinse the bottle several times with distilled water. Determine the temperature of the distilled water by placing a thermometer into a beaker containing 50-100 ml of distilled water. Wait at least 10 minutes for the thermometer to equilibrate. By using following observations we can determine the density of the liquid.

1.Weight of empty specific gravity bottle (W) =……………… gm

2.Weight of empty specific gravity bottle +Water = (W1) =……………gm

3. Weight of Water = (W1-W) =……….gm

4. Weight of empty specific gravity bottle +liquid =(W2) =……………gm

5. Weight of liquid=(W2-W)= …….gm

Density of liquid= Weight of liquid / Weight of water =…………… gm/cm^3

Relative density can be calculated directly by measuring the density of a sample and dividing it by the density of the references. The density of the sample is simply its mass divided by its volume. The relative density of a liquid can be measured using a **hydrometer**. This consists of a bulb attached to a stalk of constant cross-sectional area. First the hydrometer is floated in the reference liquid and the displacement is marked. The reference could be any liquid, but in practice it is usually water. The hydrometer is then floated in a liquid of unknown density. The change in displacement is noted. In the example depicted, the hydrometer has dropped slightly in the green liquid, hence its density is lower than that of the reference liquid. It is of course, necessary that the hydrometer floats in both liquids.

As far as determination of viscosity of liquid is concerned, it can be determined by using different types of viscometers such as Falling Ball viscometer, Falling piston viscometer, Oscillating piston viscometer, Vibrational viscometer, Rotational viscometer, Electromagnetically spinning sphere viscometer ,Stabinger viscometer ,Bubble viscometer ,Micro slit viscometer ,Ostwald's viscometer etc.

Determination of viscosity of liquid by Ostwald's viscometer (Glass capillary viscometer) Most commonly used viscometer is Glass capillary viscometer.

Procedure: 1 Take clean and dry viscometer and fix it in a perfectly vertical position by clamping the broad tube using wooden stand.2.

Take carefully 15 ml of the given liquid and introduce into the apparatus through the broad tube.3.Suck the liquid from capillary side by means of rubber tube above the mark ‘ X’(Do not allow the liquid to come into rubber tube) 4.Press the rubber tube firmly by folding it so that the level of the liquid does not get disturbed.5.Now allow the liquid to flow down through the capillary by releasing the fold on the rubber tube.6.Note time required(in seconds) for the flow between marks ‘X’ and ‘Y’.

7.Repeat the procedure three times for the same liquid and find the mean time of flow(t_A).8.Remove the liquid through the broad tube and clean the viscometer with the acetone. Take exactly same volume (15 ml) of distilled water in it .Find the mean time of flow(t_w).Then by using the following formula viscosity of the given liquid can be calculated.

$$\eta_A = \frac{t_A \,.\, d_A}{t_W \,.\, d_W} \times \eta_W$$

η_A = Viscosity of given liquid =............poise.

t_A = Mean time flow for liquid =...........Sec

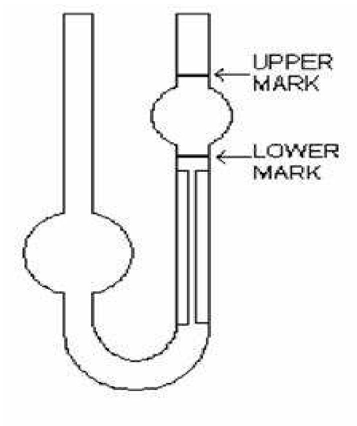
t_W = Mean time flow for water =............Sec

d_A = Density of liquid =............gm/cm^3

d_W = Density of water =............gm/cm^3

η_W = Viscosity of water =............poise

Viscosity can be converted into Poise or centipoises and then it is being converted into other units.



(Ostwald’s viscometer)

The viscosities have been determined by using Ostwald viscometer with an accuracy of 0.001 Nsm^{-2}.

Using measured values of ultrasonic velocity (U), density(ρ), and viscosity(η) some acoustical parameters have been calculated using following standard expressions.

Ultrasonic velocity (U) = $V\lambda$ ms^{-1}

Specific acoustic Impedance (Z) = ρU(Kgm^{-2} S^{-1})

Adiabatic compressibility (β) = $1/U^2\rho$ (Kg^{-1}m s^{-2})

Intermolecular free length (Lf) = $k\sqrt{\beta}$ (m)

Relaxation time (τ) = $4\eta/3\rho U^2$ s

Free volume (Vf) = $[M_{eff} U/k\eta]^{3/2}$ m^3

Internal pressure (π_i) = $bRT(k\eta/V)^{1/2}.(\rho^{2/3}/M_{eff})^{7/6}$ atm

Cohesive energy (CE) = $(\pi_i)V_m$ KjMol^{-1}

Available volume (V_a) = V_m (1-U/U_) m^3

Lenard jones potential (LJP) = 6 V_m/V_a

Free energy of formation (ΔG) = –RTlnK Kjmol^{-1}

Free energy of activation (ΔG^{s}) =
–KsTln(h/τKsT) Kjmol^{-1}

Stability Constant(K) = $Y/(b-y)^2$ dm^{3}mol^{-1}

Excess ultrasonic velocity (U^E) = U_{exp} –$(X_1U_1+X_2U2)$ ms^{-1}

Excess velocity (η^E) = η_{exp}– $(X_1\eta_1 + X_2\eta_2)$ Nsm^{-2}

Excess free length $L_f^{\,E}$ = $L_{f\,(exp)}$ –$(X_1L_{f\,1}+X_2L_{f\,2})$ m

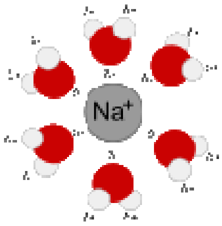
Excess Acoustic Impedance Z^E = Z_{exp} –$(X_1Z_1+X_2Z_2)$ Kg^{-2} S^{-1}

Excess available volume V_a^E = $V_{a\,(exp)}$ –$(X_1V_{a1}+X_2V_{a2})$ m^3

Result and discussions:

Ultrasonic velocity measurements are used in understanding the molecular interactions in pure liquids and binary / ternary mixtures since the deviations from the linear dependence of velocity and compressibility on the mole fractions provide an insight into the physicochemical properties of liquid mixtures such as molecular association and dissociation as well as the strength of interaction between the components. The molecular interaction studies have been made on liquid mixtures. Interaction between ion and solvent is totally depend upon the solvation. Solvation is an interaction of a solute with the solvent which leads to stabilization of the solute species in the solution. One may also refer to the solvated state, whereby an ion in a solution is complexed by solvent molecules. The concept of the salvation interaction can also be applied to an insoluble material, e.g : solvation of functional groups on a surface of ion–exchange resin.

Solvent and intermolecular interactions: Polar solvents are those with a molecular structure that contains dipoles. Such compounds are often found to have a high dielectric constant. The polar molecules of these solvents can solvate ions because they can orient the appropriate partially charged portion of the molecule towards the ion in response to electrostatic attraction. This stabilizes the system and creates a solvation shell(or hydration shell in the case of water).Water is the most common and well studied polar solvent, but others exist, such as acetonitrile, dimethyl sulfoxide, methanol, propylene carbonate, ammonia, ethanol and acetone. Solvation involves different types of intermolecular interactions: hydrogen bonding, ion-dipole and dipole-dipole attractions or vanderwaals forces. The hydrogen bonding, ion-dipole and dipole-dipole interactions occur only in polar solvents. Ion-ion interactions occur only in ionic solvents. The solvation process is thermodynamically favored only if the overall Gibb's energy of the solution is decreased, compared to the Gibb's energy of the separated solvent and solid. This means that the change in enthalpy minus the change in entropy is a negative value, or that the Gibb's energy of the system decreases.



Ion – solvent Interactions (e.g. NaCl in water)

Thermodynamic considerations: For solvation to occur, energy is required to release individual ions and molecules from the crystal lattices in which they are present. This is necessary to break the attractions the ions have with each other and is equal to the solids lattice energy(the energy released at the formation of the lattice as the ions bonded with each other).The energy for this comes from the energy released when ions of the lattice associate with molecules of the solvent. Energy released in this form is called the free energy of salvation.

The enthalpy of the solution is the solution enthalpy minus the enthalpy of the separate systems, whereas the entropy is the corresponding difference in entropy. Most gases have a negative enthalpy of solution. A negative enthalpy of solution means that the solute is less soluble at high temperatures. Although early thinking was that a higher ratio of a cations ion charge to ionic radius, or the charge density, resulted in more salvation, this does not stand up to scrutiny for ions like iron(III) or lanthanides and actinides, which are readily hydrolysed to form insoluble (hydrous)oxides. As solids, these are it is apparent, not solvated.

Enthalpy of solvation can help explain why solvation occurs with some ionic lattices but not with others. The difference in energy between that which is necessary to release an ion from its lattice and the energy given off when it combines with a solvent molecule is called the enthalpy change of solution. A negative value for the enthalpy change of solution correspond to an ion that is likely to dissolve, whereas a high positive value means that salvation will occur. It is possible that an ion will dissolve even if it has a positive enthalpy value. The extra energy required comes from the increase in entropy that results when the ion dissolves. The introduction of entropy makes it harder to determine by calculation alone whether a substance will dissolve or not. In general, thermodynamic analysis of solution is done by modeling them as reactions. For example: If you add sodium chloride to water, the salt will dissociate into the ions sodium(+aq) and chloride(-aq).The equilibrium constant for this dissociation can be predicted by the change in Gibb's free energy of this reaction.

Max born has developed the first quantitative model for salvation of ionic compounds. Moore and Fort measured the ultrasonic velocity, density and adiabatic compressibility and other acoustical parameters for fourteen liquid mixtures.

The structure of a molecule determines its function. In turn, the forces between the atoms determine the structure of the molecule. The interactions between the atoms in a molecule are classified as strong or weak, depending on whether or not the interaction can be disrupted by weak forces like thermal motion. The primary structure of the macromolecules is made of strong interactions such as the covalent bonds. Higher order structures like secondary, ternary and quaternary structures.

Weak interactions, on the other hand, not only help to determine the three-dimensional structure but also are involved in the interactions between different molecules. Any interaction within a molecule or between molecules can be understood as a sum of the interactions between pairs of atoms. Hydrogen bonds and Vander Waals' interactions are classified as weak forces. Vander Waals' forces act between all atoms and ions in all solids but the effect cannot be felt in the presence of strong interactions like covalent, ionic or metallic bonds. Vander Waals' forces are basically electrostatic in nature. In that, they involve interaction between electric dipoles. There are three components of the Vander Waals' forces namely, the permanent dipoles in the molecule, the dipoles induced by an external electric field, and the one induced by the London-dispersion effect. The relative contribution of each to the total force varies and depends on the type of the molecule. The hydrogen bonds are weaker than covalent bonds but are stronger than Vander Waals' forces.

In general, when two liquids are mixed together the structure of each of the two liquids is the same. The components change structurally in both aqueous and non-aqueous solutions. The phenomenon of preferential interaction between unlike molecules (solvation) or similar ones (association)is observed, depending on the degree of affinity between the components. Many researchers have studied binary mixtures at various temperatures (such as at 303.15 K, 308.15 K, 313.15 K, 318.15 K .

It is observed that there is slight increase in velocity suggesting weak ion-solvent interactions. e.g. In aqueous Mg^{++} ion solution, Mg^{++} ion form a core compact structure with the solvent molecules through ion-dipole forces. Due to this effect the compressibility decreases. It is observed that acoustic impedance also increases which shows strong ion-solvent interactions. The decreased compressibility brings the molecules to a closer packing resulting in a decrease of intermolecular free length. The solvation number in $MgSO_4$ + H_2O Solution decreases with increase in concentration and temperature shows the weakening of ion-solvent interactions. In some cases velocity, density and viscosity increases with increase in concentration and corresponding decrease in the experimental parameters with increase in temperature except ultrasonic velocity. The increase in density with increasing concentration of solute ions suggest a moderate strong electrolyte nature in which the electrolyte ions tends to attract the water molecules. The gradual increase in velocity ,density and viscosity with solute concentration at all temperatures may be due to interactions between solute ions and water molecules. In aqueous ion solution, solute ions form a core compact structure with solvent molecules through ion-dipole forces. Due to this effect the compressibility decreases. When temperature increased the mean distance between solute ions and water molecules tends to increase with corresponding increase in compressibility and hence increase in the ultrasonic velocity showing strong ion-solvent interactions. Adiabatic compressibility (β) decreases with increase in concentrations and temperature of ions in water confirms the presence of ion-solvent interactions through ion-dipole interactions. The compressibility of a solvent is higher than that of solution. In binary mixture acoustic impedance vary linearly with increase in solute concentrations in water. For dilute solution ion-solvent interaction is very less. Acoustic impedance increases with increase in temperature. Intermolecular free length shows similar behavior as reflected by the compressibility values. The decrease in compressibility values brings the molecules to a closer packing which results in a decrease of intermolecular free length. The solvation number in binary mixture decreases with increase in concentration. This suggests the structure promoting nature of solution as well as presence of ion-dipole interaction between solute ion and water molecules.

Conclusion:

The experimental parameters such as ultrasonic velocity, density ,viscosity and the other acoustical properties gives valuable information regarding ion-solvent interactions in aqueous solutions. There is uniform decrease in density and increase in intermolecular free length with increase in temperature indicating the loosening of intermolecular forces.

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