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Understanding Molecular Interactions in Methanol and m-Toluidine Mixtures Through Acoustical and Viscosity Analysis

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Abstract: ***The viscosity (n), and Density (p) have been calculated for methanol, m-toluidine and their binary mixtures at room temperature. Ultrasonic Velocity (U) have been measured for pure methanol, m-toluidine and their binary mixtures using Ultrasonic interferometer at 2MHz frequency. Experimental data have been used to calculate some derived parameters such as adiabatic compressibility (β), acoustical impedance (Z), relaxation time (τ), free length (L_f) and free volume (V_f). Also, the excess parameters such as excess ultrasonic velocity ΔU, excess acoustical impedance (ΔZ), excess relaxation (Δτ), excess free length (ΔL_f) and excess free volume (ΔV_f). These parameters have been evaluated and discussed in light of intermolecular interaction in these mixtures.***

Keywords: Ultrasonic velocity, acoustic parameters, excess parameters

1. Introduction

Ultrasonic and acoustic studies in solutions are instrumental techniques used to investigate the behavior of sound waves as they propagate through liquid mixtures. [1]. These studies offer a profound understanding of molecular interactions, structural changes with the mixture and how these properties respond to variations in factors like temperature and pressure. Study of molecular interactions between solute and solvent has a great importance in many fields of science and technology as such industrial, medicinal and biochemistry. Ultrasonic velocity is highly sensitive to the structure and interactions present in the liquid mixtures as it is fundamentally related to binding process between constituents. [2] An investigation in the possible change of acoustic properties of mixtures and their degree of deviation from ideality has been found to be excellent quantitative way to procure information about molecular structure and intermolecular forces in the liquid mixtures. This has given impetus to the theoretical and experimental investigation of excess acoustic properties of liquid mixtures.

Alcohols have found various applications and commercial use in medical and other fields, for example methanol is a versatile chemical with many uses in industry, transportation and every day products [12]. M-toluidine is used as an intermediate chemical in the production of dyes and pigments, including those used in in textiles, leather and printing inks. Therefore, it seemed important to examine the ultrasonic study of methanol with M-toluidine.

2. Experimental Details

Methanol and M-toluidine used were of AR grade with minimum assay of 99.9% procured form S. D. fine chemicals and Spectrochem Pvt. Ltd. Mumbai. These chemicals are used without further purification. Samples of solution with different mole fraction m-toluidine were prepared. The density (ρ) and viscosity (η) of pure liquids and liquid mixtures were determined by using 10 ml Specific gravity bottle and Ostwald's viscometer respectively. The Ultrasonic velocity (U) in the liquid and liquids mixtures have been measured using an Ultrasonic Fixed-frequency interferometer (Mittal type Model F-05.) [2] The interferometer is fixed frequency (2MHz) variable path type. Ultrasound of constant frequency is generated at the bottom of cylindrical sample cell using quartz crystal and sent into the medium under study. The propagated waves after getting reflected at the reflector surface held at the top of the cell, again travels back through the same medium forming a standing wave pattern in the medium. Thus, moving the reflector plate for a fixed number of nodes or antinode positions, the distance moved for known number of waves can be known. Using frequency with these data will gives ultrasound velocity in the medium.

The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U) were used to calculate various acoustical parameters such as adiabatic compressibility (β_{ad}), Acoustical impedance (Z), free length (L_f), free volume (V_f), relaxation time (τ) using following expressions [14]

$$\beta_a = \frac{U^2}{\rho} \quad \text{(i)}$$

$$Z = U\rho \quad \text{(ii)}$$

$$L_f = K_T {\beta_a}^{1/2} \quad \text{(iii)}$$

$$V_f = \left[\frac{M_{eff}U}{\eta K}\right]^{3/2} \quad \text{(iv)}$$

$$\tau = \frac{4}{3}\eta\,\beta_a \quad \text{(v)}$$

Where, K_T is temperature dependent constant having value of 199.53×10^{-8} in MKS system and K is temperature dependent constant whose value is 4.28×10^9 in MKS system
$M_{eff} = \sum X_i M_i$ Where X is mole fraction and M is molecular weight in of i^{th} components

The strength of interaction between the component molecules is well reflected in the deviations, in excess viscosity (Δη) Excess Adiabatic compressibility ($\Delta\beta_{ad}$), Excess Acoustic impedance (ΔZ), Excess intermolecular free length (ΔL_f) excess free volume (ΔV_f) etc. These parameters were calculated using the relation.

$$\Delta Y = Y_m - (X_1Y_1 + X_2Y_2) \text{ (vi)}$$

Where, ΔY is any excess parameter, and Y refers to above mentioned parameter. The subscripts m, 1 and 2 used in the above equation are respectively for the mixture, component 1 and component 2, X_1 and X_2 are the mole fractions of two components in the liquid mixture.

3. Result and Discussion

The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U) were used to calculate various acoustical parameters such as adiabatic compressibility (β_{ad}), Acoustical impedance (Z), free length (L_f), free volume (V_f), relaxation time (τ) for Methanol, M-toluidine and their binary mixtures are listed in table (1) and the values of excess viscosity (Δη), excess ultrasonic velocity (ΔU), Excess adiabatic compressibility ($\Delta\beta_{ad}$), Excess intermolecular free length (ΔL_f) and excess free volume (ΔV_f) are reported in table (2).

Ultrasonic velocity of sound waves in a medium is fundamentally related to the binding forces between the molecules. From fig. (1), it is observed that ultrasonic velocity (U) increases with mole fraction of M-toluidine. The velocity increases non-linearly with concentration indicates that there is intermolecular interaction exists with mixture on the basis of the model for the sound propagation proposed by Eyring and Kincaid [10] ultrasonic velocity (U), increases on increase mole fraction of m-toluidine [8]

The variation in the values of adiabatic compressibility indicate that the free dipoles of methanol molecules would induce moments in the neighbouring molecules of the M-toluidine resulting in dipolar induced dipolar interaction leading to contraction in the volume This leads to subsequent variation in the adiabatic compressibility (β_{ad}) as well as intermolecular free length (L_f) [12].

Specific acoustic impedance (Z) of the medium is governed by the inertial & elastic properties of the medium [9]. In the present system the acoustic impedance (Z) varies with increase in concentration of M-toluidine variation trend of acoustic impedance supports the possibility of the molecular interaction between solute and solvent molecules. Also, free volume (V_f) have same trend with that of ultrasonic velocity. This indicates significant molecular interactions[12].

The excess parameters of a binary liquid system is a measure of deviation from the ideal behaviour of the mixture and are more sensitive towards the molecular interactions in the liquid mixture. The respective excess parameters have been calculated and are shown in table 2 and in figures 2 to 4 which indicates that the parameters are negative over a wide range of mole fraction. Being the excess values, these reveled the extent of non-ideality of the system at the respective mole fraction. The magnitudes of positive excess viscosity and excess acoustic impedance (ΔZ) are continuously varies with increasing mole fraction of M-toluidine. Thus, the strong interaction existing between the components were confirmed.

4. Conclusion

1) Acoustic parameters in Methanol and M-toluidine system suggest strong molecular interaction in unlike molecules of system.
2) Non-linear behavior of acoustic parameters suggests the formation of complex in the binary mixtures

Table 1

The values of density (ρ), ultrasonic velocity (U), adiabatic compressibility (β_{ad}), intermolecular free length (L_f), Acoustic impedance (Z), free volume (Vf) and relaxation times (τ) of the binary liquid mixture of methanol+ m-toluidine with mole fraction of M-toluidine at room temperature

Mole fraction of m-toluidine (X)	ρ (Kg m^{-3})	Viscosityη $x10^{-3}$	U (ms^{-1})	ßad (10-10m2 N-1)	L_f (A^0)	Z ($10^6 kgm^{-2}s^{-1}$)	(V_f) X^{10-8} m^3mol^{-1}	τ $x10^{-13}$ sec
0	783	0.6039	1290	6.193	0.496	1.1201	6.3499	4.98
0.0700	839.5	0.762	1340	6.008	0.4810	1.1812	6.7382	6.10
0.1662	883.9	0.9597	1380	5.855	0.4828	1.2202	6.2667	7.50
0.3095	916.2	1.1578	1390	5.731	0.47767	1.2603	7.018	8.84
0.5446	955.6	1.9731	1408	5.821	0.48168	1.2801	4.5972	15.31
1	981	2.7706	1436	6.120	0.49383	1.2650	4.67	22.60

Table 2

The values of Excess viscosity (Δη), Excess ultrasonic velocity (ΔU), Excess adiabatic compressibility ($\Delta\beta_{ad}$), Excess intermolecular free length (ΔL_f) and excess acoustic impedance (ΔZ) of the binary liquid mixture of methanol+m-toluidine with mole fraction of M-toluidine at room temperature

Mole fraction of toluidine (X)	*(Δη)*	*(ΔU) ms⁻1*	*Δ ßad (10-10m2 N-1)*	*Δ L_f (10^{-12}m)*	*ΔZ ($10^6 kgm^{-2}s^{-1}$)*
0.0000	0.0000	0.000	0.0000	0.0000	0.0000
0.0700	.006431	39.78	- 0.17989	- 0.0148	0.0509
0.1662	0.3243	262.708	0.84552	0.0817	0.2353
0.3095	0.49512	437.11	1.688122	0.1442	0.4177
0.5446	1.44583	774.994	3.211	0.2641	0.7061
1	0.0000	0.0000	0.0000	0.0000	0.0000

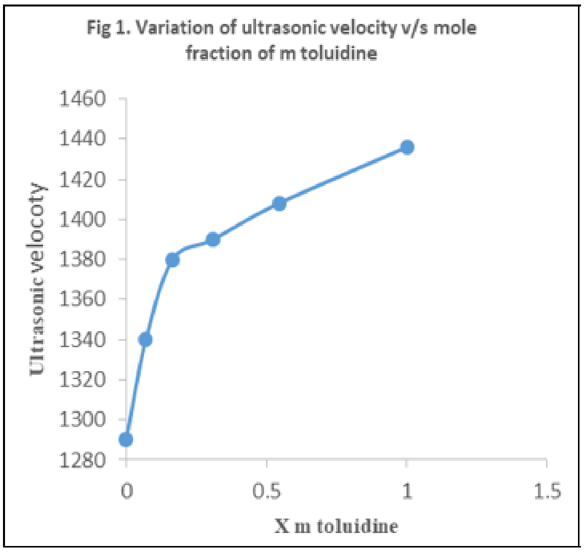

Fig 1. Variation of ultrasonic velocity v/s mole fraction of m toluidine

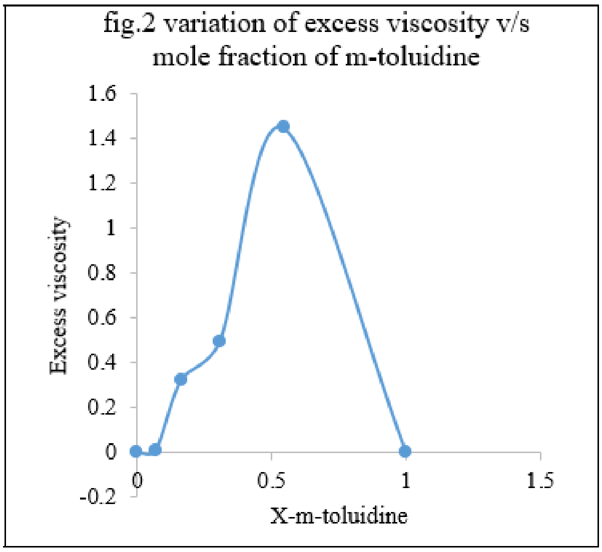

fig.2 variation of excess viscosity v/s mole fraction of m-toluidine

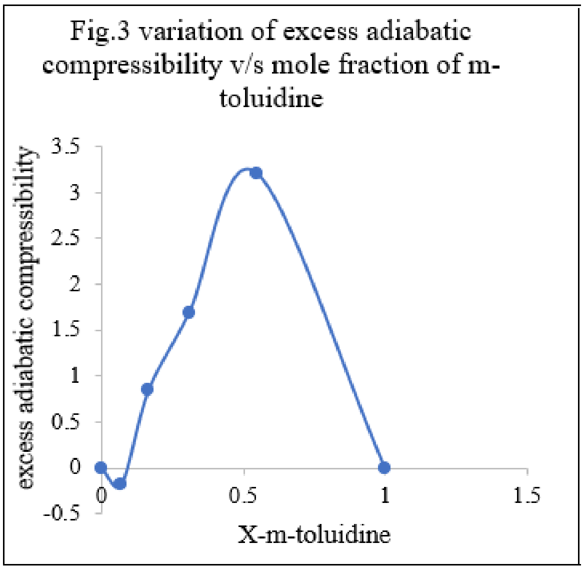

Fig.3 variation of excess adiabatic compressibility v/s mole fraction of m-toluidine

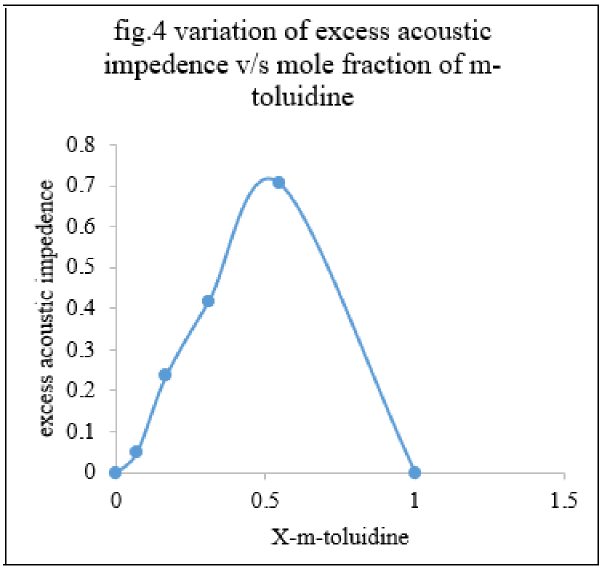

fig.4 variation of excess acoustic impedence v/s mole fraction of m-toluidine

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