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Interaction between Solvent-Solvent Molecules in A Tertiary Mixture at Different Temperatures by Ultrasonic Technique

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ABSTRACT - The basic parameters like viscosity (η), density(ρ) and velocity (U) have been measured for tertiary liquid mixture by ultrasonic Interferometer. From these three parameters various thermodynamical and acoustical parameters such as specific acoustic impedance (Z), Intermolecular free length (L_f), adiabatic compressibility 's (β) etc can be estimated using standard relations from measured values of Ultrasonic viscosities, densities and viscosities in the wide range of concentrations at 35^0 C, 40^{0}C and 45^{0}C temperatures for Aniline + Propanol-2 +Toluene tertiary system. The solvent-solvent interactions are studied on the basis of increase or decrease in ultrasonic velocity, density, viscosity and other derived acoustical parameters in terms of structure making and structure breaking tendencies of various solvent molecules.

***Keywords*: density, ultrasonic interferometer, ultrasonic velocity, viscosity, water bath, picnometer.**

I. INTRODUCTION

The study of molecular interactions in the liquid mixtures is of considerable importance in the elucidation of the structural properties of the molecules. Lagemann and Dunbar [4] were the first to point out the sound velocity approach for qualitative determination of the degree of association in liquids. Recent developments have made it possible to use ultrasonic energy in medicine, engineering, agriculture and other industrial applications.[5,6] .Ozawa and Minamisawa [7] have observed concentration of ultrasonic velocity invariant with respect to temperature in alcohol-water mixtures. Hanel[8] has measured sound velocity and thickness of thin samples by time –resolved acoustic microscopy. Bae and Yun [9] have studied the ultrasonic velocity in binary solutions of silicon dioxide and water. Knowledge of thermodynamic and acoustical properties is of great importance in studying the physio-chemical behavior and molecular interactions in a variety of liquid mixtures(1,3). The compositional dependence of thermodynamic properties has proved to be a very useful tool in understanding the nature and extent of pattern of molecular aggregation resulting from intermolecular interaction between components. In the present, work, ultrasonic techniques have been employed for the evaluation of the molecular interaction in the tertiary mixtures containing aniline, propanol-2 and toluene at 308 K.

II. EXPERIMENTAL DETAILS

Ultrasonic velocity for the mixture was measured using the ultrasonic interferometer (Model M 81) supplied by Mittal Enterprises, New Delhi, that has a reproducibility of ± 0.4 m/s at 25^0 C with a fixed frequency of 3 MHz. The temperature was maintained constant by circulating water from a thermodynamically controlled water bath (accuracy ±0.1 ^{0} C). The temperature of the cell as measured using a thermocouple was found to accurate to ± 0.25 ^{0} C. The density of the mixtures has been measured using a sensitive pycnometer with an accuracy of 0.5 kg/m^3. Chemicals used in this study are ultra pure ,supplied by Sigma-Aldrich Ltd and used without purification. Tertiary system is studied at different temperatures, 35^0 C, 40^{0}C and 45^{0}C with different concentrations of the system .Especially for this system ultrasonic velocities, densities and viscosities of the mixtures have been measured at different temperatures.

III. THEORY

Other acoustical parameters such as adiabatic compressibility ((β),Intermolecular free length (L_f) ,Molar Sound velocity(R), Specific acoustic impedance (Z) etc can also be determined.

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

Adiabatic compressibility (β)= $\frac{1}{U^2\rho}$ (2)

Where k values for different temperatures were taken from the work of Jacobson[29]; at 35,40 and 45^o C the K values are 637, 642 ,647 respectively.

Molar sound velocity (R) $=U^{1/3}V$ (3)

Molar compressibility(B) = $\left(\frac{M}{\rho}\right)\beta^{-1/7}$ (4)

where V and M are the molar volume and molecular weight of the mixtures, respectively.

Specific acoustic impedance (Z) $=\rho U$ (5)

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The excess adiabatic compressibility (β^E) and excess intermolecular free length (L_f^E) are evaluated by the following expression

$$B^E = \beta_{exp} - \beta_{ideal} \quad (6)$$

$$(L_f^E) = L_{f.exp} - L_{f.ideal} \quad (7)$$

For β_{ideal} and $L_{f.ideal}$, the densities and the ultrasonic velocities of various components in pure state at the three given temperatures have been measured. Further, the velocities of both the systems at different concentrations and temperatures have been evaluated theoretically using volume additive rule[21] as :

$$U_{ideal} = U_1\emptyset_1 + U_2\emptyset_2 + U_3\emptyset_3 \quad (8)$$

Where $U_1, U_2,$ and U_3 are the velocities of the three components of the ternary liquid mixture in pure state and $\emptyset_1$,$\emptyset_2$ and $\emptyset_3$ are their volume fractions .

Similarly, ideal density is evaluated using :

$$P_{ideal} = \rho_1 \emptyset_1 + \rho_2 \emptyset_2 + \rho_3 \emptyset_3 \quad (9)$$

Finally β_{ideal} and $L_{f.ideal}$ are evaluated using following equations :

$$\beta_{ideal} = \frac{1}{U^2_{ideal.}\ \rho_{ideal}} \quad (10)$$

and

$$L_{f.ideal} = K\beta^{1/2}_{ideal} \quad (11)$$

Table 1 Conversion of CGS units to SI units.

No	Parameter	CGS units	SI units
1	Ultrasonic velocity (U)	1 cms^{-1}	$10^{-2} ms^{-1}$
2	Density (ρ)	1 g cm^{-3}	10^3 Kg m^{-3}
3	Adiabatic compressibility (β)	1dyn^{-1} cm^2	10 $N^{-1}m^2$
4	Intermolecular free length(L_f)	1A°	10^{-10} m
5	Molar sound velocity (R)	1 cm^3 mol^{-1} $(cm\ s^{-1})^{1/3}$	$10^{-20/3}$ m^3 mol^{-1} $(ms^{-1})^{1/3}$
7	Molar compressibility (B)	1 cm^3 mol^{-1} $(dyn^{-1}\ cm^2)^{-1/7}$	$10^{-43/7}$ m^3 mol^{-1} $(N^{-1}m^2)^{-1/7}$
8	Wave number (λ)	1 cm^{-1}	10 m^{-1}

Table 2- Standard values of dipole Moment(D),density(ρ), ultrasonic Velocity(U),viscosity (η),Isothermal compressibility(βT),Thermal expansibility(α),and specific heat capacity(CP)at constant pressure of the experimental liquids at 303 K

Liquid	D	ρ kgm^{-3}	U ms-1	$\eta \times 10^3$ Nsm^{-2}	$B_T \times 10^{12}$ Pa^{-1}	$\alpha \times 10^3$ K^{-1}	CP $kJkg^{-1}$ K^{-1}
Aniline	**1.13**	**1010.9**	**1640**	**3.036**	**453**	**0. 81**	**2.167**
Toluene	**0.37**	**857.8**	**1287.2**	**0.526**	**681.7**	**1.07**	**1.70**

Table 3 Ultrasonic velocity, Density and viscosity of Tertiary mixture at different temperatures

Temp	Mole Fraction (Aniline) X_1	(Propanol-2) X_2	(Toluene) X_3	Ultrasonic velocity(U) ms^{-1}	Density (ρ) Kgm^{-3}	Viscosity (η) $NSec^{-2}$
35 ⁰ C	**0.8000**	**0.000**	**0.2000**	**1331.1**	**857**	**0.711**
	0.8100	**0.001**	**0.1800**	**1350.7**	**865**	**0.740**
	0.8200	**0.002**	**0.1400**	**1358.9**	**871**	**0.768**
	0.8300	**0.003**	**0.1200**	**1374.0**	**871**	**0.783**
	0.8400	**0.004**	**0.1000**	**1390.6**	**879**	**0.794**
	0.8500	**0.005**	**0.0800**	**1404.5**	**886**	**0.802**
	0.8600	**0.006**	**0.0650**	**1406.6**	**894**	**0.809**
	0.8700	**0.007**	**0.0500**	**1477.4**	**898**	**0.840**
	0.8800	**0.008**	**0.0112**	**1493.2**	**901**	**0.844**
	0.8900	**0.009**	**0.0120**	**1498.7**	**902**	**0.849**
40⁰ C	**0.8000**	**0.000**	**0.2000**	**1492.3**	**903**	**0.853**
	0.8100	**0.001**	**0.1800**	**1495.6**	**908**	**0.857**
	0.8200	**0.002**	**0.1400**	**1498.6**	**912**	**0.860**
	0.8300	**0.003**	**0.1200**	**1501.4**	**914**	**0.864**
	0.8400	**0.004**	**0.1000**	**1506.7**	**918**	**0.867**
	0.8500	**0.005**	**0.0800**	**1511.2**	**916**	**0.870**
	0.8600	**0.006**	**0.0650**	**1545.0**	**919**	**0.873**
	0.8700	**0.007**	**0.0500**	**1548.8**	**921**	**0.875**
	0.8800	**0.008**	**0.0112**	**1549.0**	**925**	**0.878**
	0.8900	**0.009**	**0.0120**	**1561.2**	**927**	**0.878**
45⁰ C	**0.8000**	**0.000**	**0.2000**	**1571.3**	**938**	**0.884**

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	0.8100	0.001	0.1800	1574.3	942	0.891
	0.8200	0.002	0.1400	1578.1	943	0.895
	0.8300	0.003	0.1200	1582.0	945	0.897
	0.8400	0.004	0.1000	1584.3	946	0.902
	0.8500	0.005	0.0800	1589.0	949	0.906
	0.8600	0.006	0.0650	1590.1	953	0.907
	0.8700	0.007	0.0500	1596.7	958	0.910
	0.8800	0.008	0.0112	1599.6	964	0.916
	0.8900	0.009	0.0120	1604.1	967	0.921

Table 4 Acoustic Impendence(Z), Adiabatic Compressibility(β) & Intermolecular free length (L_f)

Temp	Mole Fraction (Aniline) X_1	(Propanol-2) X_2	(Toluene) X_3	Acoustic Impendence (Z) $/10^6$ $Kgm^{-2}S^{-1}$	Adiabatic Compressibility (β) $/10^{-10}$ $Kg^{-1}ms^2$	Intermolecular free length (L_f) $/10^{-11}$ m
35 ^{0} C	0.8000	0.000	0.2000	1.1420	6.5658	5.618
	0.8100	0.001	0.1800	1.1683	6.3367	5.1692
	0.8200	0.002	0.1400	1.1836	6.2173	5.1203
	0.8300	0.003	0.1200	1.2077	6.0261	5.0409
	0.8400	0.004	0.1000	1.2320	5.8366	4.9610
	0.8500	0.005	0.0800	1.2556	5.6704	4.8899
	0.8600	0.006	0.0650	1.2631	5.6283	4.8717
	0.8700	0.007	0.0500	1.3311	5.0848	4.6305
	0.8800	0.008	0.0112	1.3468	4.9723	4.5790
	0.8900	0.009	0.0120	1.3518	4.9358	4.5622
40^0 C						
	0.8000	0.000	0.2000	1.3475	3.1702	3.6562
	0.8100	0.001	0.1800	1.3580	3.6818	3.9402
	0.8200	0.002	0.1400	1.3667	3.6583	3.9276
	0.8300	0.003	0.1200	1.3722	3.6430	3.9194
	0.8400	0.004	0.1000	1.3831	3.6432	3.9195
	0.8500	0.005	0.0800	1.3842	3.6148	3.9042
	0.8600	0.006	0.0650	1.4198	3.6124	3.9029
	0.8700	0.007	0.0500	1.4264	3.5215	3.8535
	0.8800	0.008	0.0112	1.4328	3.5052	3.8445
	0.8900	0.009	0.0120	1.4472	3.4890	3.8357
45^0 C						
	0.8000	0.000	0.2000	1.4738	3.3924	3.7822
	0.8100	0.001	0.1800	1.4829	3.3710	3.7702
	0.8200	0.002	0.1400	1.4881	3.3597	3.7506
	0.8300	0.003	0.1200	1.4949	3.4450	3.8114
	0.8400	0.004	0.1000	1.4987	3.5746	3.8114
	0.8500	0.005	0.0800	1.5079	3.3156	3.8815
	0.8600	0.006	0.0650	1.5153	3.2938	3.7391
	0.8700	0.007	0.0500	1.5296	3.2687	3.7268
	0.8800	0.008	0.0112	1.5420	3.2427	3.7126
	0.8900	0.009	0.0120	1.5511	3.1625	3.6978

IV. RESULTS

Ultrasonic velocity, density and viscosity for the tertiary system, Aniline + Propanol-2 +Toluene have been listed in table 2 & acoustic Impendence(Z), adiabatic Compressibility(β) & Intermolecular free length (L_f) for the same tertiary system have been listed in table 3 .The appropriate conversion of CGS units to SI units have been provided in Table 1 .

V. CONCLUSION

Aniline is an organic chemical compound specifically a primary aromatic amine. It consists of benzene ring attached to an amino group. Aniline is oily and slowly oxidized and resinified in air to form impurities which can give it a red brown tint. Its boiling point is 184 degree centigrade and its melting point is -6 degree centigrade. It is a liquid at room temperature. Like most volatile amines it possesses somewhat unpleasant odor of rotten fish and also has a burning aromatic taste. It is seen from that at 35^0 C,40^{o}C and 45^{o}C ultrasonic velocity (U) increases with increasing concentration . The non- linear variation of ultrasonic velocity with concentration indicates occurrence of complex formation between unlike molecules. The molecular association becomes maximum at those concentrations where velocity maxima occurs. This may be interpreted due to the formation of strong hydrogen bonding resulting into complex formation producing displacement of electrons and nuclei. The chemical interaction may involve the association due to hydrogen bonding, due to dipole –dipole interaction or due to the formation of charge transfer complexes. All these processes may lead to strong interaction of forces.(fort and Moore,1965). Aniline and Propanol-2 involves in strong attraction due to their polar nature. Toluene is unsaturated but behaves like a saturated compound .In the presence of Toluene molecules as electron donor will have higher stability to the carbocation of Propanol-2 and hence toluene can not provide strong interaction. Aniline is having higher dielectric constant(6.8012) and toluene (2.362) is found to

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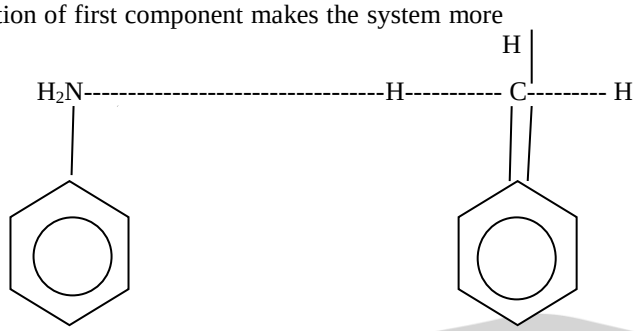
be stronger. When aniline is added with toluene the interaction exists between the lone pair of electrons on nitrogen and H^+ of the hyper conjugative structure of toluene. The probable interaction structure of aniline and toluene is depicted below. The density and viscosity of the tertiary solution increases with increases in concentration of the aniline which is due to the dipole –induced dipole interactions existing between the lone pair of electrons of nitrogen and H^+ of the hyper conjugative structures of toluene. Table 2 indicates that the ultrasound velocity ,density and viscosity increases with the mole fraction of first component. The increasing trend of the density shows that the addition of first component makes the system more compact. As toluene molecules are heavier than alcohol sound velocity and density increases with increase in mole fraction of toluene. Aniline and Toluene being aromatic behaves as electron donors but in ternary system aniline behaves as electron donor. It supports the dominating dipole or induced dipole type interactions of aniline with toluene rather than the inherent dispersive type of toluene in the ternary system. Table 3 indicates that alike ultrasound velocity ,density and viscosity the specific acoustic Impendence ,adiabatic compressibility and Intermolecular free length increases with the mole fraction of first component.



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