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Ultrasonic Studies of Molecular Interactions of 1,4 Diazabicyclo 2,2,2- Octane in Different Solvents at 303 K

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ABSTRACT

The ultrasonic velocity, density and viscosity have been measured for 1,4 Diazabicyclo-2,2,2-Octane with different solvents at 303 K for a constant frequency of 2 MHz. Acoustic parameters like adiabatic compressibility, molar volume, intermolecular free length, acoustical impedance, free volume, relaxation time, Gibb's free energy and cohesive energy for the solution have been computed. The results have been analyzed and interpreted in terms of molecular interaction between solute and solvent.

Keywords :

Ultrasonic studies are highly sensitive to molecular interaction in liquid mixtures (Anwar Ali et. al.,2004; Aralaguppi and Barragi, 2006). This helps in better understanding the nature of solute–solvent interactions. The solution properties of liquid mixtures consisting of polar and nonpolar components find applications in industrial and technological process (Krishnamurthi and Thenmozhi, 2012). The present study is focused on ultrasonic studies of one of the amine components, 1, 4 Diazabicyclo 2,2,2- Octane. Generally amines have solubility that are independent of polar and nonpolar solvents and these are readily suitable to explore solute-solvent interaction.

Several researchers have worked on 1, 4 Diazabicyclo 2,2,2- Octane (Zi-Rong Zheng et al., 2000; Gerhard Laus et. al., 2008; Gerhard Laus et. al., 2012). It is widely used as, catalyst, complexing ligand (Gerhard Laus et. al., 2012), undergoes charge transfer interaction with bromine, carbontetrabromide (Gerhard Laus et. al., 2008) numerous crystal structures of its salt and as coordination compounds (Gerhard Laus et al., 2008; Laus et. al., 2011). It is found that no reports has been made on ultrasonic investigation of 1,4 Diazabicyclo 2,2,2- Octane (DABCO) in different solvents.

Hence an attempt is made to investigate the ultrasonic studies of DABCO in different solvents, such as Water, DMF, Acetonitrile, Acetone, and Methanol is discussed. For the better understanding of the molecular interaction between the components of mixture, ultrasonic velocities together with density and viscosity have been measured. The trends of variation of the acoustic parameters such as velocity, adiabatic compressibility, molar volume, free volume, viscous relaxation time, acoustic impedance, internal pressure, Gibb's free energy, intermolecular free length and cohesive energy are presented in the paper.

MATERIALS AND METHOD

1,4 Diazabicylo 2,2,2 Octane (DABCO) 98% is purchased from OTTO kemi, Mumbai. The solvents were analytical grade reagent (AR) procured from Fischer Scientific, Mumbai, India. The density of the solution systems was determined using a 10 ml specific gravity bottle. The viscosity of the solution systems were measured using Ostwald's viscometer with an accuracy of $\pm 0.0001 Nsm^2$. The velocity of ultrasonic wave has been measured using Ultrasonic Interferometer at the frequency of 2 MHz supplied by PICO (Model BL-02), Chennai. The acoustic and thermodynamical parameters were calculated from the following equations.

Adiabatic compressibility (β), $\beta = 1 / U^2\rho$

Intermolecular free length (L_f), $L_f = K\beta^{1/2}$

Where, K is the Jacobson temperature dependent constant (4.281×10^9)

Free volume (V_f) $V_f = (M_{eff}U/K\eta)^{3/2}$

Where, M_{eff} is the effective mass of the solution system.

Molar volume (V_m) $V_m = (M_1f_1 + M_2f_2) / \rho_{12}$

Where, M_1 is the molecular weight of solute, M_2 is the molecular weight of solvent, f_1 is the mole fraction of solute, f_2 is the mole fraction of solvent, ρ_{12} is the density of the solution system.

Internal pressure (π_i) $\pi_i = bRT (K\eta/U)^{1/2} (\rho^{2/3}/M^{7/6})$

Where, b stands for cubic packing, which is assumed to be 2 for all the liquids, T is the absolute temperature in Kelvin, R is the universal gas constant.

Relaxation time (τ), $\tau = 4/3(\beta\eta)$

Acoustic impedance (Z) $Z = U.\rho$

Gibb's free energy (ΔG) $\Delta G = kT Ln (kT \tau/h)$

Where, k is the Boltzmann constant, h is the Plank's constant

Cohesive energy (CE) $CE = V_f \cdot \pi_i$

Results and Discussion

Table 1 shows the experimental data of velocity (U), viscosity (η) and the density (ρ) of DABCO in different solvents at 303 K. It is observed that density decreases with decreasing polarity of solvents, thus decreases the viscosity and velocity. This is further supported by the adiabatic compressibility, free volume and free length. The increase in compressibility, free length and free volume with decrease in velocity indicates that DABCO and polar protic solvents posses strong molecular interactions.

According to Erying and Kincaid (1938) the ultrasonic velocity should increase if the intermolecular free length decreases and vice versa. Infact the molecular association in the DABCO solution systems which is presented in table 2, shows that ultrasonic velocity and acoustic impedance increases with decrease in intermolecular free length and adiabatic compressibility in order of increasing polarity of solution system. The decrease in the value of intermolecular free length with increase in ultrasonic velocity further strengthens the strong molecular association between unlike molecules through hydrogen bonding. Thus it is evident from the table 2, that DABCO water solution system is found to have strong molecular association.

Table 1. Values of density, viscosity and velocity of DABCO solution system at 303K

Solute	Solvent (polarity)	Solution system ($f_1 + f_2$)	Density (r) Kgm^{-3}	Viscosity (Π) Nsm^{-2}	Velocity (U) ms^{-1}
DABCO	Water (9)	DABCO +Water (0.00407 + 0.9959)	1152.4	0.001	1520
	DMF (6.4)	DABCO+DMF (0.013043 +0.9869)	1084	0.00095	1489
	Acetonitrile (5.8)	DABCO+Acetonitrile (0.00925 + 0.9907)	888.8	0.000407	1221
	Acetone (5.1)	DABCO+Acetone (0.01965 +0.9803)	915	0.00046	1139
	Methanol (5.1)	DABCO+Methanol (0.00723 +0.9927)	919.4	0.0007	1107

Table 2. Values of adiabatic compressibility, molar volume, intermolecular free length, free volume and acoustic impedance of DABCO solution system at 303K

Solution system	Adiabatic Compressibility (b $x10^{-11} N^{-1}m^2$)	Molar Volume (Vm m^3mol^{-1})	Inter molecular Free Length ($L_f x10^{-10}$ m)	Free Volume ($V_f x10^{-7} m^3mol^{-1}$)	Acoustic Impedance (Z $x10^6$ kgm^2s^{-1})
DABCO + WATER	43.28	0.0159	0.415	2.6172	1.7516
DABCO+ DMF	41.578	0.068	0.404	2.491	1.614
DABCO+ ACETONITRILE	75.4	0.0458	0.5479	4.915	1.085
DADCO+ ACETONE	84.12	0.0642	0.578	3.853	1.0428
DABCO+ METHANOL	89.73	0.03548	0.597	1.979	1.0178

The acoustic impedance increases with an increase in the polarity of the solution system. This indicates that there is a possibility of strong interaction between the components of the mixture. It is also significant that there is more strong interaction for DABCO water solution system.

Free volume for the molecules of liquid are not closely packed to each other there is always a free space between them, moreover it is an inverse function of internal pressure. In table 2, It is observed that free volume increases or decreases with increasing polarity of solution system. This decrease in volume can be attributed to close association between DABCO and protic solution molecules. Thus, it is concluded that there exist solute solvent interactions.

From the table 2, it has been revealed that the molar volume has been increased with respect to the size of the solvent molecules.

Table 3. Values of Gibb's free energy, internal pressure, relaxation time and cohesive energy of DABCO solution system at 303K

Solution system	Gibbs Free Energy (ΔG $x10^{-20}$ K J mol^{-1})	Internal Pressure (p_i $x10^6$ Pa)	Relaxation Time (t x 10^{-12}s)	Cohesive Energy (kJ/mol)
DABCO + WATER	0.54114	978.75	0.57706	15.56213
DABCO+ DMF	0.49636	182.912	0.5193	12.43802
DABCO+ ACETONITRILE	0.38944	231.295	0.4021	10.59331
DADCO+ ACETONE	0.4936	169.24	0.5159	10.86521
DABCO+ METHANOL	0.69614	422.61	0.8374	14.9942

Internal pressure provides an excellent basis for examining the solution phenomena and studying the various properties of liquid state. It is the measure of cohesive or binding force between the solute and solvent interaction. It is found that internal pressure is more for solution system consisting of polar protic solvents. This is due to existence of the strong binding force between the solute and solvent for a protic solution system.

The values of relaxation time are given in table 3. The relaxation time is in the order of 10^{-12} sec is due to structural relaxation process (Kinser and Fray,1989) and the molecule get rearranged due to cooperative process (Ali Hyder and Nain 2000). The relaxation time is comparatively more for DABCO methanol solution system because of less free volume. Hence it takes longer time to appear as translational energy from excitational energy. Gibbs free energy confirms the relaxation time from the measured value given in table 3. This indicates the need for longer time for the rearrangement of molecules in mixture.

The experimental values yielded clearly that the intermolecular interactions are strong between DABCO and protic solution system.

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