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Study of solvent-solvent interaction in tertiary mixture 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 viscosity (η), density(ρ) and velocity (U), thermodynamical and acoustical parameters.

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 [1] 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.

METHODOLOGY

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 Type equation here.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 ultrapure, 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 these system ultrasonic velocities, densities and viscosities of the mixtures have been measured at different temperatures.

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)

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

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

$(L_f^E)= L_{f.exp}-L_{f.ideal}$ (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 :

$U_{ideal} = U_1\emptyset_1 + U_2\emptyset_2 + U_3\emptyset_3$ (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 :

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

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

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

and

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

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.

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} $(ms^{-1})^{1/3}$
6	Molar compressibility (B)	1 cm^{3} mol^{-1} $(dyn^{-1}\ cm^{2})^{-1/7}$	$10^{-43/7}$ m^{3} mol^{-1} $(N^{-1}m^{2})^{-1/7}$
7	Wave number (λ)	1 cm^{-1}	10 m^{-1}

Table 2:

Temp	Mole fraction			Ultrasonic Velocity(U)	Density(ρ)	Viscosity (η)
	X_1	X_2	X_3	m/sec	gm/cm^3	Centipoise
35 ^{0} C	0.02792	0.03271	0.6251	875	1.4841	0.4920
	0.2790	0.03891	0.6248	878	1.4790	0.4917
	0.02787	0.03893	0.6241	879	1.4732	0.4913
	0.02783	0.03897	0.6238	882	1.4714	0.4911
	0.02771	0.03901	0.6238	883	1.4652	0.4909
	0.02767	0.03904	0.6235	895	1.4648	0.4899
	0.02760	0.03910	0.6234	892	1.4635	0.4892
	0.02756	0.03915	0.6231	890	1.4623	0.4889
	0.02751	0.03918	0.6229	886	1.4600	0.4885
	0.02699	0.03922	0.6222	884	1.4591	0.4880
40^0 C						
	0.02792	0.03271	0.6251	881	1.321	0.4820
	0.02790	0.03891	0.6248	883	1.319	0.4817
	0.02787	0.03893	0.6241	885	1.316	0.4815
	0.02783	0.03897	0.6238	892	1.316	0.4810
	0.02771	0.03901	0.6238	895	1.314	0.4804
	0.02767	0.03904	0.6235	898	1.310	0.4804
	0.02760	0.03910	0.6234	887	1.308	0.802
	0.02751	0.03918	0.6229	882	1.305	0.4795
	0.02751	0.03918	0.6229	879	1.301	0.4794
45^0 C						
	0.02699	0.03922	0.6222	864	1.299	0.4794
	0.02792	0.03271	0.6251	862	1.317	0.4654
	0.02790	0.03891	0.6248	866	1.315	0.4651
	0.02787	0.03893	0.6241	867	1.311	0.4648
	0.02783	0.03897	0.6238	870	1.309	0.4641
	0.02771	0.03901	0.6238	877	1.307	0.4638
	0.02767	0.03904	0.6235	890	1.707	0.4621
	0.02760	0.03910	0.6234	888	1.307	0.4617
	0.02751	0.03918	0.6229	865	1.301	0.4610
	0.02751	0.03918	0.6229	863	1.298	0.4602
	0.02699	0.03922	0.6222	840	1.295	0.4599

DISCUSSION

It is seen from that at 35^0 C ultrasonic velocity (U) increases with increasing concentration attains a maximum value at 0.03904 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). With increase of concentration of solution, the density and viscosity of the mixture decreases.

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