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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) can be measured by ultrasonic Interferometer. From these three parameters various thermodynamical and acoustical parameters such as specific acoustic impedance (Z), Intermolecular free length (Lf), adiabatic compressibility 's (β) etc can be estimated using standard relations from measured values of Ultrasonic viscosities, densities and velocities in the wide range of concentrations at 350 C, 400C and 450C 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.

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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 (Lagemann, 1995) 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 (Hanel, 1985 and Bae, 1998). Ozawa and Minamisawa (Rastogi, 2003) have observed concentration of ultrasonic velocity invariant with respect to temperature in alcohol-water mixtures. Hanel (Rastogi, 1999) has measured sound velocity and thickness of thin samples by time –resolved acoustic microscopy. Bae and Yun (Khasare, 1987) 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 (Lagemann, 1995 and Blokhra, 1991).

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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.

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 is 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.

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

Temp	Mole Fraction (Acetone) X_1	(Propanol) X_2	(Chloroform) X_3	Ultrasonic velocity m/sec	Density(ρ) gm/cm^3	Viscosity (η) centipoise
35 ^{0} C	0.2432	0.06832	0.7892	845	1.2700	0.4982
	0.2431	0.06834	0.7894	847	1.2692	0.4979
	0.2429	0.06836	0.7895	849	1.2689	0.4971
	0.2427	0.06839	0.7896	849	1.2688	0.4969
	0.2425	0.06842	0.7898	852	1.2682	0.4965
	0.2421	0.06845	0.7900	854	1.2580	0.4964
	0.2418	0.06847	0.7904	851	1.2580	0.4962
	0.2416	0.06847	0.7913	850	1.2578	0.4961
	0.2415	0.06850	0.7915	849	1.2575	0.4961
	0.2413	0.06852	0.7918	849	1.2574	0.4955
40^0 C	0.2432	0.06832	0.7892	849	1.2575	0.4954
	0.2431	0.06834	0.7894	851	1.2571	0.4953
	0.2429	0.06836	0.7895	853	1.2571	0.4951
	0.2427	0.06839	0.7896	856	1.2569	0.4947
	0.2425	0.06842	0.7898	858	1.2569	0.4946
	0.2421	0.06845	0.7900	865	1.2567	0.4943
	0.2418	0.06847	0.7904	861	1.2565	0.4943
	0.2416	0.06847	0.7913	860	1.2564	0.4940
	0.2415	0.06850	0.7915	858	1.2564	0.4938
	0.2413	0.06852	0.7918	857	1.2563	0.4930
45^0 C	0.2432	0.06832	0.7892	857	1.2564	0.4931
	0.2431	0.06834	0.7894	860	1.2561	0.4928
	0.2429	0.06836	0.7895	864	1.2559	0.4927
	0.2427	0.06839	0.7896	865	1.2550	0.4926
	0.2425	0.06842	0.7898	867	1.2549	0.4924
	0.2421	0.06845	0.7900	870	1.2540	0.4921
	0.2418	0.06847	0.7904	865	1.2538	0.4919
	0.2416	0.06847	0.7913	864	1.2535	0.4919
	0.2415	0.06850	0.7915	862	1.2533	0.4910
	0.2413	0.06852	0.7918	860	1.2532	0.4908

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) =ρU ……(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.

Simillarly 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:

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

and

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

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.

Conclusion

It has been observed that at 35^0 C ultrasonic velocity (U) increases with increasing concentration of the solution which attains a maximum value at 0.2421 mole fractions. The non-linear variation of ultrasonic velocity with concentration indicates occurrence of complex formation between unlike molecules. The molecular associations become 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). The density and viscosity of the tertiary solution decreases with decrease in concentration of the solution. The study shows that the mixture can be used in agriculture, industry and hospitals as a medicine at different temperatures to the some extent .Major drawback is that the solution mixture can not be used at higher temperature because of the less interaction between the solvent solvent molecules.

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