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STUDY OF SOLVENT-SOLVENT INTERACTION IN A AQUEOUS MEDIUM AT DIFFERENT TEMPERATURES BY ULTRASONIC TECHNIQUE

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ABSTRACT

The basic parameters like viscosity (η), density(ρ) and velocity (U) can be measured 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 n estimated using standard relations from measured values of Ultrasonic viscosities, densities and velocities in the wide range of concentrations at 35^0 C, 40^0C and 45^0C temperatures for Acetone + Propanol-2 +chloroform 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

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.

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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 bycirculating 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, 40^0C and 45^0C 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.

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

$$\text{Adiabatic compressibility } (\beta) = \frac{1}{U^2\rho} \quad (2)$$

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.

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

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

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

$$\text{Specific acoustic impedance } (Z) = \rho U \quad (5)$$

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

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

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

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 .

Simillarly ideal density is evaluated using :

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

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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^o	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

Temp	Mole fraction			Ultrasonic	Density(ρ)	Viscosity (η)
Velocity(U)	X_1	X_2	X_3	m/sec	gm/cm^3	Centipoise
35 ^{0} C						
	0.09578	0.06893	0.83527	991	1.3692	0.5870
	0.07108	0.10232	0.82659	995	1.3419	0.5608
	0.0709	0.1530	0.77601	997	1.3119	0.5422
	0.07054	0.20823	0.72145	998	1.2799	0.5337
	0.07031	0.25386	0.67558	999	1.2517	0.5314
	0.07025	0.30837	0.62575	995	1.2032	0.5234
	0.07019	0.35363	0.57517	993	1.1672	0.5189

0.07001	0.40314	0.52683	991	1.1316	0.5180
0.06984	0.45240	0.47777	990	1.1014	0.5001
0.06966	0.50142	0.4291	975	1.1075	0.4992

40^0 C

0.09578	0.06893	0.83527	965	1.3493	0.5495
0.07108	0.10232	0.82659	970	1.3286	0.5415
0.0709	0.1530	0.77601	974	1.3000	0.5315
0.07054	0.20823	0.72145	976	1.2631	0.5328
0.07031	0.25386	0.67558	982	1.2358	0.5214
0.07025	0.30837	0.62575	979	1.1879	0.5210
0.07019	0.35363	0.57517	975	1.1615	0.5200
0.07001	0.40314	0.52683	971	1.1233	0.5199
0.06984	0.45240	0.47777	969	1.0944	0.5010
0.06966	0.50142	0.4291	965	1.0651	0.4984

45^0 C

0.09578	0.06893	0.83527	997	1.3434	0.5272
0.07108	0.10232	0.82659	1120	1.3235	0.5130
0.0709	0.1530	0.77601	1016	1.2906	0.5125
0.07054	0.20823	0.72145	1028	1.2561	0.5210
0.07031	0.25386	0.67558	981	1.2323	0.5208
0.07025	0.30837	0.62575	978	1.1705	0.5200
0.07019	0.35363	0.57517	977	1.1584	0.5198
0.07001	0.40314	0.52683	972	1.1158	0.5150

0.06984	0.45240	0.47777	969	1.0902	0.5130
0.6966	0.50142	0.4291 3	963	1.0614	0.5058

IV RESULTS

Ultrasonic velocity, density and viscosity for the acetone-propanol-2 and chloroform have been listed in table 2.The appropriate conversion of CGS units to SI units have been provided in Table 1 .

V CONCLUSION

It is seen from that at 35^0 C ultrasonic velocity (U) increases with increasing concentration attains a maximum value at 0.0703 mole fractions. 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).

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