STUDY OF MOLECULAR INTERACTION BETWEEN ACETOPHENONE AND ETHYL METHYL KETONE WITH ACETONE BY ULTRASONIC MEASUREMENT

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ABSTRACT

Binary liquid mixture find practical applications in most chemical processes, their properties are less known. Derived parameters from ultrasonic speed measurement and the corresponding excess functions provide qualitative information regarding the nature and strength of interactions in liquid mixtures. The use of acetone in preparing a large number of aromatic compounds is well known. Acetone is also used as solvent in various organic synthesis. Thus, acetonephenone and ethyl-methyl ketone with acetone mixed solvents would enable us to have a large number of solvents, with appropriate physico-chemical properties, which can be used for a particular chemical process. Moreover literature survey indicates that no ultrasonic study on these binary systems has been reported. Therefore, present study was undertaken in order to have deeper understanding of the intermolecular interaction between the components of the above binary liquid mixtures. Thus, a study of physical properties data on the binary mixtures containing acetone has attracted considerable interest in our present study.

INTRODUCTION

The study of thermodynamic properties of binary liquid mixtures has proved to be a useful tool in elucidating the structural interactions components[1-5]. Many researchers have shown the important and fundamental role of the molecular details of the solvent species to determine the specific interactions which are responsible for macroscopic thermodynamic and other related properties in non-electrolyte solutions. When binary or more complex mixtures are used as solvent media, specific solvent-cosolvent interactions can intervene to modify the structural properties and the molecular arrangement of the pure liquids. Thus, the knowledge of the structure of mixed solvent systems becomes an essential prerequisite to interpret and to understand the interaction patterns between ions, ions-pairs and ionic aggregates, and bulking solvent molecules. Excess thermodynamic functions which depend on the composition, temperature and pressure of the system which are of great importance to a chemical engineer in the design of industrial separation process and to a chemist for arriving at theories of liquid mixtures. In principle, the interaction between the molecules can be established from a study of

the characteristics abrupt departure from ideal behavior of some physical properties, like volume, compressibility, viscosity etc.

Accurate knowledge of thermodynamic properties of organic liquid mixtures has relevance in understanding the molecular interaction between the components of the mixture, in developing new theoretical model, and also in carrying out engineering applications in the process industry. Data of these properties can be obtained experimentally or by using generalized methods that permit the calculation of the properties of mixtures. The development of a calculation method requires that an adequate database should be available. Although many tabulated value of the above properties are generally available for the pure solvents, literature data relative to various binary mixtures are of the lacking.

Densities of liquid mixtures and related volumetric properties are required for many applicative aspects as well as for theoretical calculations. In particular, their knowledge is indispensable when the classical and the thermodynamic approach is to be used to relate and to compute the equilibrium properties of such mixtures. From this point of view, they are of strategically importance for both the test of existing theories and the development of new models for mixture behaviors. For this point of view, they are of strategically importance for both the test of existing theories and the development of new models for mixture behaviors. For practical purposes (tank design, pipe-lines etc.) the knowledge of volume of liquid mixtures is important than the corresponding density values.

Numbers of studies on the measurements of ultrasonic speeds and isentropic compressibilities of liquid-liquid mixtures have been carried out as it has gained much importance in investigating the physicochemical behavior of liquid mixtures such as molecular association and dissociation. Ultrasonic speed and related data of liquid mixtures are found to be the most powerful tool in testing theories of liquid stage. In addition, some more useful properties of liquid mixtures which are not easily accessible by other means can be deduced by means of data obtained from ultrasonic speed measurement.

It is well recognized that speed of sound, isentropic compressibility, and molar volume of liquid mixtures provide information on molecular interactions. The high precision of speed of sound measurements make it possible to calculate reliable values of two parameters characterizing deviations of the system from ideality, the excess molar isentropic compressibility which proves to be one of the most reproducible of the excess molar properties and deviation u^D of the speed of sound u, from those in ideal mixtures u^{id}. Molecular association in solution and some important correlation with various parameters e.g. ratio of the heat capacities γ, molar isentropic and isothermal compressibilities $K_{S.m}$ and $K_{T.m}$, free volume V_f, apparent molar compressibility $K_{S.i}$, ϕ available volume V_a, isentropic compressibility K_S, deviation in isentropic compressibility ΔK_S, mixing function Δu etc can be very well studied through speed of sound measurement in liquid mixtures. In recent years, there has been an increased interest in the determination of either isothermal or isentropic compressibilities. The role that isentropic

compressibilities play in the thermodynamic characterization of binary mixtures is also subject of a recent review.(6).

It has been pointed out by several workers that excess thermodynamic functions are sensitively dependent not only on the difference in intermolecular forces; but also on the difference in the size of the molecules. It is obvious that the study of excess compressibilities and excess molar volumes gives important information on intermolecular forces determining the properties of mixtures. Solute-solute interactions can be investigated from speed of sound and density data using statistical theory of solutions.

REVIEW OF STUDIES

An extensive literature survey reveals that considerable data have been accumulated on thermodynamic and ultrasonic studies of liquid-liquid mixtures.

Published literature on the accumulation of experimental data such as density, viscosity and speed of sound in the binary mixtures has been truly exhaustive. It is thus beyond the scope of this dissertation to cite all the references. Only the representative papers will be cited. In many of these studies, the properties that have been measured are density, refractive index, dielectric constant, viscosity, vapor pressure, enthalpy, heat capacity and speed of sound. From these properties, excess parameters of interest have been calculated. However, in the present thesis, discussions will be centered around the measurement of four physical properties, viz., density, excess molar volumes, viscosity, and speed of sound. Using these data, the mixing quantities have been evaluated to investigate their effects in terms of the binary interactions.

Kolling, O.W.(1) studied the trends in dielectric constant as a function of mole fraction for eighteen solvent pairs containing acetone. He found that generally nonlinear usually shows negative deviation from ideal behavior. Based upon a linear solvation energy relationship, the sizes of the deviations at the maximum or minimum condition are related to the dipolarities and polarizing abilities of the added cosolvents in most cases. However, the three strongly associated hydrogen bonding cosolvents, formamide, N-methylacetamide and water, are exceptions to that pattern.

Reilly, J.T. et al.(2) studied an investigation into the solvent properties of liquid carbon dioxide which was done by means of FT-IR spectroscopy. A high-pressure, circulation-type apparatus was designed and built specifically for this study. The spectra for the combination bands for carbon dioxide showed that there are interactions between methanol and carbon dioxide. However, the spectra of the fundamental O-D vibration of deuterated methanol in liquid carbon dioxide indicate that there is no hydrogen bonding. Therefore, we concluded that the interactions between carbon dioxide and methanol are Lewis acid-base interactions rather than hydrogen bonding. This conclusion is supported by experiments where acetone is introduced into the

CO_2/methanol-*d* binary system. FT-IR measurements show the hydrogen bonding of acetone with deuterated methanol.

Petrov, N. Kh.[3] reviewed the published data on the dynamics of nonspecific preferential solvation in binary solvents, as obtained by fluorescence spectroscopy (in particular, by magnetic spin fluorescence method) using probe molecules in which strong charge redistribution yielding dipoles and ion pairs takes place upon excitation. The dynamics of preferential solvation of the excited probe in a binary solvent is described by a sequence of consecutive equilibrium reactions, in which each step is the absorption of a molecule of the polar component by the solvation shell of the excited probe, where transport from the bulk solution occurs via translational diffusion. The characteristic effect of the time saturation of solvation is attributed to the energetically unfavorable process of interface formation between the solvation shell, which a polar nanosized cluster, and the homogeneous binary mixture. Such polar clusters may affect the course of photochemical reactions involving charged species or particles with a large dipole moment. Simple model concepts, such as the Frenkel theory of heterophase fluctuations, the Onsager model, and the Hildebrand theory of solubility used for the description of the physical picture of preferential solvation, are considered.

RESULTS & DISCUSSION

Acetone is a versatile liquid, which finds use for the preparation of number of aromatic compounds which have got variety of uses in the modern world. Thus, a study of physical properties data on the binary mixtures containing acetone has attracted considerable interest in the literature[1-3]. Hence, the experimental denstities and speed of sound data at 303.15K for the binary mixtures of acetophenone with acetone and ethylmethylketone with acetone have been presented. From the experimental data, deviations in various acoustical properties such as isentropic compressibility, intermolecular free length, ultrasonic speed of sound and relative association have been computed.

Deionized water was taken and a little $KMnO_4$ and 2 or 3 pallets of NaOH were added to it. The solution was double distilled in an all glass double distillation assembly and the first fraction was rejected.

An ultrasonic interferometer is a simple and direct device to determine the ultrasonic velocity in liquid with a high degree of accuracy. With the help of an ultrasonic interferometer we can determine various thermodynamic parameters like ultrasonic velocity, Adiabatic Compressibility (β_{ad}), Isentropic Compressibility (β), Isothermal Compressibility (β_T), Effective Debye Temperature (Q_D), Grunesian Parameters (T), Intermolecular Free Path length (L_f), Internal Pressure (π_i), free volume (V_f), Rao's constant (R) , Surface Tension (S_t), Mean Square Thermodynamic Fluctuation, Vander Waal's Constant (b), Wada Constant (W), Space Filling Factor (r) and Relative Association (R_a). With the help of these thermodynamic properties calculated with the help of ultrasonic interferometer, we can study phenomenon like

azeotropism, intermolecular interactions, miscibility and compatibility of binary liquid mixture, phase transition between various phases, various thermodynamic properties of binary and ternary liquid mixture, transport related phenomenon and various properties related with transport phenomenon etc.

WORKING PRINCIPLE OF ULTRASONIC INTERFEROMETER:

An ultrasonic interferometer is a simple and direct device to determine the ultrasonic velocity with a high degree of accuracy. The principle used in the measurement of velocity is based on accurate determination of the wavelength (λ) in the medium. Ultrasonic waves of known frequency are produced by a quartz plate fixed at the bottom of the cell. The waves are reflected by a movable metallic plate kept parallel to the quartz plate. If the separation between these plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. The acoustic resonance gives rise to an electrical reaction on the generator driving the quartz plate and the anode current of the generator becomes maximum.
If the distance is now increased or decreased and the variation is exactly one half wavelength or multiple of it, anode current again becomes maximum. From the knowledge of wavelength, the velocity can be obtained by the relation;

Velocity = wavelength × frequency

$$V = \lambda \times \nu$$

The determination of adiabatic and isothermal compressibility's may be done by the following formula;

$$V = \sqrt{\frac{1}{\rho\beta_{adaib}}} = \sqrt{\frac{\gamma}{\rho\beta_{isotherm}}}$$

Where, γ is the ratio of specific heats, ρ is the density of liquid, β_{adaib} is adiabatic compressibility's and $\beta_{isotherm}$ is the isothermal compressibility's.

EXPERIMENTAL DETAILS OF ULTRASONIC INTERFEROMETER STUDY

High purity grade acetone purchased from Qualigens Fine Chemicals, 99.8%, India was used without further purification, except drying over molecular sieves. acetophenone was obtained from S D fine Chemicals, A R Grade 99.4% are purified by standard procedure[(4)]. The mixtures were prepared by weight and were kept in special airtight bottles.

The densities of pure liquids and binary mixtures were measured using a single capillary pycnometer (made of borosil glass) of bulb capacity 8 * 10^{-3} dm^3. The marks of the stem were calibrated with triple distilled water. The ultrasonic speeds in pure liquids and in their binary mixtures were measured using single crystal variable path length ultrasonic interferometer

(Mittal Interprises, New Delhi, Model: M-82) operating at 2 Mhz by the method described elsewhere[5,6]. Experimentally determined values of densities and speeds of sound, whichever available, for the pure liquids are compared with the literature.

Isentropic compressibility, intermolecular free length and relative association have been calculated by the following formulae [1]:

$$k_S = \frac{1}{u^2 \rho}$$

$$L_F = K\, k_S^{1/2}$$

$$R_A = \frac{\rho}{\rho_0}\left(\frac{u_0}{u}\right)^{1/3}$$

Where ρ_0 and u_0 are the densities and ultrasonic speed of pure solvent, ρ and u are the density and ultrasonic speed of mixtures respectively and K is the temperature dependent Jacobson constant (6.0816×10^4 at 35^0C).

The deviation parameters of the binary liquid mixtures have been evaluated using the general equation:

$$\Delta y = y_{mix.} - x_1 y_1 + x_2 y_2$$

Where, y indicates the parameters such as isentropic compressibility, intermolecular free length and ultrasonic speed; x_1 and x_2 are the mole fractions of components 1 and 2 respectively. Δy , y_1 , y_2 , and $y_{mix.}$ are the deviations parameter, parameters of the components 1 and 2 and observed parameter respectively.

Graphical representation of Δk_S as a function of mole fraction of acetone, x_1 is given in Figure

The dependence of on mole fraction of acetone is fitted to a Redlich-Kister type equation [2];

$$\sigma\ \Delta k_S = \left[\sum \frac{\Delta k_{S,obsr} - \Delta k_{S,cal}}{n-m}^2\right]^{1/2}$$

Where, n is the total number of experimental points and m is the number of coefficients.

CONCLUSION

Mixed solvents, rather than pure solvents, find practical applications in most chemical processes, their properties are less known. Derived parameters from ultrasonic speed measurement and the corresponding excess functions provide qualitative information regarding the nature and strength

of interactions in liquid mixtures. In the manuscript, we report the results of our study on the binary mixtures of acetone with acetophenone and ethylmethylketone, covering the entire composition range, at 303.15K. Acetone is commonly used for preparation of various organic compounds. Thus, acetone + acetophenone/ethylmethylketone mixed solvents would enable us to have a large number of solvents, with appropriate physiochemical properties, which can be used for a particular chemical process. Therefore, present study was undertaken in order to have deeper understanding of the intermolecular interaction between the components of the above binary mixtures.

PROPOSED RESEARCH WORK

In the present work, an attempt has been made to find experimental densities and speed of sound at 30^0C between acetonephenone and ethylmethyl ketone with acetone binary liquid mixtures covering entire composition range with the help of ultrasonic interferometer. From the experimental data, deviations in various acoustical properties such as isentropic compressibility, intermolecular free length and relative association will be computed.

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