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Physico-Chemical and Excess Thermodynamic Properties of Acrolein with Methanol at 298K Temperature and 10 MHz Frequency.

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ABSTRACT

The densities (ρ), viscosities (η) and Ultrasonic velocity (U) of binary liquid mixture of Acrolein with the solvent methanol were measured over the entire composition range at the temperature 298K for the frequency 10MHz. The observed experimental data have been utilized to evaluate some of the derived thermodynamic parameters such as adiabatic compressibility (β_a) , free length (L_f), free volume (V_f), internal pressure (π_i), relaxation time (τ) and acoustic impedance (Za). The behavior of these parameters with composition of the mixture has been discussed in terms of molecular interaction between the components of liquids. The excess values of adiabatic compressibility (β_a^E), free volume (V_f^E) and free length (L_f^E) were evaluated and discussed in the light of molecular interactions in the mixture.

Keywords: Molecular interaction, ultrasonic velocity, binary liquid mixture, excess parameters, Acrolein, methanol and Hydrogen bonding.

INTRODUCTION

Ultrasonic studies of the liquid mixtures are of great importance because of their extensive use in the textile, leather and pharmaceutical industries [1, 2].The ultrasonic velocity has been measured in order to understand the nature of molecular interactions in pure, binary and ternary liquid mixtures [3, 4].

Organic solvents usually form Hydrogen bond in the solutions. The functional group of the organic solvents can form H-bonds due to hydrophilic effects in the mixture, while the hydrocarbon part of the solvent is responsible for the hydrophobic part [5]. The practical application of the organic solvents in industrial and biological process has been recognized all over the world as they provide wide choice of solutions with appropriate properties. The evaluated thermodynamic parameters from the experimental acoustical data have been interpreted in terms of the molecular interactions between the components of the mixture [6, 7]. Further, these measurements are found to be greatly significant in studying the structural changes associated with the liquids. They also provide importance information about the molecular packing and various types of intermolecular interactions and their strength influenced by the size, shape and the chemical nature of the component molecules [8]. A thorough knowledge of the thermodynamic and transport properties of the liquid systems is essential in many industrial applications such as design, calculation, heat transfer, mass transfer, fluid flow and so forth [9, 10].

The acoustical and excess thermodynamic properties of the binary liquid mixture of Acrolein with the organic solvent methanol at 298K temperatures have been studied in the present paper. The liquids under investigation have been chosen on the basis of their industrial applications [11]. These applications have greatly stimulated the need of extensive information on the thermodynamic, acoustic and transport properties of the solvent and their mixture. On the basis of ultrasonic studies, it is interesting to note that the thermodynamic result of the binary mixture gives useful information of the molecular interaction [12, 13]. In the present investigation, the acoustical and excess thermodynamic properties of Acrolein with methanol binary mixture at 298K temperature have been studied.

METHODOLOGY

In the present work, the chemicals used, are Analytical Reagent (AR) and Spectroscopic Reagent (SR) grades of minimum assay of 99. 9% obtained from E-Mark, Germany and Sd Fine chemical, India. The purities of chemical were checked by the density measurements at the temperature 298.15K and compare with available literature values. The binary liquid mixtures of different known composition were prepared by mole fraction (x) basis. The density, viscosity and ultrasonic velocity were measured as a function of the binary liquid mixtures of solute Acrolein and with solvent methanol at the temperature 298.15K.

The density was determined using a specific gravity bottle (10ml) using relative measurement method. The weight of the sample was measured using an Electronic Digital Balance with an accuracy of ±0.1mg. An Oswald's viscometer (10ml) was used with an accuracy of ±0.001Nsm^{-2} for the viscosity measurement. Efflux time was determined by using digital timer with an accuracy of ±0.01s. An Ultrasonic Inetervelometer (UTI-101, Innovative Instrument, Hyderabad) having fixed frequency of 10MHz has been used for velocity measurement. The overall accuracy in the velocity measurement is ±0.1ms^{-1}. An Electronically digital operated constant temperature water bath has been used to circulate the water through a doubled walled measuring cell made up of stainless steel containing the experimental solution at the desire temperature. The accuracy in the temperature measurement is ±0.1K. Extreme care was taken to avoid contamination during mixing. The present work was conducted under normal pressure.

The calculated parameters are Adiabatic compressibility (β_a), Intermolecular free length (L_f), free Volume (V_f), Internal Pressure (π_i), specific acoustical impedance (Za), relaxation time (τ), excess adiabatic compressibility (βa^E), excess free volume (V_f^E) and excess free length (L_f^E)

i. Adiabatic compressibility (β_a):

The adiabatic compressibility (β_a) has been calculated from the ultrasonic velocity (U) and the density (ρ) of the medium using the equation as:

$$\beta_a = 1/ (U^2 * \rho) \quad \text{---------- (1)}$$

ii. Intermolecular free length (L_f):

Intermolecular free length has been determined as:

$L_f = K_J (\beta_a)^{1/2}$ ---------- (2)

Where K_J is the temperature dependent Jacobson's constant [14] but independent of the nature of liquid.

iii. Free volume (V_f):
The free volume has been calculated in terms of ultrasonic velocity (U) and viscosity (η) of the liquid as:

$V_f = [(Me_{ff} U) / (K \eta)]^{3/2}$ ---------- (3)

Where, Meff (Effective mass) = Σ mi xi, in which mi and xi are the molecular weight and the mole fraction of the individual constituents respectively. K is the temperature independent constant, which is equal to $4.28 * 10^9$ for all liquids and η be the viscosity.

iv. Internal pressure (πi):
On the basis of statistical thermodynamics, Suryanarayana [15], derived an expression for the determination of internal pressure (π_i) by the use of free volume concept as:

$\pi i = (b RT)[(K * \eta) / (U)]^{1/2} * [(\rho^{2/3}) / (Me_{ff}^{7/6})]$ ------(4)

Where, b is the cubic packing which is assumed to be 2 for all liquids and solutions, K is the temperature independent constant, T is the absolute temperature, R is universal gas constant, η be the viscosity and Meff the effective molecular weight .

v. Relaxation time (τ):
The relaxation time (**τ**) can be calculated from the relation as:

$\tau = (4/3) \beta a * \eta$. ---------- (5)

Where βa and η are adiabatic compressibility and viscosity of the liquid and liquid mixtures.

vi. Acoustic impedance (Za):
The specific acoustic impedance is given by,

$Za = U * \rho$. ---------- (6)

Where U and ρ are the ultrasonic velocity and density of the liquid respectively.

Excess parameters (A^E) represent the difference between the parameters of real mixtures (Aexp.) and those corresponding to an ideal mixture ($Aid_.$).

$A^E = A_{exp.} - A_{id.}$ …… (7)

Where $Aid_. = \sum A_i X_i$, i = 1, 2, 3, n. A_i is any acoustical parameters and x_i the mole fraction of the liquid components.

RESULTS AND DISCUSSION

In the present study the Table-1 summarizes the values of density (ρ), viscosity (η) , ultrasonic velocity (U), adiabatic compressibility (β_a), free length (L_f) and free volume (V_f) for the binary system of Acrolein + methanol at the temperature 298.15K. The calculated values of Internal Pressure (π_i), specific acoustical impedance (Za), relaxation time (τ), excess adiabatic compressibility (βa^E), excess free volume (V_f^E) and excess free length (L_f^E)) with respect to concentrations at 298K temperature were shown in the Table-2.

The variations of Velocity (U), Density (ρ), Viscosity (η), Adiabatic compressibility (β_a) and Intermolecular free length (L_f) ,free Volume (V_f) ,excess adiabatic compressibility (βa^E), excess free volume (V_f^E) and excess free length (L_f^E) with respect to concentration (x) of the binary system: Acrolein + Methanol at 298K temperature are shown in Fig. (A), Fig. (B), Fig. (C), Fig. (D), Fig. (E), Fig. (F), Fig. (G), Fig. (H) and Fig. (I) respectively.

From the Table**–**1, it is noted that, the density (ρ) and ultrasonic velocity (U) increases with increase in mole fraction of Acrolein the binary system: Acrolein + methanol. While viscosity decreases with increase in mole fraction of the solute in the binary system: Acrolein + methanol. The increase in the velocity is due to decrease in adiabatic compressibility and free length**.** It has been observed that for a given concentration, as the number of CH-group or Chain length changes, the sound velocity changes. This may lead to the presence of specific molecular interaction between the molecules of the liquid mixture. The adiabatic compressibility and free length are the deciding factors of the ultrasonic velocity in the liquid

systems. The internal pressure decrease and free volume increase with increasing mole fraction of the salute in the system. The internal pressure may gives information regarding the nature and strength of forces existing between the molecules. It represents the presence of weak interaction between the solute and solvent molecules. Acoustic impedance (Za) increases with increase in the mole fraction of the solute in the system**.** The relaxation time (τ) decreases with increasing the mole concentration of the solute in the system. The dispersion of the ultrasonic velocity in the system may contain information about the characteristic time (τ) of the relaxation process that causes dispersion. The relaxation time in the order of 10^{-12}sec., is due to structural relaxation process **[**16**]** and in such a situation, it is suggested that, the molecules get rearranged due to co-operative process **[**17**].**

The excess adiabatic compressibility (β_a^E) is overall positive over the entire composition range of the mixture for the system. The positive value of excess adiabatic compressibility indicate that the liquid mixture is less compressible than the pure liquids forming the solution and the molecules in this mixture are more tightly bound in the liquid mixture than in pure liquids. Thus positive value of excess adiabatic compressibility of this system indicates strong specific interaction between the component molecules and interstitial accommodation of small molecules in the voids created by bigger molecules. The excess free volume (V_f^E) is negative for the system over the entire composition range of the mixture. The negative value of excess free volume (V_f^E) for the systems suggests the component molecules are more closed together in the liquid mixture than in the pure liquids forming the mixture, indicating that, strong attractive interactions between component molecules such as hydrogen bonding and dipole-dipole interactions. The variation of excess free length (L_f^E) is positive over the entire range of composition, for the system. The positive value of excess free length (L_f^E) for the system, indicate structural readjustment in the liquid mixture toward a less compressible phase of fluid and closer packing of the molecule [18, 19].

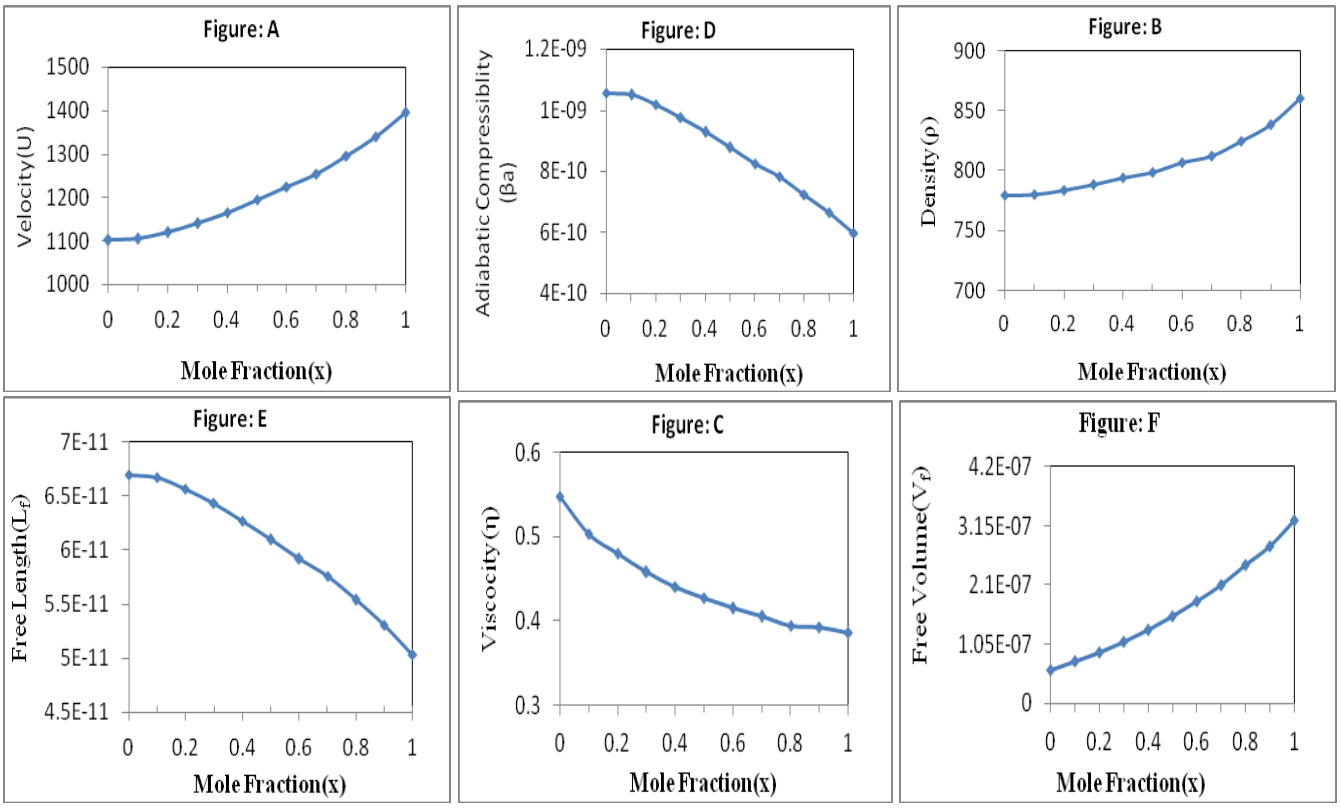
Table 1: The experimental values of Velocity (U), Density (ρ), Viscosity (η) , Adiabatic compressibility (β_a), Intermolecular free length (L_f) and free Volume (V_f) for the system: Acrolein + Methanol at 298K temperature.

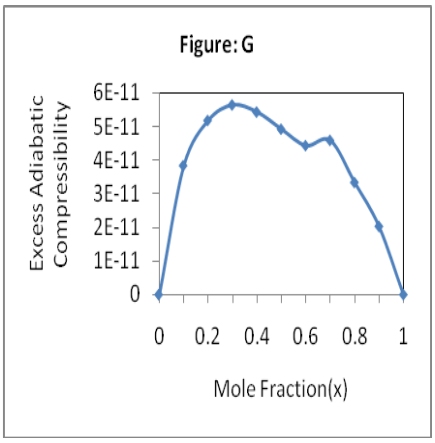
Mole fraction (x) of Acrolein in Methanol	U (m/s)	ρ (kg/m^3)	η 10^{-3} (CP)	β_a 10^{-10}(Pa^{-1})	L_f 10^{-10} (m)	V_f 10^{-7}(m^{3}mol^{-1}**)**
T= 298K						
0.0	1101.50	779.30	0.548	10.58	0.669	0.583
0.1	1105.00	780.00	0.503	10.50	0.667	0.743
0.2	1120.10	783.54	0.480	10.17	0.656	0.900
0.3	1140.10	788.33	0.458	09.76	0.643	1.090
0.4	1165.00	793.90	0.441	09.28	0.627	1.303
0.5	1195.15	798.43	0.427	08.77	0.609	1.546
0.6	1225.10	806.53	0.415	08.26	0.591	1.813
0.7	1255.10	812.04	0.405	07.82	0.575	2.104
0.8	1295.10	824.25	0.395	07.23	0.553	2.460
0.9	1340.10	838.15	0.393	06.65	0.530	2.795
1.0	1394.14	860.00	0.386	05.98	0.503	3.254

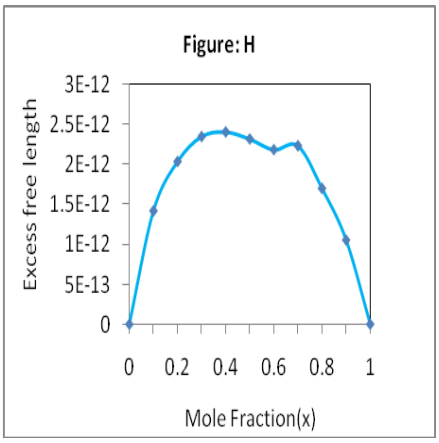
Table 2: The calculated values of Internal Pressure (π_i), specific acoustical impedance (Za), relaxation time (τ), excess adiabatic compressibility (βa^E), free volume (V_f^E) and free length (L_f^E) with respect to concentrations of system: Acrolein + Methanol at 298K temperature.

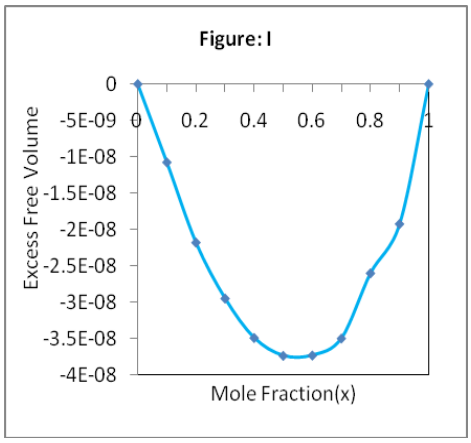
Mole fraction of Acrolein in Methanol	Πi 10^8 (P_a)	Za 10^6(kg/m^2s)	τ 10^{-13} (s)	β_a^E 10^{-10}(Pa^{-1})	L_f^E 10^{-11}(m)	V_f^E $10^{-7}m^3mol^{-1}$
T=298K						
0.0	10.72	0.85	7.73	0	0	0
0.1	9.43	0.86	7.04	0.38	0. 14	-0.11
0.2	8.48	0.87	6.51	0.50	0. 20	-0.22
0.3	7.66	0.89	5.96	0.53	0. 23	-0.30
0.4	6.97	0.92	5.46	0.54	0. 24	-0.35
0.5	6.37	0.95	4.99	0.49	0. 23	-0.38
0.6	5.87	0.98	4.57	0.47	0. 22	-0.37
0.7	5.42	1.01	4.22	0.45	0. 21	-0.35
0.8	5.03	1.06	3.81	0.33	0. 17	-0.26
0.9	4.73	1.12	3.48	0.20	0. 11	-0.20
1.0	4.44	1.19	3.07	0	0	0

Figure: The variations of Velocity (U), Density (ρ), Viscosity (η), Adiabatic compressibility (βa) , Intermolecular free length (L_f) , free Volume (V_f) ,excess adiabatic compressibility (βa^E), free volume (V_f^E) and free length (L_f^E) with respect to concentration (x) of Acrolein in Methanol at the 298K temperature are shown in Fig. (A), Fig. (B), Fig. (C), Fig. (D), Fig. (E), Fig. (F), Fig. (G), Fig. (H) and Fig. (I) respectively.









CONCLUSION

The dependence of ultrasonic velocity and other derived parameters on composition of the mixtures is the indication of the presence of molecular interactions. The interaction primarily of dipole-dipole and solute-solvent type. The molecular interactions present in Acrolein with methanol as a solvent have been studied by viscosity, density and ultrasonic velocity study. The result indicates the existence of molecular interaction between the solute and the solvent in their solutions. The result is also shows the presence of higher degree of molecular interaction between Acrolein and methanol in solution. The excess thermodynamic parameter such as excess compressibility (β_a^E), excess free length (L_f^E) and excess free Volume (V_f^E) for different mole concentration of solute for the above binary system is evaluated and these parameters suggests the presence of weak molecular interactions.

Conflicts of interest: The authors stated that no conflicts of interest.

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