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The electromagnetic theory of Clerk Maxwell furnishes a great unifying principle; it indicates that the wireless waves which convey speech and music from one corner of the earth to another, the infrared radiation which give us warmth, the visible light rays which enables us to see the things around us, the ultraviolet radiations which bring about photochemical reactions, the \( \chi \)-rays that reveal the internal architecture of crystalline solids and the \( \gamma \) rays that shoot out from radioactive bodies are all fundamentally of the same physical nature. They constitute a whole gamut of radiations having widely different frequencies and wavelengths. According to Maxwell’s theory, all these radiations travel through the space with the same unique velocity of \( 3 \times 10^8 \) m/s and their essential difference is one of frequency or the number of vibrations per second. Indeed, considered from phenomenological standpoint, it is difficult to conceive of an upper limit to the frequency spectrum of the electromagnetic radiation.

If we now consider the vibrations of material media which constitute ‘sound’ in its broadest sense, we have a similar, though not identical, state of affairs. Sound is defined as a mechanical vibratory form of energy which is propagated through a medium by means of the motion of the particles of the medium. The phenomenon of propagation is a complex interplay between the parameters of the sound wave and the characteristics of the medium. An upper limit to the frequency spectrum of sound can, however, is fixed when it is remembered that the idea of sound wave propagation in a medium ceases to have any precise meaning when the wavelength is of the same of
the order of magnitude as the intermolecular distance \[^1\]. Since sound velocity is of the order of a thousand meter per second, and the intermolecular distance of the order of a few Angstrom units \((10^{-8} \text{ cm})\), the upper frequency limit of the acoustic spectrum can be fixed at about a million \((10^{12})\) vibrations per second \[^1\].

The acoustic spectrum extending from the very lowest frequencies up to the highest conceivable, can thus is divided into three broad ranges. The audible range of frequencies lies between 20 Hz and 20 KHz. Ordinary methods of producing sustained sounds do not enable us to excite vibrations of frequencies far above this range. For generating vibrations of higher frequencies, we have to resort to electro-acoustical methods which consist in transforming electrical oscillations into mechanical oscillations of the same frequency by taking advantage of the piezo-electric property exhibited by crystalline quartz\[^2\]. In this manner, we can generate mechanical oscillations of hundred million \((10^8)\) vibrations per second, and such inaudible sounds are known as “Ultrasonics”. It is impossible to excite artificially sound waves of frequency higher than, say \(10^9\) vibrations per second. However, the discovery that the thermal agitation always present in fluids and solids can be identified with spontaneous sound waves of very high frequency pervading such media is one of the triumphs of modern physical theory. In the ever-present heat motion of the molecules of a medium, nature has thus placed at our disposal sound waves of frequencies far beyond the range of artificial excitation. These can be conveniently designated as “Hypersonics”\[^1\].

Any material that has elastically can propagate ultrasonic waves. The propagation of ultrasonic waves is through the displacement of successive elements of the medium. If the substance is elastic there is a restoring force that tends to bring
each element of material back to its original position. Since all such media possess inertia, the particle continues to move after it returns to the position from which it started and finally reaches another different position, past the original one. From the second point, it returns to its starting position about which it continues to oscillate with constantly diminishing amplitude. The elements of materials will execute different movements as wave passed through them. As the wave travels through the material successive elements in it experience these displacements, each such element in the wave path moving a little later than its neighbour. In other words, the phase of wave of vibration changes along the path of wave transmission.\[2,3\]

An ultrasonic wave being transmitted through a substance is of two types. Each type causes a specific movement in the elements of medium and the paths that these elements follow as they move in response to the wave are called their orbits. These orbits may be parallel to the line of propagation in which case, the waves are called longitudinal waves. If the path followed by the elements is normal to the direction of propagation, the waves are called transverse waves or shear waves. Since liquids do not possess shear elasticity, transverse waves cannot exist in liquids. Rectilinear propagation is a characteristic exhibited by ultrasonic waves because of their short wavelength.\[2,3\]

The accurate measurement of the sound speed is very inconvenient for sound of audible frequency due to its long wave length and the consequent large size of the apparatus.\[4\] However, measurements at frequencies above the audible range (ultrasonic frequencies) can be readily made on samples of liquid of about 100 cc or less. The short wavelength of the ultrasonic waves is the factor that has been made possible the application of these waves in many cases. Such sound waves are
generated by applying an alternating electric field of suitable frequency to a crystal of quartz which is thereby set into resonant longitudinal oscillations (piezoelectric effect). Ultrasonic waves are generated from the free surface of an oscillating crystal and their wavelengths can be measured by setting up standing waves in the liquid between the crystal surface and a parallel reflector. By this and similar methods using the oscillating quartz, the ultrasonic speed can be measured.[4]

The study of the propagation behaviour of ultrasonic waves in solids, liquids, liquid mixtures, electrolyte solutions, suspensions, polymers, etc is now rather well established as an effective means for examining certain physical properties of materials or medium.[4-11] This thesis deals with the ultrasonic study of certain binary and ternary liquid mixtures. Ultrasonic velocity in the samples is measured using Ultrasonic Interferometer velocity measuring system. In addition, the density and viscosity of the samples are measured. Various thermo-acoustical parameters and excess functions are computed. The nature and type of intermolecular interactions taking place in the liquid mixtures are explained on basis of the computed parameters.

1.1. Peculiarities of Liquid State

The most obvious resemblance between liquids and gases is their lack of rigidity. As such, neither of them offers a permanent resistance to a shearing stress. An immediate consequence of this is that, neither liquid nor a gas possesses a shape of its own; both assume the shape of the container. Every solid on the other hand possesses a definite form and will always offer a resistance to shearing stress. Between liquids and solids, the most prominent similarity is that both possess cohesion, which enables them to maintain a free surface, whereas a gas always fills
any container. The next and less fundamental property common to liquids and solids is their relative incompressibility compared to gases. While the compressibility of solids are usually of the order of $10^{-6}$ atm\(^{-1}\), those of liquids are only slightly larger, $10^{-5}$ atm\(^{-1}\). But the compressibility of a gas, which is roughly equal to the reciprocal of the pressure, (at a pressure of one atmosphere) is about $10^5$ times as great as that of a liquid. Closely allied to this similarity between liquids and solids, is their similarity in density. The density change which takes place when a solid melts is usually of the order of 10 to 15 percent, but on vaporization, the density decreases by 100 to 1000. From these simple facts, considerable information can be obtained about the nature of the molecular arrangement in the liquids. From the density considerations, for example, the mean distance between the molecules (the word ‘molecule’ is used for simplicity to indicate ‘atom, molecule or ion’) can be calculated. In the solid the molecules are in contact. In the liquids, there is a little space, about 5% of the molecular diameter between the molecules. In a gas, the space between the molecules is about six times the molecular diameter.

Forces between molecules are of short range and act through a distance of only two to three molecular diameter. In a gas, these forces are of little importance and any regular arrangement of the molecules will be destroyed by the thermal motion of the molecules. Thus, the usual assumption that the molecule of a gas are arranged in random is justified.

In a solid, on the other hand, the close packed arrangement of the molecule prevents any molecule from moving away from its original position which in turn, results in the rigidity of the solid. The low compressibility of the solid is due to the fact that there is no free space between the molecules, so that any compression must
be accomplished only by reducing the size of the molecules themselves. If the liquid maintains the solid-like molecular arrangement, it is difficult to explain its fluidity. The molecules are packed so close together that the interior molecule cannot change its position more than the molecule of the solid can. The only conceivable way in which flow could take place would be, by the simultaneous displacement of a whole plane of molecules. Such a motion, however, would require a simultaneous lengthening of a large number of molecules and intermolecular spaces and needs a large energy of activation for the flow process. To avoid this difficulty, it is obviously necessary to assume that only a few molecules move at a time, and that it must be relatively easy for molecules to get displaced from the regular lattice.

The problem of packing so many spheres into a given volume does not permit a large variation from the regular close packed structure. In fact the only reasonable modifications are:

(i) There may be local irregularities, caused by groups of molecules coming together, leaving wider space elsewhere in the structure.

(ii) There may be gradual distortions of structure as we go from molecule to molecule, so that the pattern becomes irregular over a large distance, although the pattern in the immediate neighbourhood of a given molecule may be quite regular.

1.2. Evidence in X-ray Diffraction

In considering the degree of order in a liquid, it is valuable to consider the results of X-ray diffraction experiments. The X-ray diffraction pattern of a solid single crystal consists of symmetrically placed points of high intensity (Laue’s spots). In the X-ray diffraction pattern of crystalline powders, it is found that as the particle...
size of the powder decreases, the peaks increase in width and become diffuse, until for very small particle size, the diffraction maxima become completely blurred out. If a liquid had no regularity of structure, it should give a continuous scattering of X-rays without maxima. In fact, there are a few maxima and minima, and these occur at distances corresponding to those in some ordered close-packed structures. This is interpreted as showing that liquids possess a certain amount of short-range order, but long-range disorder.

To oversimplify, solids are always “solids”; Gases are always “fluids”; Liquids are “solid-like” at short times and short ranges, but “fluid-like” at long times and long ranges.

The existence of some similarity in the X-ray diffraction pattern in liquids and solids should not be considered as evidence that a liquid is more like a solid than a gas. Short range order is a necessary consequence of the similar high packing densities. Gases at low density have no X-ray diffraction pattern; but if they are compressed to high density, then a pattern typical of a liquid appear.

The results of X-ray diffraction studies on liquids reveal another important characteristic of the liquid structure. The area under the first peak in radial distribution function (resulting from X-ray studies) indicates almost always, the number of neighbours to be smaller than that in the crystal at or near this distance. There are thus definite gaps in the packing of the atoms. It is obvious that the fluidity of the liquids depend directly on their (gaps) presence. It should be noted that the decrease in density in the melting process is only partly accounted for, by hole formation. The remainder arises from the increase in the average distance between nearest neighbours.
1.3. Structural Differences between Solids, Liquids and Gases

The structure of a gas has been described simply in terms of the chaotic motion of molecules (thermal motion), which are separated from one another by distances that are very large compared with their own diameter. The influence of intermolecular forces and finite molecular size is very small and vanishes in the limit of zero pressure.

Since in a liquid the molecules are separated by a distance of the same magnitude as the molecular diameter, the volume occupied by a liquid is about the same as the volume of the molecules themselves. At these close distances the effect of the intermolecular forces is very large, with the result that each molecule has a low potential energy compared with its energy in the gas. The difference in potential energy between gas and liquid is the energy that must be supplied to vaporize the liquid. The motion of the molecules in the liquid is still chaotic, but since the liquid occupies a much smaller volume, there is less randomness in the space distribution of the molecules. The liquid has a very low compressibility simply because there is very little empty space left between the molecules. The liquid is capable of flow under stress because the molecule does have freedom to move anywhere within the volume; it must, however, push other molecules aside to do so, and as a consequence the resistance to flow is greater than for the gas.

The molecules in a solid are locked in a regular pattern; the spatial arrangement is not random as in the gas or liquid, but completely ordered. The solid does not flow under the application of a small stress, as do liquids or gases, but deforms slightly, snapping back when the stress is removed. This highly ordered arrangement is always accompanied by a lower potential energy, so that energy is
required to convert the solid to a liquid. The ordered arrangement usually has a somewhat smaller volume (perhaps 5 to 10%) than the liquid volume. The solid has a coefficient of compressibility that is about the same magnitude as that of the liquid.

The distribution of energies in solids and liquids is essentially the same as in the gas and, so long as the temperature is sufficiently high, is described by the Maxwell-Boltzmann distribution function. The motion in gases is characterized by kinetic energy only; in solids and liquids there is a potential energy as well. The motion in solids consists purely of vibration. In liquids, some of the molecules are moving through the liquid while others are momentarily caged by their neighbours and are vibrating in the cage. The motion in the liquid has some of the characteristics of the unhampered motion of molecules in the gas and some of the characteristics of the vibration of molecules in the solid. Overall, any liquid bears a closer resemblance to a solid than to a gas.

1.4. Methods of Studying Molecular Interactions

Intermolecular interaction in different liquid state theories is always expressed as a potential. The understanding of the liquid state therefore requires detailed information about the atomic or molecular interactions. This is the first step towards the construction of potential function. The molecular interaction study in liquids provides information regarding the internal structure, molecular association, complex formation, internal pressure, etc. The experimental techniques available to study molecular interactions are Nuclear Magnetic Resonance, Microwave, Ultra-violet and Infrared spectroscopy, X-ray and Neutron scattering and Ultrasonic investigation. While NMR technique reflects the effect on the proton-bearing molecule, the
Microwave absorption provides information through the dielectric constant. The X-ray and Neutron scattering help in the study of molecular motion. The spectroscopic techniques provide information of interactions, when interaction energies involved are large. Weak molecular interactions cannot be resolved from the observed spectra. Ultrasonic techniques can however reveal weak intermolecular interactions due to its useful wavelength range. Ultrasonic parameters are also directly related to a number of thermodynamic parameters. Since various liquid state theories are based on thermodynamic considerations, ultrasonic velocity determination helps a lot in their study.

1.5. Ultrasonic Study of Molecular Interactions

The study of propagation behaviour of ultrasonic waves in liquid systems is now rather well established as an effective tool for examining certain physical properties of the materials. It is particularly well adapted to examining changes in such physical properties while they occur. The data obtained from ultrasonic propagation parameters *i.e.*, ultrasonic velocity and its variation (i) with concentration of one of the components (ii) with temperature helps to understand the nature of molecular interaction. Varieties of models correlating the observed ultrasonic parameters with the structural arrangements of the constituents of the liquid mixtures and interactions amongst them have been proposed. Owing to the sensitivity to very low population densities at high energy states, ultrasonic methods have been preferred and these methods are reported to be complementary to other techniques like dielectric relaxation, infrared spectroscopy, nuclear magnetic resonance etc. In other words ultrasonic studies are extensively used in the conformational analysis of
organic molecules. Several empirical and semi-empirical formulae have been
developed correlating ultrasonic velocity with other molecular parameters and a brief
count of theoretical aspects are given in Chapter 4.

1.6. Liquid Mixtures

In a true solution of two substances it is found that every part is like every
other part and the true solution is a homogeneous phase, an example being sugar
dissolved in water. As far as liquid solutions are concerned, only three types of
solutions are to be considered (1) The solution of a solid in a liquid (2) The solution
of a gas in a liquid (3) The solution of a liquid in a liquid, i.e., a liquid mixture.

The present work is pertaining only to completely miscible liquids and so
discussion on completely immiscible and partially immiscible liquid mixtures will be
omitted. In liquid mixtures, the possible interactions are between like molecules, as
well as, unlike molecules. These interactions are of two types, namely, long range and
short range. The long range interactions (which include electrostatic induction and
dispersion forces) arise without the overlap of the electron clouds when the interacting
molecules approach each other. The long range interactions are highly directional. On
the other hand, short range interactions such as dipole-dipole, dipole-induced dipole,
charge transfer, complex formation and hydrogen bonding arise when the molecules
come closer together resulting in a significant overlap of electron clouds.

The measurement of ultrasonic velocity (along with other data such as density,
viscosity, conductivity, absorption coefficient etc.,) has been used to study the various
types of molecular interactions in liquid mixtures and the study of ionic interactions in
mixed salt solutions. The usefulness of the above experimental data is limited.
Therefore to get additional information on the nature and strength of molecular
interactions, the related acoustical/thermodynamical parameters such as free length,
adiabatic compressibility, free volume, internal pressure, acoustic impedance, etc.,
and their excess parameters are calculated. In a mixture of liquids, one might expect a
simple rule such as, \( A_m = \sum x_i A_i \) where, \( A_i \) is a parameter (such as ultrasonic
velocity, adiabatic compressibility etc.,) of the \( i \)th component liquid in the mixture
with a mole fraction \( x_i \) and \( A_m \) is the value of the same parameter for the mixture.
However these parameters are functions of molecular packing and interactions and so
they do not obey the above rule and exhibit a complex behaviour. Thus a
macroscopic parameter, which can be experimentally determined, is utilized to
understand the microscopic behaviour of liquids and liquid mixtures. In order to study
the non-ideality of the liquid mixtures, the difference between the experimental and
ideal mixture values (excess values of the parameters), are determined using the
relation, \( A^E = A_m - \sum_{i=1}^{n} x_i A_i \)

1.7. Brief Review

Ultrasonics has long been accepted as a powerful tool in the investigation of
acoustical properties of liquids and several theories are available in the literature to
predict the ultrasonic velocity in liquids and liquid mixtures. These include different
theories of ultrasonic velocity of liquid mixtures, namely, Nomoto, Impedance
dependence, Van Dael-Vangeal, Collision factor and Nutsch-Kuhnkie's. The
experimental determination of ultrasonic velocity and calculations therefrom the
quantities like compressibility, intermolecular free length, internal pressure, Wada’s
constant, acoustic nonlinearity parameter etc. gave wave to study to nature, type and
strength of intermolecular interactions present in liquid mixtures. A brief review of
the theoretical and experimental ultrasonic studies in pure liquids, binary and ternary
liquid mixtures and of acoustic nonlinearity parameter (B/A) are given.