

Investigation of Excess Thermo-Acoustic Properties of Binary Liquid Mixture Using Ultrasonic Non Destructive Technique

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Abstract:

The acoustic parameters for binary liquid mixture namely n-hexane -Tetrahydrofuran has been determined at four different temperatures. The acoustical parameters such as adiabatic compressibility (β_a^E), intermolecular free length (L_f^E), free volume (V_f^E), acoustic impedance (Z^E), and relaxation time (E) has been computed using values of ultrasonic velocity and density. The extent of interaction existing between component molecules has been found out in n-hexane and tetrahydrofuran system. The interaction parameters values have been out to be negative suggesting the presence of dipole-induced-dipole interaction with increase in temperature.

Keywords: Binary mixture, molecular interaction, ultrasonic velocity, isentropic compressibility, intermolecular free length, and acoustic impedance.

Introduction:

The importance of liquid mixtures rather than single component liquid system^[1,2], has gained much importance during the last two decades in assessing the nature of molecular interaction and investigation of liquid mixtures consisting of polar and non-polar components is of considerable importance in understanding inter molecular interaction between the component molecules and they find applications in several industrial and technological process ^[3-5]. Such studies as a function of concentration are useful in gaining insight into the stracture and bonding of associated molecular components and other molecular processes. The measurement of ultrasonic speed and parameters derived from it has been used in understanding the nature of intermolecular interaction in liquid mixtures^[6-11]. Though a number of investigations were carried out in mixtures having n-hexane as one of the components^[12-13], binary system with tetrahydrofuran as one of the components is a solvent for resins, waxes, oils, dyes and surface coatings.

Experimental:

The chemicals n-hexane and tetrahydrofuran were used of analytical grade and obtain from Merck chemicals private Ltd. (Purity 99.5%). Special attention was given to avoid the vaporization of solution. Comparing their density with literature values checked the purity of chemicals. The mixtures of various concentrations in mole fraction were prepared.

Measurements

(i) Velocity Measurement:-The velocity of ultrasonic wave in the binary mixture have been measured using ultrasonic interferometer with an high degree of accuracy operating at 5 MHz frequencies (Model F-81) supplied by M/s Mittal





(1)

(2)

(3)

Enterprises, New Delhi. The measuring cell of interferometer is a specially designed double walled vessel with provision for temperature constancy. An electronically operated digital constant temperature bath supplied by M/s Mittal Enterprises, New Delhi, operating in the temperature range 5°C to 99.9°C with an accuracy of ± 0.1°C has been used to circulate water through the outer jacket of the double walled measuring cell containing the experimental liquid.

(ii) Density Measurement:-The densities of the mixture were measured using a 25ml specific gravity bottle. The specific gravity bottle with the experimental mixture was immersed in a temperature controlled water bath. The density was measured using the formula

 $\rho_2 - \left(\frac{w_2}{w_1}\right) \rho_1$, Where, w_1 = weight of distilled water, w_2 = Weight of experimental liquid, ρ_1 = Density of water, ρ_2 = Density of experimental liquid

(iii) Viscosity measurement:-The viscosities of the ternary mixture were measured using an Oswald's viscometer calibrated with double distilled water. The Oswald's viscometer with the experimental mixture was immersed in a temperature controlled water bath. The time of flow was measured using a digital racer stop

watch with an accuracy of 0.1 sec. The viscosity was determined using the relation,

$$\eta_2 = \eta_1 \left(\frac{t_2}{t_1}\right) \left(\frac{\rho_2}{\rho_1}\right)$$

Where, η_1 = Viscosity of water, η_2 = Viscosity of mixture, ρ_1 = Density of water, ρ_2 = Density of mixture, t_1 = Time of flow of water, t_2 = Time of flow of mixture. **THEORY:**

The adiabatic compressibility (β_a) has been calculated from sound velocity 'u' and the density (ρ) of the medium using the relation

$$\beta = \frac{1}{\mu^2 \rho}$$

Intermolecular free length (L_t) has been determined by the equation.

 $L_f = K_T \sqrt{\beta}$

Where K_T is a Jacobsen's constant.

The free volume V_f in terms of ultrasonic, velocity (u) and the viscosity (η) of a liquid is

$$V_{f} = \left(\frac{Meff u}{k\eta}\right)^{3/2}$$

Where M_{eff} is the effective molecular weight

$$M_{eff} = \sum m_i x_i \tag{4}$$

In which m_i & x_i are the molecular weights and mole fraction of individual constituents respectively and K is a temperature dependent constant equal to 4.28 \times 10⁹ for all liquids in MKS system.

Specific acoustic impedance (Z) is determined from equations,

$$Z = u \cdot \rho$$
 (5)
An excess value of ultrasonic related parameters has been calculated by using the

relations.
$$U^E = U_{expt} - \sum X_i U_i$$
 (6)
 $\eta^E = \eta_{expt} - \sum X_i \eta_i$ (7)

$$\eta^{E} = \eta_{expt} - \sum X_{i} \eta_{i} \tag{7}$$



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$\beta^{E} = \beta_{expt} - \sum X_{i}\beta_{i}$	(8)	
$V_f^E = (V_f)_{expt} = \sum X_t (V_f)_t$		(9)
$L_f^E = (L_f)_{nxpd} - \sum X_i (L_f)_i$		(10)
$Z^{\bar{E}} = Z_{oxyt} - \sum X_i Z_i$		(11)
$\tau^E = \tau_{expt} - \sum X_i \tau_i$		(12)

Where $\beta_{s^{E}}$, $V_{f^{E}}$, L_{f}^{E} and t^{E} are the excess values of molar volume, adiabatic compressibility, and free length respectively.

Result and Discussion:

Ultrasonic velocity (*u*), density (ρ), adiabatic compressibility (β_a) and other related excess thermodynamic parameters like excess adiabatic compressibility (β_a^E), excess acoustic impedance (Z^E), excess free volume (V_f^E) and excess free length (L_f^E) are evaluated for binary mixture tetrahydrofuran in n-hexane over whole concentration at 301.15 K, 305.15K, 309.15K and 313.15K and presented in Table-I, Table - II, Table - III and Table- IV respectively.

Table 1: Excess Values of Ultrasonic Velocity, Viscosity, Adiabatic Compressibility, Free Length, FreeVolume, Acoustic Impedance, Relaxation Time At 301.15K.

Mole	UE	$\eta^{E\times 10^{-3}}$	$\beta^{E \times 10^{-10}}$	$L_{f}^{E} \times 10^{-11}$	Vf ^E ×10-3	Z^{E}	T ^E ×10-13
Fraction(x)	ms-1	Kgm ⁻³	$Kg^{-1}ms^2$	m	M ³ mole ⁻¹	Kgm ⁻² s ⁻¹	S
0.0	00.00	0.00	0.0000	0.0000	0.00	0.0000	0.0000
0.1	34.71	0.00	-1.4018	-0.3075	0.79	-0.0032	-0.5315
0.2	73.75	-0.01	-2.6916	-0.6380	1.52	0.0124	-1.0769
0.3	78.13	-0.02	-2.7694	-0.6525	2.04	0.0027	-1.2233
0.4	57.31	-0.02	-2.3842	-0.5373	1.49	-0.0129	-0.9763
0.5	64.51	-0.02	-2.4024	-0.5628	1.41	-0.0077	-0.9725
0.6	47.00	-0.02	-1.9111	-0.4308	1.08	-0.0201	-0.7495
0.7	42.63	-0.01	-1.5636	-0.3572	0.76	-0.0196	-0.5768
0.8	32.81	-0.01	-1.1347	-0.2711	0.59	-0.0137	-0.4395
0.9	15.22	-0.01	-0.5370	-0.1170	0.39	-0.0190	-0.2311
1.0	00.00	0.00	0.0000	0.0000	0.00	0.0000	0.0000

Table 2: Excess Values of Ultrasonic Velocity, Viscosity, Adiabatic Compressibility, Free Length, Free Volume, Acoustic Impedance, Relaxation Time At 305.15K.

	1	,					
Mole	U^{E}	$\eta^{E \times 10^{-3}}$	$\beta^{E \times 10^{-10}}$	$L_f E \times 10^{-11}$	$V_{f}^{E} \times 10^{-3}$	Z^{E}	T ^E ×10-13
Fraction(x)	ms^{-1}	Kgm ⁻³	$Kg^{-1}ms^2$	m	$M^{3}mole^{-1}$	Kgm ⁻² s ⁻¹	S
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	17.5530	-0.0046	-0.8360	-0.1626	0.5264	-0.0114	-0.2650
0.2	62.0960	-0.0172	-2.3509	-0.5456	1.7333	0.0073	-0.9294
0.3	55.0690	-0.0188	-2.1934	-0.4884	1.8451	-0.0083	-0.9043
0.4	42.2020	-0.0191	-1.9768	-0.4226	1.4156	-0.0179	-0.7596
0.5	26.1450	-0.0210	-1.5547	-0.3011	1.0922	-0.0342	-0.5688
0.6	15.7480	-0.0160	-1.2815	-0.2336	0.6050	-0.0380	-0.3854
0.7	9.6010	-0.0190	-0.9779	-0.1653	0.6211	-0.0401	-0.3283
0.8	19.7340	-0.0155	-0.9067	-0.1895	0.6318	-0.0203	-0.3542
0.9	-4.9130	-0.0080	-0.2427	-0.0154	0.1174	-0.0001	-0.0430
1.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 3: Excess Values of Ultrasonic Velocity, Viscosity, Adiabatic Compressibility, Free Length, Free Volume, Acoustic Impedance, Relaxation Time At 309.15K.





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Mole Fraction(<i>x</i>)	U ^E ms ⁻¹	η ^E ×10 ⁻³ Kgm ⁻³	$eta^{ extsf{E} imes10^{-10}}$ $Kg^{-1}ms^{2}$	L _f ^E ×10 ⁻¹¹ m	Vf ^E ×10 ⁻³ M ³ mole ⁻¹	Z ^E Kgm ⁻² s ⁻¹	Ţ ^E ×10−13 S
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	23.7760	-0.0015	-1.2061	-0.2482	0.4541	-0.0034	-0.3277
0.2	70.1720	-0.0152	-2.8526	-0.6588	2.2686	0.0165	-1.1693
0.3	64.8380	-0.0144	-2.6938	-0.6064	1.7937	0.0038	-1.0040
0.4	59.5040	-0.0168	-2.5684	-0.5741	1.6210	-0.0011	-0.9505
0.5	51.6700	-0.0200	-2.2632	-0.4980	1.4896	-0.0088	-0.8571
0.6	43.3360	-0.0197	-1.8772	-0.4049	1.2149	-0.0160	-0.7025
0.7	25.0020	-0.0186	-1.3366	-0.2688	0.8056	-0.0227	-0.4867
0.8	12.0880	-0.0164	-0.8736	-0.1647	0.5402	-0.0213	-0.3265
0.9	4.3340	-0.0081	-0.4279	-0.0745	0.1951	-0.0150	-0.1358
1.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4: Excess Values of Ultrasonic Velocity, Viscosity, Adiabatic Compressibility, Free Length, Free Volume, Acoustic Impedance, Relaxation Time At 313.15K.

Mole	UE	$\eta^{E \times 10^{-3}}$	$\beta^{E\times 10^{-10}}$	$L_f^{E \times 10^{-11}}$	$V_{f}E \times 10^{-3}$	ZE	<i>T</i> ^E ×10−13
Fraction(x)	ms-1	Kgm ⁻³	$Kg^{-1}ms^2$	m	M ³ mole ⁻¹	Kgm ⁻² s ⁻¹	S
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	30.3930	0.0002	-1.8162	-0.3602	0.5414	-0.0006	-0.4690
0.2	96.3260	-0.0072	-4.4564	-1.0028	2.3879	0.0329	-1.5765
0.3	102.4690	-0.0139	-4.5273	-1.0259	2.7165	0.0292	-1.6706
0.4	103.8520	-0.0166	-4.3957	-1.0100	2.6453	0.0284	-1.6402
0.5	95.1150	-0.0213	-3.8749	-0.8917	2.5258	0.0199	-1.5054
0.6	83.3780	-0.0209	-3.2658	-0.7547	2.0925	0.0134	-1.2780
0.7	65.6410	-0.0183	-2.5497	-0.5911	1.5373	0.0090	-0.9991
0.8	39.9040	-0.0177	-1.6450	-0.3709	1.0665	-0.0003	-0.6809
0.9	13.1670	-0.0099	-0.6950	-0.1389	0.4062	-0.0098	-0.2651
1.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

In the binary liquid systems under investigation, the variation of ultrasonic velocity (u), adiabatic compressibility (β_a) , molar volume (V_m) , free length (L_f) and acoustic impedance (Z) are measured. In Figure-I, Figure-II, Figure-II, Figure-IV, Figure-V and Figure-VI respectively represents the variation in excess ultrasonic velocity (U^E) , excess viscosity (η^E) , excess adiabatic compressibility (β_a^E) , excess free length (L_f^E) , excess free volume (V_f^E) , excess acoustic impedance (Z^E) and relaxation time (E). These variation indicate the existence of molecular interaction between solvent and solute. The excess adiabatic compressibility (β_a^E) is negative over whole concentration range and it becomes minimum at a concentration (0.2) of tetrhydrofuran in n-hexane at observed temperatures. This indicates that the intermolecular interaction at this optimum at this concentration and it may leads to formation weak hydrogen bonded complex in binary liquid mixture. The same effects are also observed in excess volume (V_f^E) , excess free length and excess acoustic impedance.





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Fig.I: Plots of Excess Ultrasonic Velocity Vs Mole Fraction of Tetrahydrofuran(x) for nhexane - Tetrhydrofuran System at various Temperatures.



Fig.II: Plots of Excess Viscosity Vs Mole Fraction of Tetrahydrofuran(x) for n-hexane - Tetrhydrofuran System at various Temperatures.



Fig.III: Plots of Excess adiabatic compressibility Vs Mole Fraction of Tetrahydrofuran(x) for n-hexane Tetrhydrofuran System at various Temperatures.

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Fig.IV: Plots of Excess free length Vs Mole Fraction of Tetrahydrofuran(x) for n-hexane - Tetrhydrofuran System at various Temperatures.



Fig.V: Plots of Excess free volume Vs Mole Fraction of Tetrahydrofuran(x) for n-hexane - Tetrhydrofuran System at various Temperatures.



Fig.VI: Plots of Excess relaxation time Vs Mole Fraction of Tetrahydrofuran(x) for nhexane - Tetrhydrofuran System at various Temperatures.





CONCLUSION:

Experimental data of the ultrasonic velocity, density and viscosity of nhexane and tetrahydrofuran mixture have been measured over the entire composition range 301.15K, 305.15K, 309.15K and 313.15K. It has been observed that positive deviations of excess velocity, excess free volume, where as negative deviations were observed for excess free length at 301.15K,305.15K, 309.15K and 313.15K. The observed deviation of theoretical values of velocity from the experimental values is attributed to the presence of intermolecular interaction in the system studied.

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