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Studies on molecular interaction on Binary mixture of spindle oil – ethanol system: Molar Function of Ultrasonic Parameter at different concentration at 303°K

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ABSTRACT

A study has been conducted on Acoustic Parameters of Spindle oil- Ethanol system, on different concentration's [0.2%, 0.4%, 0.6%, 0.8% and 1.6%] at temperature of 303K using Ultrasonic interferometer. Parameters like Ultrasonic velocity, Viscosity, Density, Adiabatic compressibility, Acoustic Impedance, Free length, Free Volume, Relation Time, Relative Association, Adsorption Coefficient and Molar compressibility are measured and it is helpful for correlation of Molecular interaction of binary mixture spindle oil-ethanol system.

Introduction

Intermolecular interaction plays a very important role in binary and ternary liquid mixture [1, 2]. They influence the arrangement, orientation and conformation of Molecule in solution. Ultrasonic velocities of liquid mixture have been used for qualitative determination of degree of association in fluid mixtures [3, 4]. The practical application of using mixed solvent rather than single solvent in industrial and organic processes in such that it provides a wide choice of solvent or solvent mixture with desirable properties[5-7]. The rates of reaction and stability of the intermediates formed depends on the intermolecular contact of the medium. Densities, Viscosity, ultrasonic velocity were done experimentally for spindle-ethanol mixtures of different concentration at temperature 303°K. (Fig-I). Spindle oil is used as lubricating oil in cutting and tool industry. Ethanol is used as washing liquid in the cutting and tool industry so that we can able to correlate the molecular interaction [8-15] between spindle oil and ethanol. From this ultrasonic parameters like Adiabatic compressibility, Intermolecular free length, Acoustic Impedence, Relaxation time, Rao's constant, Wada constant, Available volume Relative association and adsorption coefficient were also calculated. The values are plotted against concentration. The graph obtained is explained on the basis of various intermolecular interactions present in the system and how the interactions are affected by the change of concentration at temperature 303°K.

Experimental Part

Ethanol was purified by double distillation. Solution of spindle oil-Ethanol of different concentration by volume percentage is prepared at room temperature. All of them are allowed to attain constant temperature in constant temperature bath, before carrying out the experiments. The densities of solution were carried out using a pycnometer of bulb capacity of 10 ml (Systronics India Ltd.). The Pycnometer were calibrated using double distilled water. The accuracy of density was found to be ± 0.001g/cc. The viscosities of binary mixture were determines using an Cannon-Fensky Viscometer (sigma chemical instruments).The ultrasonic velocities of pure solvent and binary mixture were measured using a single crystal path interferometer at 2MHz (Mittal Enterprises, New Delhi). The accuracy in ultrasonic velocity [16-18] was found to be ± 0.05%. The temperature of the test liquid was maintained at an accuracy of ± 0.02 in an electrical controlled thermostat water bath. The above binary mixtures are prepared by using volume percentage (%) by using jobs variation method [19-21]. From the measure density, viscosity and ultrasonic velocity u, the adiabatic compressibility b, or Ks, Intermolecular free length Lf, viscosity relaxation, acoustic impedance, adsorption coefficient Free Volume, Rao's Constant, Wada constant, Available Volume and Relative association [22- 26] were calculated using the following relation.

Adiabatic Compressibility (β)

The structural changes of the molecule in the mixture take place due to existence of electrostatic field between interacting molecules. The structural arrangement of molecules results in a considerable change in a adiabatic compressibility, which can be express as $\beta = 1/ U^2\rho$ $Kg^{-1}ms^2$ Where U is ultrasonic velocities and ρ is density of liquid mixtures.

Intermolecular Free Length (L_f)

The free length is the distance covered by sound wave between the surfaces of the neighbouring molecules and is related to ultrasonic velocity and density as

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$$Lf = K / (\rho U)^{1/2} m,\ K=(93.875 + 0.345T) \times 10^{-8}$$

Acoustic Impedance (Z)

The specific acoustic impedance is related to density and ultrasonic velocity by the relation.

$$Z=U\rho\ Kgm^{-2}S^{-1}$$

Relaxation Time (τ).

Relaxation time and adsorption coefficient are directly correlated. The adsorption of sound wave is the result of time lag between the passing of ultrasonic wave and return of molecular to their equilibrium position. It is computed using the relation $\tau = 4\eta / 3\ \rho U^2$ sec

Free Volume (V_f)

The free volume is defined as the average volume in which the centre of the molecule can move inside the hypothetical cell due to the repulsion of surrounding molecules. Free volume can be calculated by different and is given by $(V_f) = [M_{eff}\ U/\ K\ \eta]^{3/2}$ $m^3\ mol^{-1}$

Where K=4.28 X 10^9 M_{eff} = Effective molecular weight.

Effective molecular weight of liquid mixture is given by $M_{eff} = X_1M_1 + X_2M_2$

Where X_1 and X_2 are the mole fraction of the first and second component and M1and M2 are molecular weights of the first and second component respectively.

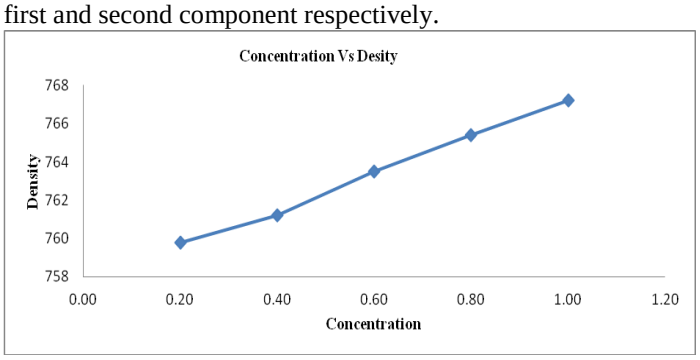

Fig I

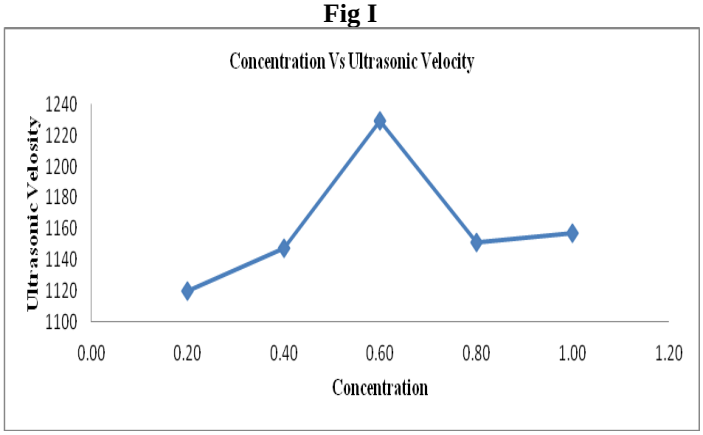

Fig II

Available Volume (V_a)

Available volume is the direct measure of compactness and strength of binding between the molecules of liquid or liquid mixture. Another parameter which can be calculate from ultrasonic velocity is the available volume and is given by $V_a = V[1-U/U\infty]\ m^3\ mol^{-1}$

Where U∞ = Schaaf's limiting value taken as 1600m/s for liquids.

Relative Association (Ra)

Relative association can be calculated from density and ultrasonic velocity and is given by

$$Ra = (\rho/\rho_o)^* (U/U_0)^{1/3}$$

Absorption coefficient (α/f^2)

Absorption coefficient is also called attenuation coefficient is a characteristic parameter of medium and it depends on external condition like temperature, pressure and frequency of measurement is given by $(\alpha/f^2) = 8\Pi^2\eta/[3\rho U^3].Npm^{-1}s^2$

Molar compressibility or Wada's constant (B)

Molar compressibility is also known as Wada's constant, which is dependent on adiabatic compressibility and density, is given by $B = (M/\rho)\ k^{-17}$

Rao's constant or molar sound velocity (R)

Rao's constant is also known as molar sound velocity and it is an additive property. It has been found to be invariant with temperature and pressure for unassociated organic and inorganic liquid. R is an relation between sound velocity and molar volume, which is given by $R = (Meff/\ \rho)\ U^{1/3}$

Results and discussion

From the variation of densities, viscosities and ultrasonic parameters with concentration and temperature, a qualitative interpretation of the intermolecular interactions in the above binary mixtures can be proposed. An increase in the density of a solution with dilution is the expected trend. For the system of Spindle oil and ethanol under study, there is increase in density, when concentration of solution increase. From the concentration of 0.2% onwards, the increase in density is practical. As the concentration increases the densities of solution of Spindle oil-ethanol system also increases (Fig:-I). The increase in density of spindle oil ethanol is pointed or sharp.

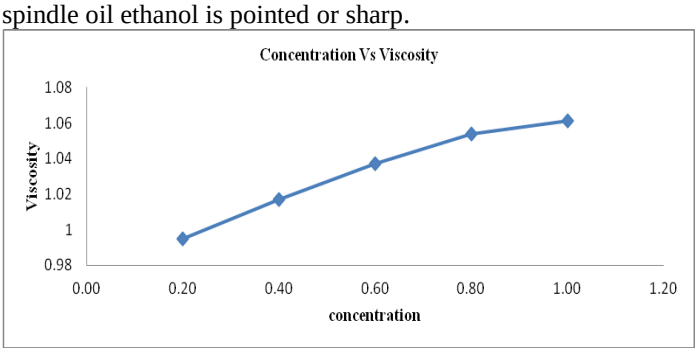

Fig III

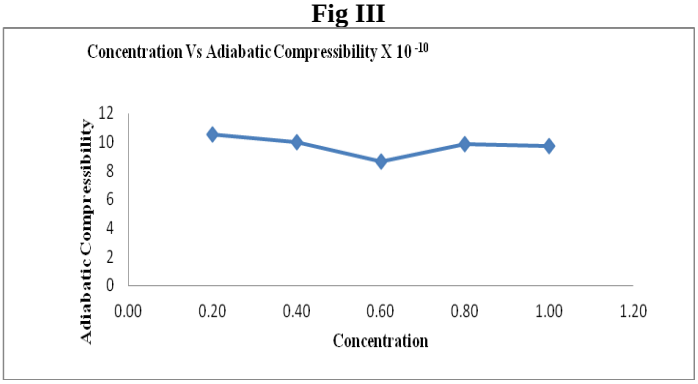

Fig IV

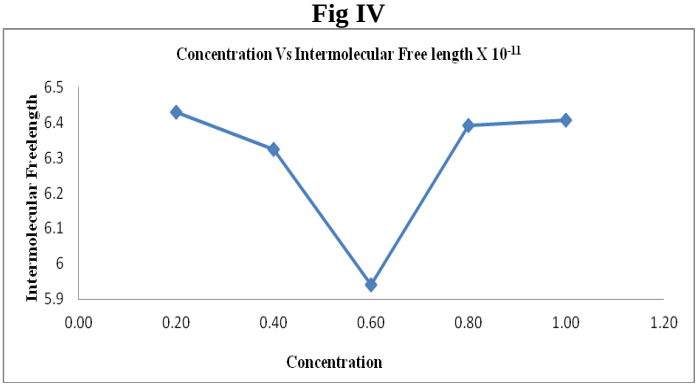

Fig V

The ultrasonic velocity is found to be lowest at very low concentration and the increase in ultrasonic velocity with increase in concentration is an expected trend. Beginning with a

concentration of 0.2 mol.%, there is sharp increase in velocity, reaching a maximum with concentration of 0.6% and then followed by a decrease (Fig-II). The increase of ultrasonic velocity from 0.2 mol.% concentration indicates the formation of strong hydrogen bonds of the solvent molecules with the larger molecules. An opposite trend is observed in the adiabatic compressibility (Fig-IV). A similar explanation for the decrease in compressibility with concentration of the liquid mixtures has been suggested by Fork and Moore. The maximum in ultrasonic velocity is observed at 0.6 mol.% concentration and at low temperatures. The decrease in ultrasonic velocity indicates that the interaction between solute molecule and solvent is becoming less dominant. This is due to the replacement of strong intermolecular attraction between solvent molecules by the weaker intermolecular interactions. This indicates that the solvent–solvent interaction is replaced by solute–solvent interaction. Generally, adiabatic compressibility decreases with increase in concentration. A high value of adiabatic compressibility for the low concentration (0.2 mol.%) indicates a positive solute –solvent interaction, and at the same time the network of hydrogen bonding formed by the solvent molecules is not much disturbed. The decrease in adiabatic compressibility with further increase in concentration indicates the breakdown of the network formed by the solvent molecules. Adiabatic compressibility reaches a minimum at 0.6 mol.% concentration. Beyond this concentration there is an increase in the adiabatic compressibility with an increase in concentration. This indicates that the solute/solvent interaction is replaced by comparatively stronger interaction between solute molecules, releasing the solvent molecules.

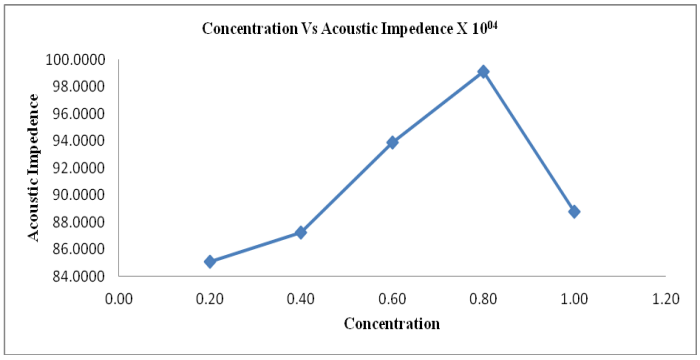

Fig VI

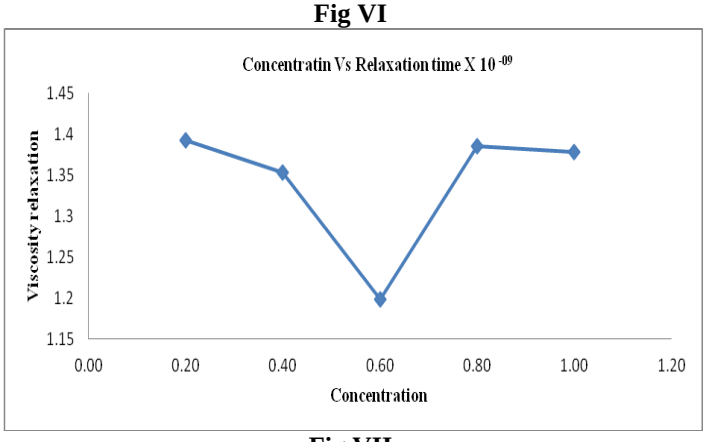

Fig VII

Further increase in adiabatic compressibility indicates change in the conformation/ orientation of the solute molecules in solution, leading to weaker inter-molecular interaction. This is attributed to the steric requirement of arranging an increasing number of larger molecules. In this situation, there steric factor takes predominance over intermolecular interactions. The changes in acoustic impedance are expected to be similar to those of ultrasonic velocity. At temperature (303K) there is a maximum at 0.6 mol.% and a minimum at 0.2 mol.%. As the concentration increases the acoustic impedance increases(Fig-VI), reaches maximum at 0.6 mol%. and then decreases. An increase in adiabatic compressibility indicates a change in the orientation of the solvent molecules around the solute molecule, which may be due to the influence of electrostatic fields around the ionized solute molecules.

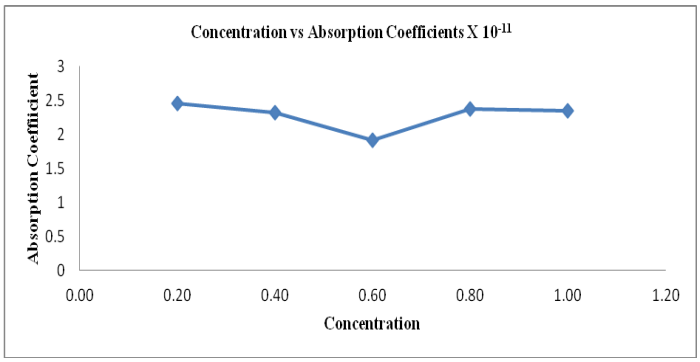

Fig VIII

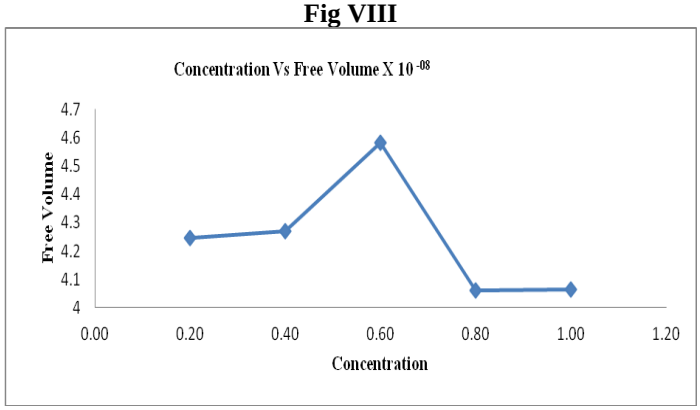

Fig IX

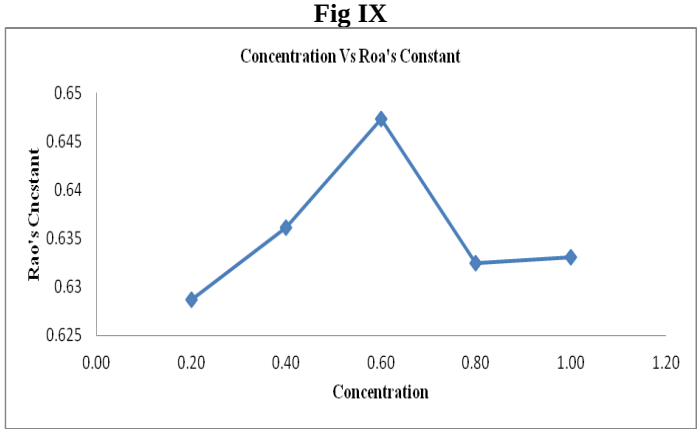

Fig X

This means that the solution becomes less compressible. It also indicates the associating tendency of the solute molecules in solution. Intermolecular free length and adiabatic compressibility are directly related to each other. Hence, the adiabatic compressibility increases with an increase in intermolecular free length. The stronger intermolecular interactions results in a tightly packed liquid structure, and, as such, the adiabatic compressibility and intermolecular free length decrease (Fig-IX). The formation of weaker intermolecular interaction leads to an increase in adiabatic compressibility and intermolecular free length. The intermolecular free length and ultrasonic velocity are inversely related to each other.

The ultrasonic velocity increases with a decrease in the intermolecular free length.

Table 1. Values of density, q, ultrasonic velocity, u, adiabatic compressibility, b, intermolecular free length, Lf of binary mixtures as a function of concentration (mol.%) at temperatures (303K).

Temperature @ 303^{O}K	Concentration				
	0.2%	**0.4%**	**0.6%**	**0.8%**	**1.0%**
Ultrasonic Velocity	1119.6	1147.2	1229.6	1151.2	1156.8
Density	749.8	761.2	763.5	765.4	767.2
Viscosity	0.995	1.02	1.04	1.05	1.06
Adiabatic Compressibility * 10^{-09}	1.0500	9.9821	8.663	9.8585	9.7404
Intermolecular Free length * 10^{-11}	6.4291	6.3232	5.9413	6.3921	6.4076
AcousticImpedence * 10^{04}	85.06721	87.3249	93.8800	88.1129	88.7497
Relaxation time * 10^{-09}	1.39281	1.35371	1.19814	1.38518	1.37833
Absorption Coefficients * 10^{-11}	2.4531	2.3269	1.9215	2.3727	2.3496
Free Volume * 10^{-08}	4.2460	4.2700	4.5810	4.0624	4.0660
Rao's Constant	0.6287	0.6361	0.6473	0.6325	0.6331
Wadas Constant * 10^{-03}	2.5489	2.5581	2.5428	2.5406	2.5391
Relative Association * 10^{-02}	99.54	98.92	96.95	99.35	99.42
Available Volume * 10^{-03}	18.21	17.16	14.01	16.97	16.74

There is an initial decrease in intermolecular free length in the low concentration region, followed by a steady decrease with an increase of concentration. The decrease of intermolecular free length with increase in concentration is a normal trend. But the initial decrease in intermolecular free length indicates that strong forces are acting between solute and solvent molecules, forming tightly held aggregates. The decrease in free length can be attributed to an increase in the stronger forces of cohesion between solute and solvent.

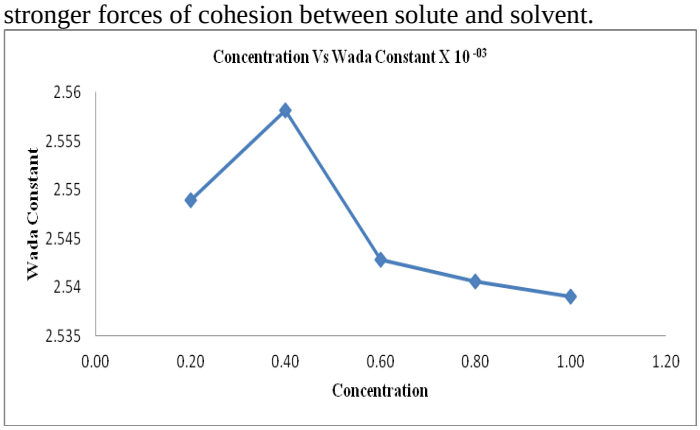

Fig XI

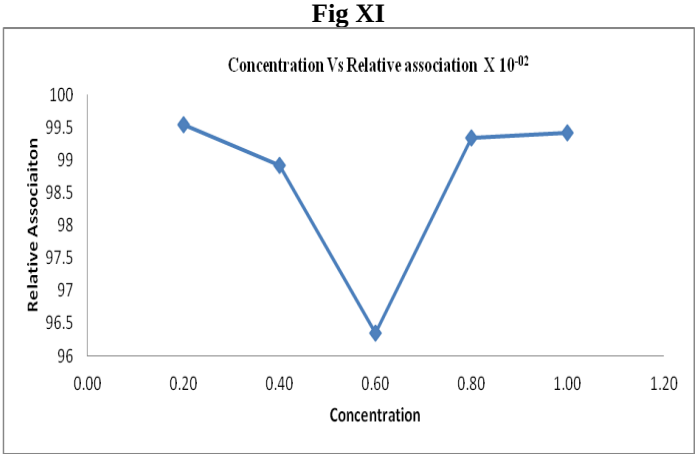

Fig XII

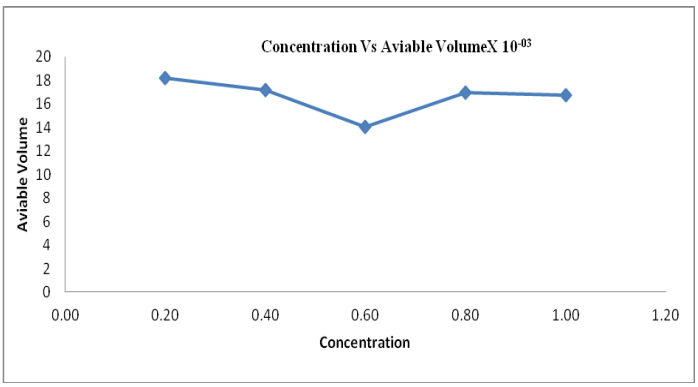

Fig XIII

The initial decrease of free length with an increase in molar concentration shows the expansion in the degree of association among solvent molecules. This is due to the breaking up of hydrogen bonds and differences in the size and shapes of molecules in the liquid mixtures. The relative association, RA, is directly proportional to q/U 1=3. This is influenced by two factors: (i) The breaking up of solvent/solvent interaction on addition of solute indicates higher value of RA. (ii) Solvation of solute indicates a lower value of Relative Association. Relative association is found to have an initial minimum value (Fig-XII) at 0.6 mol. % for temperatures 303 K. Beyond this concentration, the RA values increases, reaching a maximum at 0.2 mol. %. The maxima and minima are shifted to low concentration regions of 0.6 and 0.2 mol. %, respectively. This trend can be explained in that at low concentration, with the result being that the solvent/solvent interactions break down to give way to solvent/solute interactions. In the concentration range of 0.2–0.6 mol.%, there is a sharp increase in visible Free molar volume (Fig-IX) as the concentration increases. This clearly shows that within the concentration range a significant solute–solvent interaction is taking place. Beyond this concentration range, the decrease in molar volume is not very significant. The strength of interaction between component molecules is well reflected in deviations observed in Ks, q, u, and Lf from the expected trend. The excess parameters are

found to be more sensitive towards intermolecular interactions in the binary mixture.

Conclusions

In ethanol, molecules are held together by comparatively strong hydrogen bonds forming a network. Ethanol, being a non polar molecule, is capable of intermolecular hydrogen bonding interactions with the solute molecules, which are being slowly replaced by solvent–solute interaction. This leads to solvation of the solute molecule, resulting in an increase in density of the mixture. Increasing the temperature results in an increase in the total volume of solution, because of the weakening of intermolecular interactions. Due to solvation effects, the molecule in solution become larger in size. The study of ultrasonic parameters and excess functions for the binary mixture of spindle oil and ethanol at various concentrations and hydrogen bonding between the solute and solvent. The type and the magnitude of interaction depend on the concentration. This shows that at 0.6% mole there is strong hydrogen bonding in spindle oil and ethanol system.

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