

Molecular Level Analysis of Liquids using experimentally Observed Data involving Theoretical Methods

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Abstract

Present paper deals with problems of determining the molecular level of liquids by making use of experimentally observed data involving theoretical models which provide understanding of the fundamental problems concerned with the mechanism of chemical and biochemical catalysis and the paths of chemical reactions because this is the key to have knowledge of the structure and properties of liquids, solids and gases. The physico-chemical behaviour and nature of intermolecular interactions in the liquid mixtures has been an issue of keen interest and an interesting progress in the study of intermolecular forces has been made. The principal objective of our present analysis is that as molecular interactions define all the macroscopic properties of such systems, their knowledge has certain practical applications in many industrial operations, chemical engineering and it is also crucial to understand natural process.

1. Introduction

Molecular interactions provide understanding of the fundamental problems concerned with the mechanism of chemical and biochemical catalysis and the paths of chemical reactions because this is the key to understand the structure and properties of liquids, solids and gases. The physico-chemical behaviour and nature of intermolecular interactions in the liquid mixtures has been a subject of active interest and fascinating progress in the study of intermolecular forces has been made. Detailed theories in this regard have been given by a number of previous researchers Hirshfelder [39], Margenau [52], Kihara [43], Rowlinson [72], Hilderbrand [38] and Mollewyn-Hughes [56]. At present, the study of molecular interactions in liquid mixtures represents the main field of research for many laboratories over the whole world investigating at the frontiers of natural sciences in general and molecular biology, nanotechnology, physical chemistry, condensed matter physics in particular. The principal motive is that as these interactions define all the macroscopic properties of such systems, their knowledge has certain practical applications in many industrial operations and it is also crucial to understand natural process. Since primordial existence of human being, the materials in the world around, their spectacular behavior with respect to other materials as well as ambience has always directed his intellect, time and energy to enquire about and probe deeper into the world around. This investigation revealed what is called "atomism" in natural sciences and underlined the fact that all the objects in the universe are

composed of very small, indestructible building blocks. In due course, it was found that the nature and strength of microscopic interactions between constituents (atoms, ions or molecules) are determinants of macroscopic properties of condensed matter and thus emerged the study of molecular association, resulting from molecular interaction as one of the focus area of condensed matter physics [13,27,28,29,59,70]. On a macroscopic scale, matter is treated as a continuum which possesses certain properties clearly defined by well-known measuring operations without assuming any knowledge of the internal structure. However the microscopic point of view is aimed at a detailed knowledge of the internal structure and composition of matter. The advantage of investigation into the variation of macroscopic physical properties of the mixtures is twofold. First, this offers an indirect but convenient way to ascertain the nature and possibilities of microscopic interactions between like as well as unlike molecular species. Second, it prepares experimental background to develop, test and modify the theories for precise prediction of the properties of mixtures in varying ambience and composition, often needed in condensed matter physics [44, 51], chemistry [36, 54], chemical engineering [8, 35, 65] and industry [73, 77].

Lack of shear rigidity, in common with gases, and very low compressibility, in common with solids characterize the properties of matter in the liquid phase. It has been found that a certain amount of short-range order and long range disorder gives the liquid the characteristic property of fluidity. The liquid phase does not exist at temperatures and pressures above the critical point and is limited in temperature range between freezing point and boiling point. At low temperatures near the freezing point, the structural concept of the solid phases provides a good approximation, while at high temperature near the boiling point the statistical concepts of the kinetic theory of gases are more useful. It is noteworthy that both of these approaches are only approximation to more accurate descriptions of the liquid phase [12, 33]. Various theories and models have been proposed to describe the liquid state whose applicability and validity changes with the nature of liquids. It should be appropriate to remark here that Flory [26] used a simple partition function proposed by Eyring and Hirschfelder [23] to get reduced equation of state which is based on Vander Waals potential energy model. Regular solution theory, which is based on the assumption of no excess entropy and no volume change on mixing, provides good results in non-polar liquid [37, 74]. Moreover, the Lattice theory initially proposed by

Eyring and John [25] requires each molecule to be more or less bound to one position in space. Further, the concept of “hole” or vacant sites in the lattice is required to account for the fluidity of liquids [24, 41]. Taking into account this whole concept, Eyring and Coworkers [24, 25, 41] concluded that a liquid possesses dual characteristics of gas and solids; solid-voids experience gas like freedom while remaining part of the liquid exhibits solid like rigidity. Free “volume” or “cell” model [25, 40, 80] of the liquid state implies some amount of organization of structure in it and assumes a molecule to be confined to small region of the liquid constrained by the repulsive fields of its neighbors. By means of cell model and using the Sutherland type potential function for pair interaction between molecules, a statistical theory was formulated by Arakawa and Kiyohara [6] for binary liquid mixtures consisting of rigid spherical molecules differing in size. Investigation into the properties of dilute solutions and liquid mixtures is the most direct way to study various parameters arising from the properties of the liquids in terms of intermolecular forces. Because of the complex nature of the forces involved in a fluid, it is desired to study the molecular level interpretation of liquids using experimentally observed data apart from studies involving theoretical models proposed for liquids. Although a number of different techniques have been utilized to study the molecular interactions and its relationship with ambience parameters, viz., NMR, FTIR, X-ray, vapor pressure, dielectric, ultrasonic, viscometric, volumetric, optical etc. [11, 16, 22, 30, 45, 54, 60, 61], the dielectric, ultrasonic, volumetric, viscometric and optical techniques are widely used because of less demanding experimental technology.

2. Ultrasonic Method

Ultrasonic methods have established for themselves a permanent place in science, and every day new applications are found for the solution of many theoretical and practical problems. The mechanical longitudinal waves generated through the crystal can be propagated through the matter, namely; solid, liquid and gas. These waves may be divided roughly into the following classes according to their frequency.

- (i) Infrasonic waves (below 20 Hz)
- (ii) Audible waves (between 20 to 20 kHz)
- (iii) Ultrasonic waves (between 20 kHz to 1 GHz)
- (iv) Hypersonic waves (above 1 GHz)

Vibrational waves of a frequency above the hearing range of the normal ear are referred to as “ultrasonics”. It generally embraces all frequencies above 20 kHz [18]. Also, high-amplitude ultrasonic waves sometimes referred to as “sonic” [56]. Frequencies in the sonic range may also be used for certain ultrasonic applications. Ultrasonic, in the sense of artificially produced compressional waves at frequencies too high to affect the human ear, have been known since 1883, when Galton, adapted the edge tone generator to determine the upper limit of pitch sensation in human. In Galton’s apparatus, a jet of air debounces from a narrow slit to fall upon the sharp edge of an object which faces the slit. The jet is set in pendulation, the frequency of which can be increased by raising the velocity of efflux and reducing the separation of slit from edge. Another possible source was found in the singing arc of Duddell. In this device a spark plug or an arc of direct current to produce vibrations. Such units are based on thermal principles and are not commonly used at present. Ultrasonic wave can be produced by transducers based on piezo-electric effect or the magnetostrictive effect. The effect known as piezoelectricity was discovered by brothers Pierre and Jacques Curie. The piezo-electric is a phenomenon resulting from a coupling between the electric and mechanical properties of a material. When mechanical stress is applied to a piezoelectric material, an elastic potential will be produced. Vice-versa, when an electric potential is applied to the material, a mechanical changes will occur. Piezoelectric materials thus have numerous applications in piezoelectric devices. The most generally used crystals for ultrasonic wave generation are quartz, Rochelle salt, ammonium dihydrogen phosphate (ADP), lithium sulphate (LH), dipotassium tartrate (DKT), potassium dihydrogen phosphate (KDP). Magnetostrictive is another method for producing high frequency ultrasonic waves. Magnetostriction is a phenomenon only found in ferromagnetic materials. When an alternating current is passed through a coil in which a ferromagnetic rod is kept along the axis of the coil then the length of the rod will change twice in each cycle of the magnetic field of the coil due to magnetostriction, because the change in the length is independent of the direction of the magnetic field. The periodic change in the length of the rod produces ultrasonic waves when applied current is of suitable frequency. Laser beam ultrasound (LBU) is also a modern technique for producing ultrasonic wave. LBU is a remote implementation of conventional ultrasonic inspection systems that normally use contact transducers, squirter transducers, or immersion systems. LBU systems operate by first generating ultrasound in a sample using a pulsed laser. When

the laser pulse strikes the sample, ultrasonic waves are generated through a thermoelastic process or by ablation. Its accuracy and flexibility have made it an attractive new option in the non-destructive testing market.

The velocity of sound wave is the most important parameter that can be measured experimentally. The speed of ultrasound in a homogenous medium is directly related to both elastic modulus and density; thus changes in either elasticity or density will affect pulse transit time through a sample of a given thickness. High frequency sound waves can often be successfully transmitted into and out of moving materials without direct contact, through the use of a water bath or water stream as a coupling medium. Measurements can also be performed within closed containers by coupling sound energy through the wall. Because sound waves penetrate through the test specimen, material properties are measured in bulk rather than just on the surface. The study of ultrasonic can be separated into two phases:

- The study of the equipment for generation, reception, measurement etc.
- The study of the physical, chemical, biological etc.

The most outstanding physical effects of ultrasonics are cavitations, local heating, and the production of fog. Cavitations are a generic term applied to a number of ultrasonic effects characterized by the formation and collapse of bubbles in a liquid. The results of cavitations may be spectacular and many ultrasonic effects are ascribed to the accompanying cavitations [15, 69]. Heating effects become greater with increase of frequency because of increased absorption. Fog production is resulted by the jet of liquid thrown up when intense waves hit an interface between a liquid and air. Laser ultrasonic testing combines the sensitivity of ultrasonic inspection with the flexibility of optical systems in dealing with complex inspection problems. It works well in the testing of metals, composite materials, ceramics, and liquids. Its remote nature allows the rapid inspection of curved surfaces on fixed or moving parts. These applications could be possible only because of the ability to produce a highly directive and focused beam of vibration and to concentrate high powers in a small area. The study of propagation of ultrasonic wave in liquids is well established for examining the nature of intermolecular and intramolecular interaction in liquid system. Therefore, the ultrasonic velocity measurements in liquids and gases and its variation with temperature, pressure, frequency etc. provide

detailed information regarding the properties of the medium, such as absorption, compressibility, intermolecular forces and molecular interactions, chemical structure and the energies of the molecules in motion [1, 21].

The propagation of ultrasonic technique has been extensively used to study the physico-chemical behaviour of pure liquids [47, 49, 71, 76]. Lagemann and Dunbar [46] were the first to point out the sound velocity approach for qualitative determination of the degree of association in liquids. Ultrasonic velocity in conjunction with density measurements permits the direct estimation of isentropic compressibility, intermolecular free length and other related parameters, which cannot be easily deduced by any other method. A large number of noteworthy researchers have examined the validity of various theories [2, 19, 20, 42, 54, 61, 63, 64, 67, 75] by ultrasonic velocity and density measurements.

3. Viscometry

Viscometry describes the study of the variation of viscosity with temperature and composition of liquid mixture. It is the property which opposes the relative motion of adjacent portions of the liquid and can consequently be regarded as an internal friction or resistance to a flow. The co-efficient of viscosity η is defined as the force per unit area.

When a liquid flows through a capillary, it is probable that the thin layer of liquid in contact with the walls is stationary. As a result of viscosity, therefore, the next layer will be slowed down to some extent, and this effect will continue, to a diminishing extent, up to the centre of the capillary. If a liquid with a co-efficient of viscosity (η) flows with a uniform velocity, at a rate of volume (V) in time (t) through a capillary of radius (r) and length (l) under driving pressure of (P), then according to J. L. M. Poiseuille:

$$\eta = \frac{\pi P r^4 t}{8 V l} \quad (3.1)$$

The equation (3.1) is the basis of methods for determining co-efficient of viscosity of liquids [31].

The information based on the viscosity of pure liquid and liquid system is important in chemical engineering applications, such as in the determination of flow of fluid, mass-transfer and heat-transfer operations. Extensive experimental

data on viscosity together with the study of ultrasonic velocity and density, has led to the determination of Gibb's free energy, free volume, internal pressure and enthalpy can be found in [4, 9, 81].

4. Volumetry

Density is an intensive property of matter which defined as the ratio of an object's mass to its volume. Density describes the degree of compactness of a substance - in other words, how closely packed together the atoms of an element or molecules of a compound are. An extensive and exhaustive study of density give an insight into the nature of strength and possibilities of microscopic interaction and it prepares an experimental background to develop, test and then modify theories for the liquid mixture and their transport properties. Liquid densities are needed in many engineering problems such as process calculations, simulations, pipe design and liquid metering calculation. Molar volume can be easily measured from the experimental data of density and mole fraction and provides an efficient and convenient tool to study the interactions at molecular level. Non-zero values of excess molar volume, which measures the deviation of molar volume from ideality has been interpreted by many workers [53,62,66,78] as a commutative manifestation of three effects such as physical, chemical and structural.

5. Refractometry

The study of refractive index and molar refraction of the medium in different environment is called refractometry. Refractive index (n) of any medium is a quantitative measure of the response of constituent molecules of the medium to the electromagnetic waves and is defined as the ratio of the velocity of electromagnetic wave in vacuum to that in the medium. H.A. Lorentz, on the basis of electromagnetic theory of light and L.V. Lorenz, on the basis of wave theory of light, independently deduced following relationship between the refractive index (n) and density (ρ).

$$\left[\frac{n^2 - 1}{n^2 + 2} \right] \frac{1}{\rho} = C \quad (5.1)$$

The constant C inequation (5.1) is called specific refraction. The molar refraction (R_m) is a derived quantity and is defined as [31]

$$R_m = \left[\frac{n^2 - 1}{n^2 + 2} \right] V_m \quad (5.2)$$

where n and V_m are the refractive index and the molar volume of the medium respectively.

Measurements of the bulk properties such as refractive indices provide better insight into the molecular arrangement in liquids and help one to understand the thermodynamic properties of liquid mixtures. The study of the variations of refractive index of a liquid with temperature and with mixing of different solutes in varying concentration gives valuable inferences about the structure of liquids or liquid mixtures. Literature survey reveals that enormous work has been done to measure or evaluate the refractive index of liquids and liquid mixtures [5, 7, 10, 14, 17, 32, 50, 58, 68].

6. Excess Parameter

The analysis of excess thermodynamic properties of mixtures offers a convenient means to understand the inter-relationship between the observed macroscopic properties of the mixtures and the microscopic interactions among like and unlike molecules. The advantage of in depth and wide study of this inter-relationship is two-fold: first, it provides experimental background to develop, test and improve thermodynamical models for calculating and predicting fluid phase equilibrium and second, it offers a wide range of possibilities for continuous adjustment of physical properties of a given solvent. Properties such as molar volume, ultrasonic velocity, refractive index and viscosity, their deviation from ideality and variation with temperature and composition of binary mixtures are useful in chemical and biological industries [3], and to test theories of solutions [48]. It has been reported by earlier workers [34] that three main types of contributions to the excess thermodynamic properties of a mixture are:

- Physical: due to non-specific Vander Waals type interactions
- Chemical: due to hydrogen bonding
- Structural: due to changes in interstitial accommodation and free volume.

The experimental determination of the ultrasonic velocity, density and viscosity, enables us to calculate many more important parameters such as the Gibb's activation energy for viscous flow, internal pressure, available volume, free volume,

enthalpy etc. These functions are also found to be sensitive towards difference in size and shape of the molecules. Excess values of these derived parameters reflect the variation of nature of molecular units and provide significant inferences about the nature of interaction [79].

7. Molecular Thermodynamics

For many years the chemical industry has recognized the importance of thermodynamic and physical properties in design calculations involving chemical separations, fluid flow and heat transfer. The development of flow calorimeters, continuous dilution dilatometers, and vibrating tube densimeters has enabled the experimental determination of excess enthalpies, heat capacities and volume of liquid mixtures with convenience and accuracy. The utilization of continuous dilution techniques has reduced the experimental time needed for the determination of Gibb's free energy through conventional vapour-pressure measurements. Recent advances in gas-liquid chromatography have enabled infinite dilution activity coefficients to be measured with accuracies. But even with modern instrumentation it is not possible to measure the thermodynamic properties of all conceivable multicomponent mixtures. To overcome this problem, researchers have turned to predictive methods as a way to generate desired quantities. Although much progress has been made in recent years, we are still far from a "perfect method", as is demonstrated by the large number of new methods appearing in the literature each year. For mixtures of non-polar molecules, the Scatchard-Hildebrand solubility parameter theory provides a good first approximation of vapor-liquid equilibria. Better predictions can often be made if one uses a more sophisticated solution model based on non-random mixing or local compositions. Group contribution methods are available for predicting multicomponent properties from molecular structure. Associated solution theories provide reasonable approximations whenever there is independent evidence that strong chemical forces operate in the liquid mixture. To a large extent the selection of a predictive method depends on the type of solution and on the information already available. A number of statistical mechanical theories have been developed to study properties of liquids and liquid mixtures. Flory statistical theory (FST) [26], which was initially proposed for n-alkenes and was subsequently extended for non-polar molecules differing in size and shape, has been extensively used to evaluate various thermodynamic and transport properties of simple and complex liquid mixtures due to its simplicity and precision. Sutherland type potential function

for pair interaction between molecules and by means of cell model, a statistical theory was formulated by Arakawa and Kiyohara [6] for binary liquid mixtures consisting of rigid spherical molecules differing in size. These statistical mechanical theories of liquid mixtures lead naturally to the prediction of theoretical values of ultrasonic velocity and excess functions viz. excess energy, excess entropy and excess enthalpy.

Molecular thermodynamics constitutes a means for going beyond the limitations of classical thermodynamics in solving chemical problems. By using a microscopic approach it is frequently possible to start with independently known physico-chemical properties and from these to estimate P-V-T relationships, enthalpies, entropies and free energies. The reason for establishing such relationships is to facilitate meaningful correlations for calculating from a minimum number of experimental determinations such phase equilibrium data as are needed for either engineering design or laboratory applications.

8. Conclusion and Discussion

The knowledge of physico-chemical properties of multi-component mixtures is indispensable for many chemical process industries. For accurate designing equipment, it is necessary to know the interaction between the components of mixtures. Physico-chemical analysis method can be used for obtaining sound information for a specific interaction between the components and the structure of the binary liquid mixtures. The study of ultrasonic velocity of mixtures helps in obtaining information about the intermolecular and intramolecular interactions and association through the bonding between the atoms of component molecules in liquid mixtures. Density, refractive index and viscosity data are of importance in engineering applications. Hydrogen bonding plays a vital part in the genetic coding in the vast molecules like DNA. Liquid mixtures are the most direct source for studying the various parameters. Therefore the density, ultrasonic velocity, refractive index and viscosity have been measured in binary mixtures of butylamine + 1-butanol and butylamine + *tert*-butanol at a fixed frequency and at temperatures 293, 303 and 313K because amines are used as a starting material for the manufacture of azo dyes. Alcohols are widely used in industry and science as reagents or solvents because of its low toxicity and ability to dissolve non-polar substances. In organic synthesis, alcohols frequently serve as versatile intermediates and also used as a preservative to preserve specimens. Also alcohols often have an odor described as 'biting'

that hangs in the nasal passages. The combination of aldehyde with other molecules results in several familiar plastics. Many aldehydes are large scale industrial materials, useful as solvents, monomers, perfume ingredients and intermediates. Acoustical, volumetric, viscometric and optical properties of binary mixtures of benzaldehyde with ethanol and methanol have been measured at temperatures 293, 303 and 313K.

Thermodynamic parameters like excess molar volume, ultrasonic velocity deviation, viscosity deviation, molar refraction deviation, excess Gibb's free energy of activation for viscous flow, excess free energy and excess free volume etc., have also been computed in order to ascertain the nature and strength of association. A number of empirical and semi-empirical theories and mixing rules are applied for predicting the thermodynamic parameters like ultrasonic velocity, isentropic compressibility and refractive index. A comparative study of these mixing rules, using experimental data available from various sources, can provide background for the preferential use of one model over the other. The study of thermodynamic function such as excess energy, excess entropy and excess enthalpy and various other thermodynamic functions are useful in understanding the nature of intermolecular interactions between component molecules. Moreover, we remark here that the statistical mechanical theory proposed by Arakawa [6] has been introduced and some thermodynamic excess functions like energy and entropy for two binary mixtures of tetrahydrofuran with 1-propanol and 2-propanol at varying temperatures have been evaluated in our another paper. Schaaff's equation has been incorporated in the calculations enabling us to evaluate excess functions directly from the density and ultrasonic velocity data only.

The significant reasons for the present study are:

- The appearance of new phenomenon, which are absent in pure liquids but present in liquid mixtures, can be studied. The most interesting of these are the new type of phase equilibria which are introduced by the variation in the properties of the pure components.
- A precise correlation between microscopic and macroscopic properties can be made by using more than one technique to establish the nature of interaction because results of one experimental technique often contradict the results obtained from other technique.
- The temperature sensitivity of the complexes formed gives inference about the strength of molecular interaction. The

difference in the temperature sensitivity of the complexes formed between molecular species gives an indication about relative tendency of molecular species towards complex formation.

- Scrutiny of various mixing rules and models for the prediction of ultrasonic velocity, refractive index and viscosity in different mixtures prepares an experimental background to develop, modify and test them.

9. References

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