Ultrasonic Studies of Molecular Interactions in Binary Liquid Mixture of Dibutylamine with Ethanol

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ABSTRACT

Ultrasonic properties of Binary liquid mixture of Dibutylamine with Ethanol were studied and investigated various parameters at the temperature 303 K. Ultrasonic measurements were determined using simple interferometer device with special designed double walled quartz crystal.Ultrasonic velocity,density,viscosity,adiabatic compressibility,intermolecular free length and molar valume were calculated. Some other excess parameters like excess adiabatic compressibility,excess viscosity,excess molar volume and excess intermolecular free length were calculated theoretically. Ultrasonic velocity increases with increasing mole fraction DBA(X_1) and increases velocity with decreasing mole fraction EAOH(X_2).Molar volume also follows the same trend. Adiabatic compressibility and inter molecular free length are decreases with increasing mole fraction (X_1) and with decreasing molefraction(X_2).Density and viscosity also follows similar behavior i.e. density increases with increasing molefractionupto X_1=0.128331 then density decreases with further increasing molefraction X_1 similarly density increases with decreasing mole fraction upto X_2=0.871669 then decreases with continuous decreasing molefractionX_2. Viscosity also follows the similar behavior.Excess adiabatic compressibility, Excess intermolecular free length and excess viscosity obtain the negative values and follows similar behaviori.e these parameters are decreases with increasing mole fraction upto X_1=0.186341(X_1=0.255689 for excess viscosity) with decreasing mole fraction upto X_2=0.813659 (X_1=0.255689 for excess viscosity) then both excess parameters are increases with molefractionX_1 and with decreasing molefraction X_2. In case of excess viscosity is increases with increasing mole fraction X_1=0.186341 and with decreases molefraction X_2=0.813659 from where excess viscosity decreases with increasing mole fraction X_1 and with decreasing molefraction X_2 except pure liquids.

Keywords: Binary liquids,Ultrasonicvelocity,Excess parameters, Ultrasonic Properties, Intermolecular Interactions,Thermodynamic Properties

I. INTRODUCTION

Propagation of ultrasonic waves through liquids and solids is the significance study to know and investigate certain physical, chemical and thermo dynamical properties of the materials.

The data obtained from ultrasonic propagation parameters in liquid mixtures and solution, ultrasonic velocity, attenuation and their variation with concentration of one of the components, helps to understand the nature of molecular interactions in the mixtures.

By varying concentration of solvents in compositions and mixtures have significant properties need to technological applications and it reveals the more information about the liquid state. Ultrasonic studies explains individually and combining liquid properties. The study of propagation of ultrasonic waves in liquids and liquid Mixtures provide an information on the nature of the inter molecular and intra molecular interactions in these liquid systems. Extensive studies of ultrasonic velocity in liquids, liquid mixtures and their interpretation in the light of molecular structure has obtained much significant during the last three decades [1-5]. Ultrasonic velocity and related data of liquid mixtures are found to be the most powerful tool in testing the theories of the liquid state. Besides, the ultrasonic velocity data can be used to derive some useful properties of liquid mixtures which are not easily accessible by other means. The indication of negative excess values says strong interactions and the positive values means weak interactions between the components liquid.

II. RELATED WORK

Ultrasonic velocity, density and viscosity have been measured by J. Glory et.al [6] in the mixture bromobenzene + (2 methoxy ethanol + n butanol) at three temperatures 30, 40 and 50^{0}C. Ultrasonic velocity are evaluated from Nomoto‘s relation, Van Dael ideal mixing relation, impedance relation, Rao‘s specific velocity relation and Junjie‘s theory by Sk.Fakruddin et.al [7] and the evaluated values are compared in the three binary mixtures of quinoline as a common component with o-cresol, m-cresol and p-cresol at 303.15, 308.15, 313.15 and 318.15 K over the entire composition range. J. N. Ramteke [8] measured the ultrasonic velocity (U), density (ρ) and viscosity (η) in binary liquid mixtures containing picolin in ethanol at 301.15 K and 305.15 K. From these data they computed some of acoustical parameters such as adiabatic compressibility (K_s), free length (L_f), free volume (V_f) and internal pressure (P_i) using the standard relations. Densities and ultrasonic speed have been measured by Sahu et.al [9] at 303K for the binary mixture of di acetone alcohol and Chlorobenzene over entire composition range. From these isentropic compressibility , intermolecular free length (L_f), acoustic impedance (Z) and their deviations namely excess isentropic compressibility (K_E), intermolecular free length (L_f), acoustic impedance (Z) have been calculated and interpreted in terms of intermolecular interactions.Ultrasonic velocity and density have been experimentally determined by R. Vadmalar [10] for binary liquid mixtures of Methyl methacrylate (MMA) with tertbutanol and iso-butanol at three different temperatures.

Jalal BasiriParsaa and MahboobehFaraji [11] measured densities and viscosities of ternary mixtures of 2-pyrrolidone + 1,2-propanediol + water and corresponding binary mixtures of 1,2-propanediol + water, 2-pyrrolidone + water and 2pyrrolidone + 1,2-propanediol over the whole composition range at 313.15 K. Partial molar volume and apparent molar volume of phenyl salicylate with protic solvents such as methanol, ethanol, 1- propanol, 2- propanol, 1-butanol and 2- butanol were evaluated by Muhammad JavedIqbal, Mansoora Ahmed Chaudhry [12] at different temperatures.

1) Dibutylamine(DBA) is used as a plasticizer in pvc materials. Polyurethane (PUR) Plastic, the production of pharmaceuticals. There are lots of applications as chemicals intermediates, e.g. corrosion inhibitors, food factory, emulsifiers, dyes, photographic chemicals, plasticizers, additives for fuels and lubricants, floatation agents, accelerators in the rubber chemical industry, catalysts, agricultural chemicals. Ethanol(C_2H_6O) is widely used in numerous industrial, they have lot of application paints printing inks.

III. Experimental Techniques

The ultrasonic velocity (c), density (ρ) and viscosity (η), have been measured in mixtures of DBA(Dibutylamine) and EAOH (Dibutylamine with Ethanol) at 303K of various mole fractions. Molar volume (v), adiabatic compressibility (k_s), inter molecular free length(L_f), excess intermolecular free length (ΔL_f), excess viscosity ($\Delta\eta$), excess molar volume (Δv) and excess adiabatic compressibility (Δk_s) were also calculated for mixture of various mole fractions (X_1 and X_2) of DBA and EAOH.

The ultrasonic velocity is determined with high degree of accuracy using simple and direct device Interferometer at 2MHz frequency and specially designed double walled quartz crystal were used for maintaining constant temperature.The principle used in this measurement is based on the determination of accurate great length in the medium. The density of liquid mixtures of chemical solutions were measured by using 10 ml of specific gravity bottle measured by using following the formulae with maximum possible percentage error in density is less than 1%:

$$\rho = \frac{\omega 2-\omega 1}{v} gm/cm^3 \qquad (1)$$

$$\rho = m/v$$

where, ω_1 is the empty bottle weight,

ω_2 is the binary mixture solution weight.

The viscosity liquid is measured by an Ostwald viscometer with using the relation is

$$\eta_2 = \eta_1\rho_2 t_2/\rho_1 t_1 \qquad (2)$$

A. **Theoretical Calculations**

The experimentally measured ultrasonic velocity (U) ,density (ρ) and viscosity (η) are used to compute parameters like adiabatic compressibility (k_s), molar volume (v), intermolecular free length (L_f), excess viscosity ($\Delta\eta$), excess compressibility (Δk_s), excess molar volume (Δv) and excess intermolecular free length (ΔL_f) by using following expressions discussion by Meshna& Rita (13) and Ali & Nain(14).

$$k_s = 1/\rho c^2 \qquad (3)$$

$$L_f = K\,(k_s)^{1/2} \qquad (4)$$

$$V_m = M_{eff}/\rho \qquad (5)$$

$$\Delta\eta = \eta_{(exp)} - \eta_{(ideal)} \qquad (6)$$

$$\Delta L_f = L_{f\,(exp)} - L_{f\,(ideal)} \qquad (7)$$

$$\Delta k_s = k_{s\,(exp)} - k_{s\,(ideal)} \qquad (8)$$

$$\Delta v = v_{(exp)} - v_{(ideal)} \qquad (9)$$

Where,

η (ideal) is ideal mixing viscosity.

L_f (ideal) is ideal mixing intermolecular free length.

k_s(ideal) is ideal mixing compressibility.

V (ideal) is ideal mixing molar volume.

$M_{eff}$is molecular weight.

K is the temperature dependent constant (Jacobson's constant).

IV. Results and Discussion

The ultrasonic velocity (U), density (ρ) and viscosity (η), have been measured in mixtures of DBA andEAOH at 303K. The values of ultrasonic velocity (U), density (ρ), viscosity (η), molar volume (v), adiabatic compressibility (k_s), inter molecular free length(L_f), for mixture of various mole fractions of DBA are presented in table-1. The table-2 shows the values of excess intermolecular free length (ΔL_f), excess viscosity ($\Delta\eta$), excess molar volume (Δv) and excess adiabatic compressibility (Δk_s).

Now the present investigations , it is observed that the ultrasonic velocity increases with mole fraction (proportionality relation) of DBA and ultrasonic velocity increases with decreasing mole fraction (Inverse proportionality relation) of indicates the intermolecular interaction exists in binary liquid mixture. Fig .1 shows the variation of ultrasonic velocity can be attributed to the molecular interaction through structural arrangement of molecules in liquid mixture. When system attains a closure packing one would expect the corresponding structural changes to result in a increased ultrasonic velocity.

TABLE 1. Values of mole fraction of DBA X_1, mole fraction of EAOH density (ρ), viscosity (Ƞ), velocity (U), compressibility (k), inter molecular free length (L_f), molar volume (V).

X_1	X_2	ρ (g/cm³)	η (mpas)	U (cm/s)	K (cm²/ dyne)	L_f (cm)	V (cm³)
0	1	0.7807	0.9942	113400	9.9607E-11	6.29759E-09	59.0090944
0.036766	0.963234	0.7812	1.056	115600	9.57904E-11	6.17576E-09	63.155072
0.079089	0.920911	0.7811	1.0965	117900	9.21013E-11	6.05567E-09	67.9276684
0.128331	0.871669	0.782	1.1165	119000	9.03024E-11	5.99624E-09	73.4805563
0.186341	0.813659	0.7812	1.1358	119800	8.91916E-11	5.95925E-09	80.0221312
0.255689	0.744311	0.7773	1.1153	120300	8.88956E-11	5.94935E-09	87.8422496
0.340059	0.659941	0.773	1.0823	120800	8.86516E-11	5.94118E-09	97.3563444
0.444924	0.555076	0.7685	1.0326	121300	8.84371E-11	5.93399E-09	109.18169
0.578787	0.421213	0.7641	0.9649	122000	8.79286E-11	5.9169E-09	124.276933
0.755604	0.244396	0.7589	0.8823	122500	8.78099E-11	5.91291E-09	144.215941
1	0	0.7524	0.7452	123400	8.72812E-11	5.89508E-09	171.775651

TABLE 2. Values of mole fraction of DBA (X_1), Mole fraction of EAOH(X_2), excess adiabatic compressibility (Δk), inter molecular excess free length (ΔL_f), excess molar volume (ΔV), excess viscosity (Δƞ)

X_1	X_2	ΔK *(Cm²/dyne)*	ΔLf Cm	ΔV Cm³	Δη m pas
0	1	0	0	0	0
0.036766	0.963234	-3.36341E-12	-1.07032E-10	-0.2692	0.070955
0.079089	0.920911	-6.53087E-12	-2.10087E-10	-0.527	0.121993
0.128331	0.871669	-7.72281E-12	-2.49698E-10	-0.9199	0.154254
0.186341	0.813659	-8.11856E-12	-2.63342E-10	-1.2108	0.187999
0.255689	0.744311	-7.55987E-12	-2.45329E-10	-1.2149	0.184767
0.340059	0.659941	-6.76389E-12	-2.1954E-10	-1.1688	0.172775
0.444924	0.555076	-5.68584E-12	-1.84525E-10	-1.0812	0.149186
0.578787	0.421213	-4.54439E-12	-1.47731E-10	-0.9824	0.114818
0.755604	0.244396	-2.48372E-12	-8.05607E-11	-0.6974	0.076245
1	0	0	0	0	0

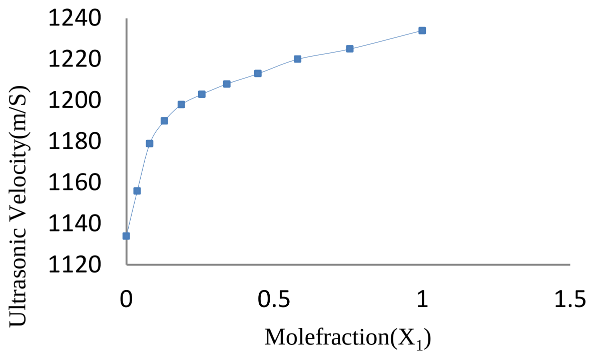

Figure 1:Variation of velocity with mole fraction of DBA

From the table.1 it is observed that the viscosity is increases with increasing mole fraction X_1=0.186341 for DAB and showing inverse relation i.e viscosity increases with decreasing mole fraction upto X_2=0.813659 for EAOH then decreases the viscosity with increasing X_1 and decreasing with X_2.The increasing and decreasing Viscosity explained on the basis of fluid resistance to flow to gradual deformation by shear stress. The high viscosity due to molecular make up gives the lot of internal friction. In case of decreases viscosity from mole fractions X_1=0.186341 and X_2=0.813659 due to molecules make up results in very little friction when it is in motion causes flow easily.Fig.2 shows the Non-linear plotted graph between mole fraction (X_1) on X-axis viscosity on Y-axis. From table- 2 the similar behavior can also seen in excess viscosity (Δη) which are all are positive values indicated strong intermolecular interactions.

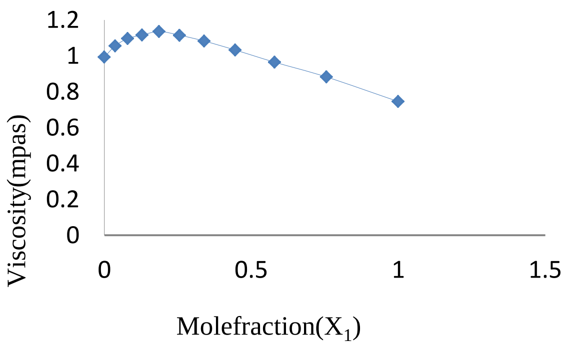

Figure2: Variation of viscosity with mole fraction of DBA

The molar volumes is studied that increases with mole fraction (X_1) shows proportionate relation and increases molar volume with decreasing mole fraction (X_2) which are tabulated in table-1. The molar volume of mole fraction X_1 increases with molar volume due to increasing molar mass converse to this molar fraction(X_2) decreases with increasing molar volume due to decreasing molar mass. Excess molar volume have been calculated from the density data .Excess molar volumes shows negative values except pure liquids . Excess molar volues decreases with increasing mole fraction(X_1) upto X_1=0.340059 then again increases with continuous increase of mole fraction(X_1). In case of mole fraction(X_2) is decreases with decreases excess molar volume uptoX_2= 0.659941 then increases with continuous decreases of molefraction (X_2). The negative values are accounted for by the effects of specific interaction and interstial accommodation. The increase and decreases excess molar values depend on density of molefractions.The variation of excess molar volume wit mole fraction(X_1) is plotted graph shows in fig.3.

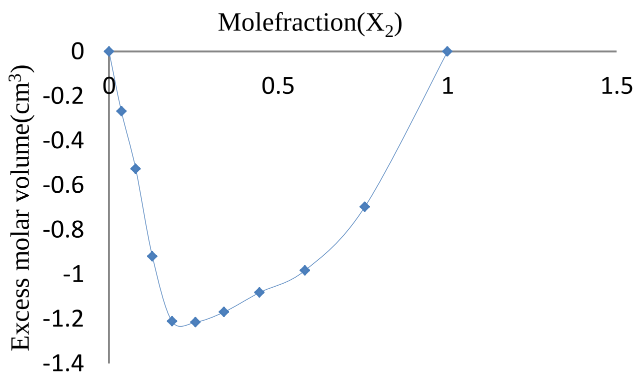

Figure 3: Variation of excess molar volume with mole fraction of DBA

Intermolecular free length (L_f) shows Inverse proportionate relation with mole fraction X_1 and proportionate relation with mole fraction X_2.This may be fact that depend on Intermolecular attraction. For mole fraction X_1, intermolecular free length decreases with increasing X_1 due to weak intermolecular attractions and strong intermolecular attractions for mole fraction X_2.From Table -2 excess intermolecular free length of mole fractions X_1 and X_2 shows negative values except pure liquids. For mole fraction X_1 it is observed that excess intermolecular free lengths are decreases with increasing molefraction(X_1) upto X_1=0.186341 then increases with continuous increases of mole fractions. Molefracrion X_2 decreases with decreasing excess intermolecular free length upto X_2=0.813659 then increases with continuous decreses of molefraction(X_2.).The negative values indicates sound wave has to travel a longer distance and the increasing and decreasing mole fraction with excess intermolecular free length depends on dominant nature of interactions between unlike molecules. The excess intermolecular free length versus molefraction graph can be shown in Fig.4 of all mole fraction(X_1). According to Jacobson [15] the adiabatic compressibility can be studied more through intermolecular free length. Increase in free length due to the process of mixing results in lowering of sound velocity. From table -1, compressibility is decreases with increasing molefraction (X_1) and decreases with molefraction (X_2). The variation of adiabatic compressibility (K) with mole fraction (X_1) of DBA is shown in fig.5.The decrease in adiabatic compressibility with increasing molefraction (X_1) and decreasing adiabatic compressibility with decreasing molefraction(X_2) depends on molecules closer and looses.

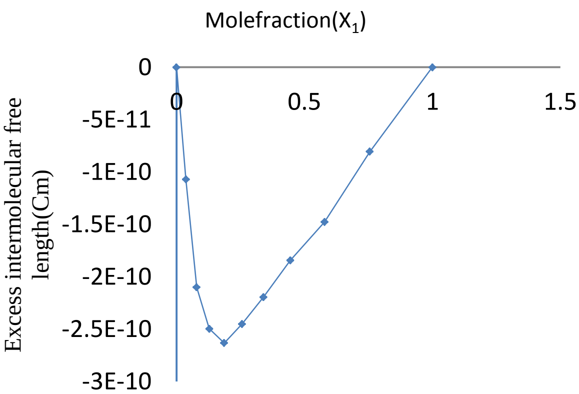

Figure 4:Variation of excess intermolecular free length with mole fraction of DBA

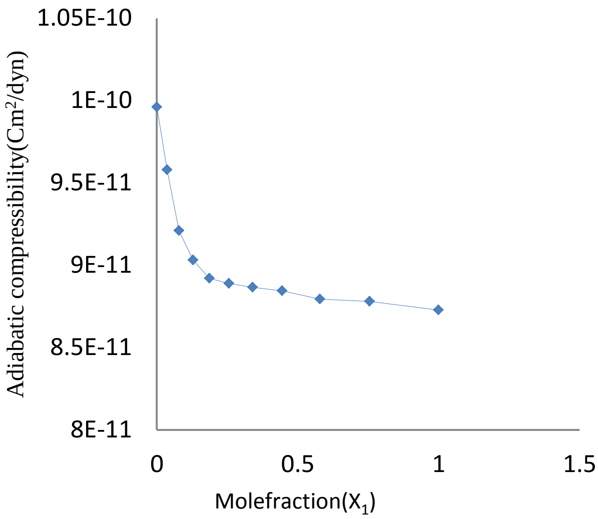

Figure 5:Variation of Adiabatic compressibility with mole fraction(X_2)

The execs adiabatic compressibility versus mole fraction of DBA is plotted and presented in fig. 6.From table-2 the excess adiabatic compressibility (ΔK) shows negative values which are decreases with increasing mole fraction (X_1) upto X_1=0.186341 then increases with continuous increases of molefraction(X_1) and decreases adiabatic compressibility with decreasing molefraction(X_2) upto X_2=0.813659 then increases with continuous decreases of molefraction(X_2). Adiabatic compressibility excess compressibility show that binary less compressible than in pure liquid. The adiabatic compressibility shows a reverse trend to that of ultrasonic indicates closure packing of component molecules which conforms the decrease in free length. The negative values of excess adiabatic compressibility , excess molar volume , excess inter molecular length and positive values of excess viscosity conform the existence of inter molecular association between the component molecules. The negative excess adiabatic compressibility indicates less compressibility.

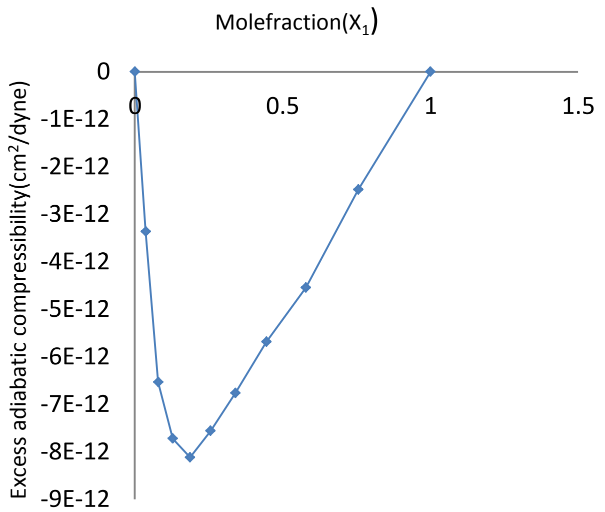

Figure 6:Variation of excess adiabatic compressibility with mole fraction of DBA

Nikos G. Tsierkezos and IoannaMolinou [16] provided information on the molecular interactions between the unlike molecules that take place at the surface and the bulk by calculating deviations in speed of sound of binary mixtures of methyl salicylate with 1-pentanol over the entire composition range at 303.15 K. The specific interactions appear to be significant at the equimolar composition and weaken with the rise of the temperature. Shengying Li et.al [17] determined excess molar enthalpies of six binary systems for acetophenone + (1-butanol, + 2-methyl-1-propanol, + 1-pentanol, + n-heptane, + cyclohexane, and + water) at T = 298.2 and 313.2 K.The experimental data of excess molar enthalpies increase with an increase in the temperature, carbon number, and branch of alcohols. It may due to fact that the increasing difficulty to form crossed associations between acetophenone and alcohols with increasing steric hindrance and aliphatic chain of alkanol. A.C. Galvão and A.Z. Francesconi [18] reports positive values of excess molar enthalpy for acetonitrile + 1-pentanol and acetonitrile + 1-hexanol mixtures and they also increase with alkanol chain length.

V. CONCLUSION

Ultrasonic Velocity increases with increasing molefraction DBA(X_1) and with decreasing molefraction (X_2) of EOAH explained on the basis of structural arrangements of molecules and showing proportionate and inverse proportionate relations with mole fractions.Viscicity of two liquids (X_1&X_2) are initially increases then decreases with increasing and decreasing of mole fractions due to fluid resistance to flow to gradual deformation by shear stress and high viscosity at particular concentration due to high internal friction.Density follows the similar behavior and high density at concentration depends on molar volume. Decreases adiabatic compressibility with decreasing and increasing molefraction explained on the basis of molecules closer and looses. Intermolecular free length with molefractions shows proportion and inverse proportion relation due to intermolecular attraction. Molar volume increases with increasing molefraction and with decreasing molefraction due to mole and density of the samples. The excess parameters except pure liquids some are showing negative values which are excess adiabatic compressibility, excess intermolecular free length,excess molar values are shows similar trend. Excess viscosity gives positive values indicates strong intermolecular interactions.The negative values of excess adiabatic compressibility , excess molar volume , excess inter molecular length and positive values of excess viscosity conform the existence of inter molecular association between the component molecules.

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