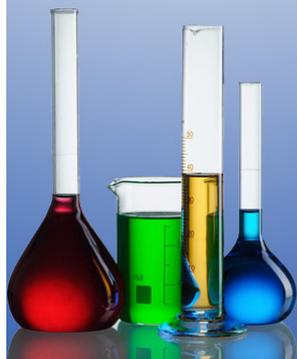


Chapter 5

ULTRASONIC VELOCITY STUDIES



CHAPTER 5

ULTRASONIC VELOCITY STUDIES

5.1: INTRODUCTION

The measurement of ultrasonic velocity has been adequately employed as a versatile tool for investigating the physical properties of matter-solid, liquid and gases. The study of ultrasonic properties of liquids and liquid mixtures is one of the rapidly developing branches of physical chemistry. Innumerable research articles have been published on the study of ultrasonic properties of the liquid and liquid mixtures. Such data are provided new sights for better understanding of thermodynamic functions in binary liquid mixtures. These studies are of very important because of their extensive use in textile industry, leather industry, pharmaceutical industry and in many others. Ultrasonic velocity measurements have proved useful in dealing with the problems of liquid structure and molecular interactions in liquid mixtures. This method has been applied both to pure liquids, liquid mixtures and to electrolyte solutions.

Ultrasonic investigations find essential applications in characterizing aspects of thermodynamic and Physico-Chemical behavior of liquid mixtures. The measurement of ultrasonic speeds and parameters derived from it has been used in understanding the nature of intermolecular interaction in liquid mixtures.

It may be mentioned here that the sound velocity is not a primary thermodynamic parameter and there is no single agreed view regarding the method of evaluation of sound velocity in an ideal mixture. Even though the sound velocity in an ideal mixture can be expressed as an additive on the mole fraction basis^{1,2} or weight fraction basis,³ the excess sound velocity so obtained does not properly characterize the deviations of the acoustic properties of the mixture from ideality. However, the attempts made by Ernst and Glinski⁴ and Kiyohara *et al.*^{5,6} indicate that sound velocities evaluated making use of thermodynamically valid expressions may

be utilized to obtain excess sound velocities which are useful in understanding the solute-solvent interactions. It is worthwhile to note here that Kudriavtsev⁷ derived expressions for evaluating theoretically the velocity of sound in pure liquids and liquid mixtures based on thermodynamically valid equations for internal energy in liquids and liquid mixtures and found that the expressions yield velocity data in good agreement with the experimental data for binary mixtures.

For four and a half decades, extensive ultrasonic velocity measurements have been carried out in a large number of liquid mixtures. Ultrasonic propagation parameters yield valuable information regarding the behaviour of binary liquid systems because of intramolecular and intermolecular association, dipolar interactions, complex formation and related structural changes affect the compressibility of the system which in turn produces corresponding variations in the ultrasonic velocity.

In many industrial applications, liquid mixtures are mostly used in processing and product formulations rather than single component liquid systems. Thermodynamic and transport properties⁸⁻¹⁰ of liquid mixtures have been extensively used to study the deviation of real liquid mixtures from ideality. In addition, these properties have been widely used to study the intermolecular interactions between the various species present in the liquid mixtures.⁸⁻¹⁰ Ultrasonic velocity and related data of liquid mixtures are also found to be the most powerful tool in testing the theories of liquid state. In addition, ultrasonic velocity data can be utilized to deduce some useful properties of liquid mixtures which are not easily accessible by other means.

The high precision of ultrasonic velocity measurements make it possible to calculate many other reliable parameters which gives information regarding deviations of the system from ideality. Molecular association in solution and some important correlations with various parameters, e.g. ratio of heat capacities, isentropic compressibilities, free volume, intermolecular free-length, available volume, internal pressure, energy of vaporization, solubility parameter, non-linearity parameter, thermo acoustical parameters etc. can be very well studied through ultrasonic velocity measurements in liquid mixtures.

It has been pointed out by several workers that an excess thermodynamic function sensitively depends not only on the differences in intermolecular forces, but also on the differences in size of molecules. It is obvious that the study of excess compressibility and other excess acoustical parameters provide important information on the intermolecular forces existing in the liquid mixtures. Through the statistical theory of solutions, using the ultrasonic velocity and density data, it is also possible to investigate the solute-solvent interactions.

5.1.1: Theory

Ultrasonic velocity measurements being faster and more accurate and non-destructive have edge over other physical methods in elucidating the structure of matter and in studying the solute-solvent interactions present in the solution etc.

A number of useful and important thermodynamic properties of liquid mixtures can be deduced from the sound velocity and density measurements under different physical conditions. Ultrasonic data when coupled with molar volume, thermal expansion coefficient and heat capacity provide information about a number of thermodynamic parameters of liquid mixtures. These parameters can further be used to study the structural molecular interactions like *solute-solute*, *solute-solvent*, and *solvent-solvent* interactions. Moreover such properties of liquid mixtures can be used to test various theories of liquid state.

5.1.2: Isentropic Compressibility (K_s)

Isentropic compressibility is an important parameter which throws light on the solute-solvent interactions in solutions. This parameter is widely used to study the behaviour of solutions.¹¹⁻¹⁹

$$K_s = 1/u^2\rho \quad \dots \quad 5.1$$

where 'u' is the ultrasonic velocity and 'ρ' is the density. The units of K_s are $m^2 N^{-1}$. The variation of K_s with concentration is widely used to study the solute-solvent interactions. If linear relation exists between K_s and concentration, then the absence of solute-solvent interactions is revealed. If the relations are nonlinear then it manifests the presence of the solute-solvent interactions in solutions.

5.1.3: Acoustic Impedance (Z)

The ratio of acoustic pressure to the associated particle velocity in a medium is defined as the acoustic impedance of the medium. The acoustic impedance (Z) is given by the relation²⁰.

$$Z = \rho u \quad \dots \quad 5.2$$

The acoustic impedance is also used for structural analysis²⁰. The deviation from linearity of Z with concentration has been attributed to the formation of molecular complexes.²¹ The units of Z are $\text{kg m}^{-2} \text{s}^{-1}$.

5.1.4: Intermolecular free-length (L_f)

The intermolecular free-length is the distance covered by a sound wave between the surfaces of the neighbouring molecules and is given by Jacobson²² as

$$L_f = K (K_s)^{1/2} \quad \dots \quad 5.3$$

where 'K' is the temperature dependant constant and 'K_s' is the isentropic compressibility. The unit of L_f is 'm'.

5.1.5: Relative Association (R_A)

Relative association between the molecules is being calculated by using the equation

$$R_A = \frac{\rho}{\rho_o} \left(\frac{u_o}{u} \right)^{1/3} \quad \dots \quad 5.4$$

where ' ρ_o ' and ' u_o ' are the density and ultrasonic velocity of solvent and ' ρ ' and ' u ' are the density and ultrasonic velocity of the mixture.

5.1.6: Excess Properties

Excess properties of the binary liquid mixtures have been evaluated by using the general equation

$$Y^E = Y_{\text{mix}} - (X_1 Y_1 + X_2 Y_2) \quad \dots \quad 5.5$$

where 'Y' indicates the parameter such as isentropic compressibility (K_s), intermolecular free-length (L_f), acoustic impedance (Z) and ultrasonic velocity (u) of the liquid mixtures. X_1 and X_2 are the mole fractions of components 1 and 2 respectively. Y^E , Y_1 , Y_2 and Y_{mix} are the excess parameter, parameters of the components 1 and 2, and observed parameter respectively.

By using the above equations, the excess ultrasonic velocity (u^E), excess isentropic compressibility (K_s^E), excess intermolecular free-length (L_f^E), excess acoustic impedance (Z^E) have been calculated from the measured density (ρ) and ultrasonic velocity (u) for the binary liquid mixtures of carbitols [2-(2-Methoxyethoxy) Ethanol (Methyl carbitol) (MC), 2-(2-Ethoxyethoxy) Ethanol (Ethyl carbitol) (EC), and 2-(2-Butoxyethoxy) Ethanol (Butyl carbitol) (BC) in different amines i.e. normal amines (n-butyl amine, n-hexylamine and n-octylamine), branched amines (sec-butyl amine and tert-butylamine) and cyclic amine (cyclohexyl amine) at 308.15 K and the results are discussed in terms of molecular interactions between the unlike components and are presented in the following sections.

The mixing quantities viz. u^E , Z^E , K^S , and L_f^E have been fitted to Redlich-Kister equation by the method of least squares using the Marquardt algorithm to derive the binary coefficients, A_j and standard deviation, σ :

$$\mathbf{V}^E (\Delta Y) = \mathbf{X}_1 \mathbf{X}_2 \sum_{\mathbf{I} = \mathbf{K}} \mathbf{A}_j (\mathbf{X}_2 - \mathbf{X}_1)^{j-1} \quad \mathbf{5.6}$$

In each case, the optimum number of coefficients, A_j was ascertained from an examination of the variation of standard deviation, σ :

$$\sigma = (\sum (Y_{\text{Cal}}^E - Y_{\text{obs}}^E) / (n-m)) \quad \mathbf{5.7}$$

Where 'n' represents the number of measurements and 'm', the number of coefficients. From the variations of ultrasonic velocity and its derived acoustical parameters and their excess parameters like u^E , Z^E , K_s^E , and L_f^E with the composition of the liquid mixtures, the molecular interactions present in the liquid mixtures under study are discussed in the following sections of this chapter.

5.2: ULTRASONIC VELOCITY STUDY OF BINARY LIQUID MIXTURES OF METHYL CARBITOL (MC) WITH AMINES AT 308.15K.

ABSTRACT

Densities and ultrasonic velocities of binary liquid mixtures of 2-(2-Methoxyethoxy) Ethanol Methyl Carbitol (MC) with amines (n-butyl amine (NBA), sec.butyl amine (SBA), tertiary butyl amine (TBA), n-hexyl amine (NHA), n-octyl amine (NOA) and cyclo hexyl amine (CHA) have been measured at 308.15 K. The observed data have been utilized to calculate various acoustical parameters like isentropic compressibility (K_S), intermolecular free length (L_f), and acoustic impedance (Z). The various excess properties like excess ultrasonic velocity (u^E), excess acoustic impedance (Z^E), excess isentropic compressibility (K_S^E) and excess inter molecular free length (L_f^E) were calculated and fitted to the Redlich-kisher equation. The results were discussed in terms of the existence of intermolecular interactions between the components in the liquid mixtures under study.

5.2.1: INTRODUCTION

In recent years, the measurement of ultrasonic velocity has been adequately employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures. The ultrasonic velocity measurements are highly sensitive to molecular interactions and can be used to provide qualitative information about the physical nature and strength of molecular interaction in liquid mixture.²³⁻²⁵ Ultrasonic velocity of a liquid is fundamentally related to the binding forces between the atoms or the molecules and has been adequately employed in understanding the nature of molecular interaction in pure liquids.²⁶⁻²⁸ The variation of ultrasonic velocity and acoustical parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interaction components as well as strongly interaction components.²⁹⁻³⁰

The ultrasonic velocity studies on intermolecular interactions of binary liquid mixtures of 2-(2-methoxy ethoxy) ethanol [Methyl carbitol (MC)] with amines [n-butyl amine (NBA), sec-butyl amine (SBA), tert-butylamine (TBA), n-hexylamine

(NHA), n-octylamine (NOA) and cyclohexylamine (CHA)] at 308.15 K and the results are discussed here in terms of molecular interactions.

5.2.2: MATERIALS AND EXPERIMENTAL METHODS:

The details of the chemicals and experimental procedures adopted in this section have been explained in chapter 2 under “Materials and Experimental methods” of this thesis.

5.2.3: RESULTS AND DISCUSSION

The density (ρ) and the ultrasonic velocity (u) have been measured over the whole composition range for the binary liquid mixtures of MC + NBA, + SBA, + TBA, + NHA, + NOA and + CHA at 308.15 K. The acoustical parameters like acoustic impedance (Z), isentropic compressibility (K_s), intermolecular free-length (L_f) and relative association (R_A) have been calculated from the measured density (ρ) and ultrasonic velocity (u) values using the relations given in Section 5.1. The results are given in Tables 5.2.1 to 5.2.6.

From the Tables 5.2.1 to 5.2.6, it is observed that the values of u , z , K_s , L_f and R_A with the mole fraction of MC (X_{MC}) is varied. This indicates the presence of interactions between the components in these binary liquid mixtures. The variation of ultrasonic velocity (u) with mole fraction of MC for all the mixtures is shown in Fig. 5.2.1 as a typical graph.

However, the excess functions which are a measure of the deviations from the ideal behavior are relatively more sensitive to the intermolecular interactions between the unlike molecules of the mixture than the pure acoustical parameters as explained above. With this in mind, the excess acoustical parameters are calculated by using the equations given in 5.1 section and are presented in Tables 5.2.1 to 5.2.6.

To have more information on intermolecular interactions in the present systems, the variations in excess acoustical parameters, like the excess isentropic compressibility (K_s^E), excess intermolecular free-length (L_f^E), excess ultrasonic velocity (u^E) and excess acoustic impedance (Z^E) with mole fraction of MC (X_{MC}) are examined from the Figs. 5.2.2 to 5.2.5 respectively.

It is evident from the Figs. 5.2.2 and 5.2.3 that K_s^E and L_f^E are negative for all the systems over the whole mole fraction range except MC + NOA systems. In general, K_s^E values depend upon two factors. (i) Increase in free-length, defined by Jacobson³¹ due to loss of dipolar association, breaking up of hydrogen bonding³² and difference in size and shapes of the component molecules and (ii) decrease in free-length as a result of dipole-dipole interactions, hydrogen bonding association³³ and complex formation between the component-1 solutions.³³

The first effect contributes to the increase in inter space between molecules in mixtures; consequently sound waves cover smaller distances in mixtures than in pure components. This would result in negative deviation in ultrasonic velocity and positive deviation in isentropic compressibility. The second effect contributes to the decrease in inter space between molecules in mixtures consequently sound waves cover larger distances in mixtures than in pure components.

The negative K_s^E and L_f^E values indicate the presence of strong interactions between unlike molecules, which may result in complex formation. The polar nature of the two components (amine and MC) leads to the interaction between the hydrogen atom of -OH group of MC with nitrogen atom of amino group of amines and also between the electron rich oxygen atom of etheric group of 2-(2-methoxy ethoxy) ethanol [Methyl carbitol (MC)] with polarised H-atom of amino group of amines. Thus, the complex formation between the two component molecules lead to a decrease in the intermolecular distances and increase in sound velocities, thereby decreasing the isentropic compressibilities of the mixtures. The negative values obtained for the K_s^E and L_f^E are in the following order:



Further, it is also observed from the experimental results that the negative contributions increase with increase in chain length of amines as well as with branching of amines.

Since 2-(2-methoxy ethoxy) ethanol [Methyl carbitol (MC)] is a liquid of proton accepting nature, N-H...O-H type of complex formation may be expected

between unlike molecules. This leads to the compact structure hence decrease in inter space between the molecules in the mixtures results which contribute to negative deviations in K_s^E and L_f^E . The variation of K_s^E and L_f^E are qualitatively similar to that of excess volumes as discussed in Chapter 4.

The change in magnitude of negative values of K_s^E and L_f^E from n-butyl amine to n-octylamine shows that increase in chain length of amines lead to less compressibility in homologous series. Further the data suggests that the strength of complex formation between unlike molecules increase from n-butyl amine to n-octylamine. This conclusion is supported by the observation made by Fort and Moore.³⁴ According to these workers, deviations in compressibility from ideality becomes increasingly negative as the strength of interactions between unlike molecules increase, for the same reason Prasad et al.³⁵ observed negative compressibilities for the mixtures of acetonitrile with polar compounds.

The negative values of excess volumes increase (cf. Tables 4.2.1 to 4.2.6) from n-butyl amine to n-octylamine. The negative values of K_s^E and L_f^E (Cf. Tables 5.2.1 to 5.2.6) also increases from n-butyl amine to n-octylamine. This shows that K_s^E and L_f^E run parallel to excess volume in its dependence on composition. This equality in trend for the above mixtures suggests that the factors contributing to V^E are similar to those that determine the values of K_s^E in the above mixtures. The values of K_s^E for the mixtures of MC with SBA and TBA are higher than the corresponding normal amine i.e. NBA. It is also observed that K_s^E and L_f^E of CHA are smaller than the corresponding normal amine i.e. n-hexylamine. These trends are similar in the case of excess volumes.

It is noticed that in the case of MC + NOA the positive K_s^E and L_f^E values are observed. An interpretation to this behavior can be given using experience made with the quantitative evaluation of alcohol + amine mixtures by ERAS model proposed by the earlier workers as explained in chapter- 4.

Figs 5.2.4 and 5.2.5 show that the variation of u^E and Z^E with X_{MC} respectively. The deviations observed in u^E and Z^E due to the close packing of molecules present in the mixture may further be explained due to strong interactions formed as a result of hydrogen bonding between unlike molecules. As expected, the

observed positive deviations in u^E and Z^E (Fig.5.2.4 and 5.2.5), where $Z = u^E/p$, and an opposite trend in the behavior of K_S^E (Fig. 5.2.2), where $K_S = 1/u^2p$ (discussed earlier), over the entire range of the mole fraction of the systems investigated again support our view that the interactions between unlike molecules are quite obvious. The u^E and Z^E values support our earlier view that interactions increase with increase in chain length of normal amines. The values of u^E and Z^E for these systems are in the following order



It has been suggested that the concentrations at which the excess functions exhibit extrema (Figs.5.2.2 to 5.2.5) indicate strong interactions between unlike molecules, leading to the formation of associates, thus formed, is reached in the concentration range where such extrema occur. However, the extrema in excess functions were viewed as due to the transition from component 1- in – component 2 solutions to component 2 – in – component solutions.

In the case of branched and cyclic amines the observed K_S^E and L_f^E values are more negative than the respective normal amines. Which may be due to the influence of geometric factors in addition to the hydrogen bond interaction and difference size of the unlike molecules. The above order observed in case of u^E , Z^E , K_S^E and L_f^E is similar to that of V^E and η^E in the mixtures under study.

It may therefore be concluded that the resultant interactions in the binary systems of the present study, is not solely dependent on the molecular structure of the component liquids, but also, influenced by other factors like dispersion forces, dipole – dipole interactions, hydrogen bonding, charge transfer interaction and /or complex formation. However it was observed that the polarity and size of the component liquids plays a significant role in determining the strength of molecular interaction in a binary mixture.

All the quantities (u^E , Z^E , K_S^E , and L_f^E) have been fitted to Redlich and Kister equations by the method of least squares using the Marquardt equation(equation 5.6) to derive the binary coefficient, A_j , and standard deviation (σ). In each case, the optimum of coefficient, A_j , was ascertained from an examination of the standard deviation (σ), using equation 5.7. The estimated values of A_j and σ for u^E ,

Z^E , K_S^E , and L_f^E , are summarized in Table 5.2.7. In all the figures, the points represent the data calculated from equation-5.5. for u^E , Z^E , K_S^E , and L_f^E respectively. The smooth curves are drawn from the best fitted data calculated from equation 5.7.

From the above discussion it is concluded that the trends in the variations of the parameters derived from the ultrasonic velocity and the sign and extent of deviation of the excess functions from rectilinear dependence on composition of these mixtures suggest the presence of molecular interactions between the components of these binary mixtures.

5.3: ULTRASONIC VELOCITY STUDY OF BINARY LIQUID MIXTURES OF ETHYL CARBITOL (EC) WITH AMINES AT 308.15 K.

ABSTRACT

Densities and ultrasonic velocities of binary liquid mixtures of 2-(2-Ethoxyethoxy) Ethanol with amines (n-butyl amine (NBA), sec-butyl amine (SBA), tertiary butyl amine (TBA), n-hexyl amine (NHA), n-octyl amine (NOA) and cyclo hexyl amine (CHA) have been measured at 308.15 K. The observed data have been utilized to calculate various acoustical parameters like isentropic compressibility (K_S), intermolecular free length (L_f), and acoustic impedance (Z). The various excess properties like excess ultrasonic velocity (u^E), excess acoustic impedance (Z^E), excess isentropic compressibility (K_S^E) and excess inter molecular free length (L_f^E) were calculated and fitted to the Redlich-kisher equation. The results were discussed in terms of the existence of intermolecular interactions between the components in the liquid mixtures under study.

5.3.1: Introduction

The thermodynamic properties derived from the measurements of density and ultrasonic speed of sound in liquid and liquid mixtures at a particular temperature or several temperatures as a function of composition are useful in chemical engineering process design and operation as well as for the development of molecular models. Additionally excess molar thermodynamics properties are of fundamental importance in understanding the molecular behavior in terms of type and extent of molecular interactions operating in the mixture. Therefore there has been considerable interest in the theoretical and experimental investigations of thermodynamic properties of different types of the liquid mixtures.³⁶⁻³⁸

Amines are important organic liquids because of their strong electron donating capability. They are weakly self associated molecules as well as can also form H-bonds either in self associated complexes or with the appropriate groups on dissimilar molecular species. Systematic studies of ultrasonic velocity and their derived acoustical parameters of binary liquid mixtures containing normal, branched and cyclic amines in a number of solvents have been made but literature reveals that their

association with carbitols are scanty. Hence it is considered important to carry out systematic studies on mixtures involving different amines in order to see the effect of normal, branched and cyclization and shape of molecules on excess thermodynamic function.

This has stimulated to undertake the systematic and detailed work on the thermodynamic and acoustic properties of different amines with polar liquids (carbitols) which will be useful for the industrial applications and theoretical development.

Now the author is reporting the measurements of density (ρ) and speed of sound (u) and derived acoustical parameters of EC +NBA,+ NHA,+ NOA,+ SBA,+ TBA,+ and +CHA and their excess functions at 308.15 K, the results are discussed from the point of view of intermolecular interactions between unlike molecules of the binary liquid mixtures under study.

5.3.2: MATERIALS AND EXPERIMENTAL METHODS: The details of the chemicals and experimental procedures adopted in this section have been explained in chapter 2 under the materials and experimental methods.

5.3.3: RESULTS AND DISCUSSION

The densities (ρ) and the ultrasonic velocities (u) have been measured over the whole composition range for the binary liquid mixtures of EC + NBA, + SBA, + TBA, + NHA, + NOA and +CHA at 308.15 K. From the measured values of density (ρ) and ultrasonic velocity (u) the thermodynamic parameters like acoustic impedance (Z), isentropic compressibility (K_s), intermolecular free-length (L_f), relative association (R_A) have been calculated for the binary liquid mixtures of 2-(2-Ethoxyethoxy) Ethanol (Ethyl carbitol) (EC) with NBA, SBA, TBA, CHA, NHA and NOA at 308.15 K over the entire composition range using the relations mentioned in the earlier Section (5.1) and the results are presented in Tables 5.3.1 to 5.3.6.

The variations of u , Z , K_s , L_f and R_A with the mole fraction of EC are observed from Tables 5.3.1 to 5.3.6. It is evident that the values of u , Z and R_A increase while those of K_s and L_f decrease with the mole fraction of EC for all the

systems except in the case of the variation of ultrasonic velocity for NOA and CHA systems. The variation of ultrasonic velocity with the mole fraction of EC for all the mixtures is shown in Fig. 5.3.1 as a typical graph. In general u and L_f have been reported to vary inverse of each other with the composition of the mixtures³⁹⁻⁴¹ as in the present case. The decrease in K_s and L_f with X_{EC} for all the mixture suggests the presence of significant interactions between unlike molecules in these mixtures. Mixing of EC with amines induces the mutual dissociation of the component molecules and possibility of formation of hydrogen bond between unlike molecules. The former effect leads to an increase in K_s and L_f values, while the latter leads to a decrease in these values. The observed decrease in K_s and L_f for all these systems studied indicates the presence of significant interactions such as hydrogen bonding between unlike molecules and it dominates over the dissociation of the component molecules.⁴² Similar trends in variations of K_s and L_f have also been reported for DMSO + MeOH^{34,43} and DMSO + n-butyl alcohols.⁴³

The increase in 'u' and corresponding decrease in L_f with X_{EC} in the present systems is in accordance with the view proposed by Eyring and Kincaid⁴⁴ In the present study, R_A is found to increase with the mole fraction of EC as shown in Tables 5.3.1 to 5.3.6. This suggests that interactions between EC and amines predominate over the breaking up of amine – amine associates. The increase in Z with X_{EC} is in agreement with the theoretical requirement as per the equation $Z = \rho.u$. Likewise the changes in behaviour of u , R_A , Z , K_s and L_f with X_{EC} in EC + amine mixtures indicate the presence of interactions between the unlike molecules.

However, the excess functions which are a measure of the deviations from ideal behaviour are relatively more sensitive to explain the intermolecular interactions between unlike molecules than those discussed above. With this view, the excess isentropic compressibility (K_s^E), excess intermolecular free-length (L_f^E), excess acoustic impedance (Z^E) and excess ultrasonic velocity (u^E) are calculated from the measured density and ultrasonic velocity using the equations explained in the earlier Section 5.1 and the results are included in Tables 5.3.1 to 5.3.6.

The variations of K_s^E , L_f^E , u^E and Z^E with X_{EC} for the mixtures under study are shown in Figs. 5.3.2 to 5.3.5 respectively. By examining the Figs. 5.3.2 and 5.3.3, Chapter 5

it is clear that K_s^E and L_f^E are negative over the entire range of composition in all these systems. The negative K_s^E and L_f^E values were found to be large and symmetrical with minima at 0.5 mole fraction of EC in all these systems.

In general negative K_s^E and L_f^E values are shown by the systems in which the strong molecular interactions exist between the components where one of the components is associated in pure state,⁴⁵ as in the present study. In view of proton donating ability of EC and proton accepting ability of amines, the negative K_s^E and L_f^E values may be regarded as an evidence for the formation of hydrogen bond between the hydrogen atom of O-H group of EC with negatively charged N atom of amino group of amines. Thus the complex formation between the two component molecules lead to a decrease in the intermolecular distance and an increase in the sound velocity, thereby decreasing the isentropic compressibility of the mixtures. The presence of minima of K_s^E and L_f^E at a particular composition might also be taken as a further evidence for the presence of molecular species with a greater degree of close packing than either of constituent liquids. A similar observation was reported for the mixtures of 2-methoxy ethanol + 2-(2-alkoxy ethoxy) ethanol by Amalendu Pal et al.⁴⁶ The negative values of K_s^E and L_f^E for all these systems fall in the order.



This order may be explained in terms of the variation in the strength of hydrogen bond between unlike molecules in the mixtures. The strength of hydrogen bond interactions between unlike molecules in the normal amines increases from n-butyl amine to n-octylamine, as the basic character of amines increases from n-butyl amine to n-octylamine has already been stated. Hence the intermolecular spaces would be reduced to the maximum extent in n-octylamine and minimum extent in n-butyl amine mixtures. Consequently the negative values of K_s^E and L_f^E would be large in EC + NOA system compared to EC + NBA system. This order is supported by the observed values of K_s^E and L_f^E and the observations of Fort and Moore.³⁴ According to these workers the deviations in compressibility tend to become increasingly negative as the strength of interaction between unlike molecules increase.

K_s^E and L_f^E values in case of SBA and TBA are more negative than the NBA and also these negative values are more for NHA than CHA. The reason may be due

to the influence of geometric factors in addition to the hydrogen bond interactions in these systems.

From Figs 5.3.4 and 5.3.5 it is noticed that the positive deviations in u^E and Z^E are observed for all the systems over the entire composition except CHA, NOA in u^E and NHA and NOA in case of Z^E range which supports our view expressed above. The positive deviations (u^E and z^E) are due to close packing of molecules present in the mixture. This close packing may be further explained due to the strong interactions formed as a result of strong hydrogen bonding between unlike molecules. Similar positive values of u^E and Z^E were reported in literature from the velocity studies of binary liquid mixtures of diethylene glycol monoethyl ether + alcohols⁴⁷ and ethanol + octanol.⁴⁸

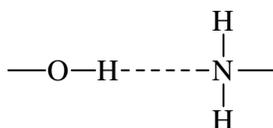
From the above figures, it is evident that the positive values of u^E for the present systems are in the following order:



Z^E values are in the following order



It has been suggested that the concentration at which the excess functions exhibiting maxima or minima indicates strong interaction between the component molecules, which in turn suggests the complex formation at this composition between the unlike molecules. The results further suggest A-B type of interactions forming.



The strength of bonding is expected to increase with increase in chain length of amines and the results of this study corroborate this fact.

All the quantities (u^E , Z^E , K_S^E , and L_f^E) have been fitted to Redlich and Kister equations by the method of least squares using the Marquardt equation (equation No.5.6) to derive the binary coefficient, A_j and standard deviation (σ). In each case, the optimum of coefficient, A_j was ascertained from an examination of the standard deviation (σ), using equation 5.7. The estimated values of A_j and σ for u^E , Z^E , K_S^E , and L_f^E are summarized in Table: 5.3.7. In all the figures, the points represent

the data calculated from equation: 5.5, for u^E , Z^E , K_S^E , and L_f^E respectively. The smooth curves are drawn from the best fitted data calculated from equation 5.7.

From the above discussion it is concluded that the trends in the variations of the parameters derived from the ultrasonic velocity and the sign and extent of deviation of the excess function from rectilinear dependence on composition of these mixtures suggest the presence of molecular interactions between the components of these binary mixtures.

5.4: ULTRASONIC VELOCITY STUDY OF BINARY LIQUID MIXTURES OF BUTYL CARBITOL (BC) WITH AMINES AT 308.15 K.

ABSTRACT

Densities and ultrasonic velocities of binary liquid mixtures of 2-(2-Butoxyethoxy) Ethanol (BC) with amines (n-butyl amine (NBA), sec.butyl amine (SBA), tertiary butyl amine (TBA), n-hexyl amine (NHA), n-octyl amine (NOA), and cyclo hexyl amine (CHA) have been measured at 308.15 K. The observed data have been utilized to calculate various acoustical parameters like isentropic compressibility (K_S), intermolecular free length (L_f), and acoustic impedance (Z). The various excess properties like excess ultrasonic velocity (u^E), excess acoustic impedance (Z^E), excess isentropic compressibility (K_S^E) and excess inter molecular free length (L_f^E) were calculated and fitted to the Redlich-kister equation. The results were discussed in terms of the existence of intermolecular interactions between the components in the liquid mixtures under study.

5.4.1: INTRODUCTION

Carbitols are a very interesting class of substances from a practical point of view, as oxygenated compounds are increasingly used as additives to gasoline due their octane enhancing and pollution-reducing properties.^{49,50} Beside this, these molecules possess both –OH group and etheric group in the same molecule, hence they show proton donating as well as proton accepting nature called amphiphilic nature and they were effectively used as surfactants with a large number of applications^{51, 52}. On the other hand, the investigation of mixtures involving alkoxyethanols makes possible the study of self-association via inter and intra molecular hydrogen bonds related to the presence of the O and OH groups in the same molecule. So, different spectroscopic techniques have been used to investigate the existence of intermolecular hydrogen bonds in these compounds⁵³⁻⁵⁵. They are present, at all conditions, even in vapour phase, whereas intermolecular H-bonds appear at higher concentrations of the cellosolve in liquid state. In solutions formed by carbitols and amines, the formation

of the intramolecular H-bonds leads to enhanced dipole-dipole interactions in comparison to those present in mixtures with homomorphic alkanols⁵⁶.

Ultrasonic wave propagation affects the physical properties of the medium and hence, can furnish information about molecular interactions of the liquid and liquid mixtures. The sign and magnitude of the non-linear deviations from ideal values of velocities and adiabatic compressibilities of liquid mixtures with composition are attributed to the difference in molecular size and strength of interaction between unlike molecules.⁵⁷⁻⁵⁹

Ultrasonic velocities have been adequately employed in understanding the nature of molecular interaction in pure liquids⁶⁰ binary and ternary mixtures.⁶¹⁻⁶³ The method of studying the molecular interaction from the knowledge of variation of thermodynamic parameters and their excess values with composition gives an insight into the molecular process. The present study⁶⁴ includes density and an ultrasonic behavior of binary mixtures of butyl carbitol with different amines over the entire composition range at 308.15 K. and results are discussed here in terms of molecular interactions between unlike molecules under study.

5.4.2: MATERIALS AND EXPERIMENTAL METHODS:

The details of the chemicals and experimental procedures adopted in this section have been explained in chapter 3 under the materials and experimental methods.

5.4.3: RESULTS AND DISCUSSION

The measured density (ρ) and ultrasonic velocity (u) are used to calculate acoustic parameters, such as acoustic impedance (Z), isentropic compressibility (K_s), intermolecular free-length (L_f), relative association (R_A) for the binary liquid mixtures of Butyl carbitol (BC) with NBA, SBA, TBA, CHA, NHA and NOA at 308.15 K over the entire composition range as a function of mole fraction of BC (X_{BC}) using the relations mentioned in the earlier section (5.1) and the results are presented in Tables 5.4.1 to 5.4.6.

Tables 5.4.1 to 5.4.6 show the variation of u , Z , R_A , K_s and L_f with the mole fraction of BC (X_{BC}). The variation of these parameters with mole fraction of BC

(X_{BC}) exhibits the presence of intermolecular interactions in these mixtures. A similar observation was made by Pal and Das⁴⁶ from the ultrasonic studies for the binary liquid mixtures of EC + n-alkanols (C_1 and C_6). The variation of ultrasonic velocities (u) of these binary mixtures with molefraction of BC is shown in Fig.5.4.1 as a typical graph and it indicates the presence of intermolecular interactions between unlike molecules of these mixtures under study.

The excess functions which are a measure of deviations from ideal behaviour are relatively more sensitive to the intermolecular interactions between unlike molecules than the ultrasonic velocity and other other properties. The excess isentropic compressibility (K_s^E), excess intermolecular free-length (L_f^E), excess acoustic impedance (Z^E) and excess ultrasonic velocity (u^E) are calculated from the measured density and ultrasonic velocity using equations explained in Section 5.1 and the results are included in Tables 5.4.1 to 5.4.6.

The variations of the excess functions K_s^E , L_f^E , Z^E and u^E with X_{BC} have been shown in Figs. 5.4.2 to 5.4.5 respectively.

From the Figs. 5.4.2 and 5.4.3 K_s^E and L_f^E are found to be negative for all the systems under study over the entire composition range. The minima for K_s^E and L_f^E is observed at $\sim 0.5 X_{BC}$ for all the mixtures. Further, the negative K_s^E and L_f^E values for the present systems are in the following order:



The dissociation of amine by the addition of BC leads to an increase in free-length in mixtures contributing to negative deviations in sound velocity and positive deviation in compressibility. However, the effect of depolymerisation and free-lengths, sound velocity and compressibility will be counteracted by the interaction due to the formation of intermolecular hydrogen bonded complexes between BC and amines. The actual values of K_s^E and L_f^E , therefore, would depend upon relative strengths of the two opposing effects.

The observed K_s^E and L_f^E values which are negative such as that the effect of interaction due to the formation of hydrogen bonded complexes between unlike molecules on compressibility dominates the physical forces which contribute to positive K_s^E and L_f^E values. Similar negative K_s^E and L_f^E values are reported by Chapter 5

Venkateswarlu et.al.⁶⁵ for the binary liquid mixtures of 2-butoxy ethanol + substituted benzenes. The behaviour of excess molar volume seems to be consistent with a minimum value of K_s^E for all the systems under study. Negative values of K_s^E and L_f^E mean that the mixture is less compressible than the corresponding ideal mixture, suggesting that there may be strong intermolecular hydrogen bonding between unlike molecules. As the amines are added to BC, thereby causing a breakdown of self-associated BC aggregates or both and hence contribute to a denser packing of the molecules through hydrogen bonding, the speed of sound increase and K_s^E decreases.

In case of BC + normal amines the K_s^E and L_f^E values increase with increase in chain length of amines. From the results it is understood that with increase in amine size, interstitial accommodation becomes less important, i.e., the molecules of two components cannot accommodate easily. This additional rigidity is a good reason for the positive values of u^E and Z^E as observed from the Figs. 5.4.4 to 5.4.5 respectively. Hence, the negative contributions in K_s^E and L_f^E and positive contribution in u^E and Z^E come from the interactions between unlike molecules, which is the most important factor in determining their magnitude.

Figs 5.4.4 and 5.4.5 show the variation of u^E and Z^E with X_{BC} respectively. The positive deviations observed in u^E and Z^E due to the close packing of molecules present in the mixture and may further be explained due to strong interactions formed as a result of hydrogen bonding between unlike molecules. The u^E and Z^E values support our earlier view that interactions increase with increase in chain length of normal amines. The values of u^E and Z^E for these systems are in the following order:



It has been suggested that the concentrations at which the excess functions exhibit extreme (Figs. 5.4.2 to 5.4.5) indicate strong interactions between unlike molecules, leading to the formation of associates. Hence, the maximum stability of the associates, thus formed, is reached in the concentration range where such extrema occur. However, the extreme in excess functions were viewed as due to the transition from component 1-in-component 2 solutions to component 2-in-component-1.solutions^{66,67}

The above order observed in case of u^E , Z^E , K_S^E and L_f^E is similar to that of V^E and η^E in the mixtures under study. The above trend suggests an increase in hydrogen bonding between unlike molecules with an increase in chain lengths of amines.

All the quantities (u^E , Z^E , K_S^E , and L_f^E) have been fitted to Redlich and Kister equations by the method of least squares using the Marquardt equation (equation No.5,6) to derive the binary coefficient, A_j , and standard deviation (σ). In each case, the optimum of coefficient, A_j , was ascertained from an examination of the standard deviation (σ), using equation 5.7. The estimated values of A_j and σ for u^E , Z^E , K_S^E , and L_f^E are summarized in Table 5.4.7. In all the figures, the points represent the data calculated from 5.5. for u^E , Z^E , K_S^E , and L_f^E respectively. The smooth curves are drawn from the best fitted data calculated from equation 5.7.

From the above discussion it is concluded that the trends in the variations of the parameters derived from the ultrasonic velocity and the sign and extent of deviation of the excess function from rectilinear dependence on composition of these mixtures suggest the presence of molecular interactions between the components of these binary mixtures.

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