THERMO ACOUSTICAL EXCESS PARAMETERS OF BINARY LIQUID MIXTURE OF 1,4 DIOXANE AND MAGNESIUM HYDROXIDE AT 7 MHZ FREQUENCY

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ABSTRACT

The ultrasonic velocity (U) density (ρ) and viscosity (η) of binary liquid mixture of 1,4 Dioxane ($C_4H_8O_2$)and magnesium Hydroxide $Mg(OH)_2$ (solvent) have been measured over the entire range of compositions at three temperatures 298K, 303K, 308K and frequency 7 MHz. The observed basic experimental data have been utilized to evaluate some of the derived thermo acoustic parameters such as adiabatic compressibility (β_a),molar volume (V_m) relaxation time (τ). The behavior of these derived parameters and their excess values of, adiabatic compressibility (β_a^E),molar volume (V_m^E) relaxation time (τ^E) were evaluated with composition of the mixture and have been discussed in terms of nature and strength of molecular interactions between the constituents. Broad classification study also helps to understand the classification of molecular interactions. .

Keywords: Ultrasonic velocity; acoustical parameters; molecular interactions; binary mixtures; 1,4 Dioxane; Magnesium hydroxide.

I. 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 important 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 1,4 dioxane with the solvent magnesium hydroxide at the temperatures 298K, 303K, 308K and

frequency 7 MHz have been studied in the present paper. The applications of the liquids under investigation have greatly stimulated the need of extensive information on the thermodynamic, acoustic and transport properties of the liquids and their mixture. US studies shows that, it is interesting to note that the thermodynamic result of the binary mixture gives useful information of the molecular interaction [11, 12].

II. EXPERIMENTAL DETAILS:

The liquids were of Analar grade and redistilled before use. The binary mixture of different mole fractions of two components namely 1,4 dioxane and magnesium hydroxide) were prepared immediately before use. For Ultrasonic velocity (U) measurement, Ultrasonic Multi frequency Interferometer (Model No. F-83, Mittal, New Delhi) was used with an accuracy of $\pm 0.1 ms^{-1}$ working at fixed frequency 1MHz**.** An electronically and digitally operated constant temperature water bath has been used to circulate water through the double walled measuring cell made up of steel containing experimental solution at the desired the temperature. The density of pure liquids and liquid mixtures was determined using pycknometer by relative measurement method with an accuracy of $\pm 0.1 Kgm^{-3}$. An Ostwald's viscometer was used for the viscosity measurement of pure liquids and liquid mixtures with an accuracy of $\pm 0.001 NSm^{-2}$. The temperature around the interferometer, viscometer and pycknometer was maintained within $\pm 0.1K$. All necessary precautions were taken to minimize the possible experimental errors. The present work was done with all precautions.

III. THEORITICAL APPROACH:

Using the experimental data of U, ρ and η, various acoustical and their excess parameters such as βa, , Vm, τ & βa^E, V^E_m τ^E were calculated by using standard equations:

$\beta a = 1/ (U^2 \rho)$ .... (1)

$\tau = (4/3)\beta\eta$ ....(2)

   Molar Volume (Vm) = M/ρ_{AB}

  $(Vm) = (MAXA + MBXB)/ \rho_{AB}$ ....(3)

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

  $A^E = A_{exp.} - A_{id.}$ ....(4)

Where $A_{id.} = \sum A_i X_i$, i = 1, 2, 3, n. A_i is any acoustical parameters and x_i the mole fraction of the liquid components. Where, K_T is the Temperature dependent Jacobson's constant in MKS system, T is the absolute temperature. M is the molecular weight, X is weight fraction, ρ_{AB} is the density of liquid mixture. After calculations, graphs were plotted for Adiabatic compressibility (βa), Molar Volume (Vm), Relaxation time (τ) and their excess values verses volume % (X) of 1,4 dioxane and magnesium hydroxide) at 7 MHz. and T K.

IV RESULTS AND DISCUSSION:

Table: 1 The experimentally measured values of ultrasonic velocity (U), density (ρ), viscosity (η) and the calculated values of adiabatic compressibility (βa), molar volume (Vm), relaxation time (τ), also excess adiabatic compressibility (a^E), excess molar volume (V_m^E) excess relaxation time ( ), w.r. to concentration (vol %) of 1,4 dioxane in aqueous magnesium hydroxide (0.1N) at temperature range 298.15K, 303.15K, 308.15K and 7 MHz frequency**.**

Volume % of 1,4 dioxan in aqueous Mg(OH)2 X	(U) m/s	Kg/m³	* 10⁻³ Ns/m² or C P	a*10⁻¹⁰ Pa⁻¹ = m²N⁻¹	Vm*10⁵ (m³/mol)	*10⁻¹² Sec	a^E* 10⁻¹⁰ Pa⁻¹	Vm^E* 10⁻⁵ m³/mol	* 10⁻¹² Sec
				T = 298.15K					
0	1568.1	1007.	0.781	4.037	5.7891		0.000	0.000	0.000
10	1582	1013.	1.262	3.943	6.0494	0.6637	-0.2300	-	0.200
20	1614.6	1019.	1.397	3.761	6.3022	0.7009	-0.5487	-	0.194
30	1624	1027.	1.167	3.691	6.5470	0.5746	-0.7547	-	0.025
40	1638	1032.	1.272	3.610	6.8022	0.6122	-0.9722	-	0.020
50	1656.6	1036.	1.513	3.514	7.0619	0.7092	-1.2036	-	0.074
60	1673	1041.	1.500	3.430	7.3159	0.6863	-1.4237	-	0.009

70	1642.6	1046.	1.540	3.541	7.5653	0.7276	-1.4492	-	0.007
80	1554	1042.	1.452	3.972	7.8808	0.7692	-1.1542	-	0.006
90	1456	1040.	1.412	4.532	8.1798	0.8535	-0.7304	-	0.048
100	1343.1	1026.	1.178	5.399	8.5810	0.8479	0.000	0.000	0.000
T=303.15K									
0	1530.1	1004.	0.709	4.253	5.8070	0.4022	0.000	0.000	0.000
10	1561	1011.	1.136	4.058	6.0610	0.6150	-0.3292	-	0.171
20	1589	1017.	1.267	3.892	6.3169	0.6576	-0.6288	-	0.173
30	1603	1025.	1.043	3.797	6.5616	0.5281	-0.8583	-	0.003
40	1614.6	1030.	1.152	3.722	6.8159	0.5720	-1.0668	-	0.006
50	1633.3	1035.	1.338	3.621	7.0718	0.6463	-1.3024	-	0.039
60	1642.2	1039.	1.324	3.566	7.3268	0.6296	-1.4913	-	-
70	1603	1043.	1.370	3.729	7.5865	0.6815	-1.4619	-	-
80	1519	1039.	1.254	4.171	7.9061	0.6978	-1.1541	-	-
90	1414	1037.	1.214	4.822	8.2078	0.7811	-0.6368	-	0.010
100	1322.3	1022.	1.088	5.593	8.6171	0.8114	0.000	0.000	0.000
T=308.15K									
0	1500.1	1000.	0.625	4.441	5.8288	0.3705	0.000	0.000	0.000
10	1526	1009.	0.914	4.255	6.0733	0.5190	-0.3240	-	0.108
20	1558.6	1014.	1.179	4.058	6.3362	0.6379	-0.6588	-	0.186
30	1572.6	1022.	0.942	3.956	6.5808	0.4973	-0.8979	-	0.005
40	1605.3	1027.	1.017	3.778	6.8387	0.5126	-1.2136	-	
50	1624	1031.	1.203	3.674	7.0947	0.5896	-1.4553	-	0.017
60	1638	1037.	1.201	3.594	7.3468	0.5756	-1.6735	-	-
70	1561	1039.	1.217	3.947	7.6140	0.6409	-1.4583	-	-
80	1498	1035.	1.105	4.304	7.9349	0.6344	-1.2383	-	-
90	1362.2	1031.	1.066	5.223	8.2510	0.7429	-0.4571	-	0.008
100	1300.1	1016.	0.998	5.818	8.6654	0.7746	0.000	0.000	0.000

Excess parameters with concentration are zero at end points with positive or negative values. They plays a vital role in assessing the compactness due to molecular arrangement and extent of molecular interaction in liquid mixtures through charge transfer, dipole –dipole and dipole –induced dipole interaction [13]. Table and fig 1 shows the variation of excess values of relaxation time τ^E verses concentration (vol. %) of 1,4 dioxane in aqueous magnesium hydroxide due to presence of strong or weak interaction [14] It is observed that, not all excess values are positive in the liquid system over the entire range of concentration. Positive excess values are varying, (shows peaks at 10-20% and 30%, 90% concentration). The positive excess values of relaxation time τ^E and Z^E ($\tau^E \propto Z^E$) indicates that, there exist a strong molecular interaction between the unlike component molecules of liquid mixture [15].

According to Reed et.al [16] the positive excess values can be attributed to specific Interaction like hydrogen bonding and charge transfer. Nature and force existing between molecules is known. (May be solvent –solute or ion –induced dipole interaction) When temperature is increased positive excess values of relaxation time τ^E slightly decreases with same trend of variation. The decrease in positive excess values of relaxation time at middle concentration, at 40%,60% & 80% & then increase up to zero, to positive excess values, is due to the possible structural relaxation process plays a predominant role over thermal relaxation process. Viscosity of constituent molecules also plays important role in some negative values of relaxation time, being a characteristic property of the individual constituents, but supports Strong interaction. Excess values of adiabatic compressibility βa^E

and excess molar volume V_m^E are negative. $\beta a \, \alpha \, 1/Za, V_m = M_{eff}/\rho$ The negative deviation of excess values is an indication of existence of strong interaction between the component molecules [17]. Also indicates strong molecular dissociation between the unlike molecules.

Table1 and fig 2A, fig 3A shows the variation of excess values of adiabatic compressibility βa^E and molar volume V_m^E verses concentration (vol.%) of 1,4 dioxane in aqueous magnesium hydroxide, respectively. In fig 2A, it is observed that, all excess βa^E values are negative in the binary liquid system over the entire range of concentration (vol.%). For excess values of adiabatic compressibility βa^E and L_f^E with the increase in concentration (vol.%) of 1,4 dioxane in aqueous magnesium hydroxide, the varying excess values of βa^E decreases negatively in magnitude and approach to minimum at around 60-70 % concentration(vol.%) and again increases up to zero. which shows that maximum structural changes take place in this region of the mixture. It further suggests that decrease in adiabatic compressibility and free length, as ($\beta a \, \alpha \, L_f$) and increase at higher concentration (βa^E and $L_f^{\,E}$) indicates the, structure breaking tendency due to hetero molecules, and existence of dispersive forces. Negative values of βa^E and $L_f^{\,E}$ shows closely packed molecules, strong interaction between the component molecules of mixture [18]. Sri Devi et al [19] suggested that the negative excess values are due to closely packed molecules, which shows existence of strong molecular interaction and positive excess values to weak interaction, between the unlike molecules. Table and fig 3A shows the variation of excess values of molar volume V_m^E verses concentration (vol. %) of 1,4 dioxane in aqueous magnesium hydroxide. It is observed that, all excess values are negative in the binary liquid system, over the entire range of composition. With the increase in concentration(vol.%) of 1,4dioxane in aqueous magnesium hydroxide, the varying excess values of V_m^E decreases negatively in magnitude and approach to minimum at around 70%, & then increases up to zero. So maximum structural changes take place in this region of the mixture. A negative excess value indicates strong interaction, strong molecular dissociation between unlike component molecules, due structural characteristic property. With increase in temperature, negative excess values of adiabatic compressibility βa^E and molar volume V_m^E again decreases keeping same variation trend separately. Table and Fig 2B (βa^E %) and Fig 3B (V_m^E %) have similar negative excess values and trend, are used in Broad classification, which gives interpretation of molecular interaction in any binary liquid-

Case No	β_a^E	V_m^E	Nature*
1	Negative	Negative	Association
2	Positive	Positive	Dissociation
3	Negative	Positive	Ordering
4	Positive	Negative	conceal

Here % Ba^E and %Vm^E are negative

CONCLUSIONS:

1. As 1,4 dioxane is non polar dipole-induced dipole type strong or weak dispersive type molecular interactions exist between solute and solvent in binary liquid mixture.

2. Non linear excess parameters plays very important role by comparing experimental and ideal (standard) values which gives knowledge about molecular interactions.

3. The heteromolecular AB interaction doesn't lead to complex formation. The system investigated is classified as case I (both % Ba^E is negative and %Vm^E is negative as per broad classification).

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