Ultrasonic Study of Molecular Interactions in Binary Mixtures at 303 K

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Abstract: The ultrasonic velocity, density and viscosity at 303 K have been measured in the binary systems of 1,4-dioxane and acetone with water. From the experimental data, various acoustical parameters such as adiabatic compressibility (β), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i), Rao's constant (R), Wada's constant (W) and specific acoustical impedance (Z) were calculated. The results are interpreted in terms of molecular interaction between the components of the mixtures.

Keywords: Ultrasonic velocity, Acoustical properties, Molecular interactions.

Introduction

Ultrasonic technique has been adequately employed to investigate the properties of any substance to understand the nature of molecular interactions in pure liquid¹, liquid mixtures²⁻⁵ and ionic interactions in electrolytic solutions^{6,7}. Though the molecular interactions studies can be best carried out through spectroscopic methods^{8,9} the other non spectroscopic techniques such as dielectric¹⁰ magnetic¹¹ ultrasonic velocity and viscosity¹²⁻¹⁴ measurements have been widely used in field of interactions and structural aspect evaluations studies. In the present work an attempt has been made to investigate the behaviour of binary solutions of water in 1,4-dioxane and acetone with regard to adiabatic compressibility, intermolecular free length and specific acoustic impedance from ultrasonic measurements at 303 K.

Experimental

Solutions of different molality (m) were prepared for each binary system. The ultrasonic velocity in the mixtures was measured using a variable path fixed frequency ultrasonic

interferometer working at 2 MHz frequency (Mittal Enterprises, New Delhi). The accuracy of sound velocity was $\pm 0.1 \text{ ms}^{-1}$. The density and viscosity of the mixture were measured using a specific gravity bottle (5 mL) and Ostwald's viscometer (10 mL) respectively. The accuracy in density measurement was $\pm 0.0001 \text{ kg m}^{-3}$ and that in viscosity measurement was $\pm 0.001 \text{ mNsm}^{-2}$.

Results and Discussion

Various acoustical parameters such as adiabatic compressibility (β), Intermolecular free length (L_f), free volume (V_f), internal pressure (π_i), Rao's constant (R), Wada's constant (W) and specific acoustical impedance (Z), were calculated using the experimental data of ultrasonic sound velocity, density and viscosity by the following equations (1-7).

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

$$L_f = k_T (\beta)^{1/2} \quad (2)$$

$$V_f = (M_{eff} U / \eta k)^{3/2} \quad (3)$$

$$\pi_i = bRT (k\eta/U)^{1/2} (\rho^{2/3}/M^{7/6}) \quad (4)$$

$$R = U^{\frac{1}{3}} V \quad (5)$$

$$W = \beta^{1/7} V \quad (6)$$

and

$$Z = U\rho \quad (7)$$

Where, all the notations having the usual meanings,

The measured parameters *viz.*, ultrasonic velocity (U), density (ρ) and viscosity (η) are given in Table 1. Table shows that, in both the systems 1 and 2, velocity increases with concentration of dioxane and acetone. This indicates that strong interaction observed at higher concentrations of X_2 . The density values also same trend with velocity in the system 1, but in case of system 2 its completely reverse trend with that of velocity. This is due to the density of acetone is less than that of water. Viscosity decreases in system 2 and increases in system 1, suggesting thereby more association between solute and solvent molecules in latter systems. The shear viscosity increases with increase in molality once again confirmed that the solute-solvent interaction.

From the same Table 1, it is observed that adiabatic compressibility (β) decreases with increase in concentration of dioxane as expected. This increase structural order of water may result in more cohesion, and leads to a decrease in (β). The decrease in (β) results in an increase in the value of (U). The free length (L_f) is another parameter which is calculated using ultrasonic velocity and adiabatic compressibility. It is observed that L_f decreases with the concentration of dioxane in system 1, whereas it increases for system 2. It has been observed that intermolecular free length decreases with mole fraction. Decrease in intermolecular free length leads to positive deviation in sound velocity and negative deviation in compressibility. This indicates that the molecules are nearer in the system.

The computed other parameters like free volume and internal pressure are given in Table 1. The variation in free volume (V_f) increases with increases in molality of dioxane in system 1. The free volume is the space available for the molecule to move in an imaginary unit cell. This reduces internal pressure. The variations in internal pressure are given in the same Table 1. As stated above the internal pressure decreases with increase in molality of dioxane. An inverse trend, as expected, is seen in the free volume changes. The observed decreases values of V_f in system 1 are due to close association between solute and solvent

molecules than system 2. Thus it is observed that in system 2 show different results from those of other three components¹³. Thus, a progressive decrease in free volume and increase in internal pressure in water-dioxane mixtures clearly indicates the existence of ion-solvent interaction, due to which the structural arrangement is considerably affected.

The acoustic impedance (Z) is the product of ultrasonic velocity and density of the solution. The value of acoustic impedance also increases with increase in concentration of dioxane. This also indicates significant interactions in the system 1. Decrease in L_f and increase of Z with the concentration of dioxane, suggest presence of solvent-solute interactions in system 1. The molar sound velocity (R) and molar compressibility (W) were increasing linearly with molality of dioxane indicating the solute-solvent interactions may occur¹⁵ in the system 1.

Table 1. Measured parameters for water + 1, 4 dioxane, benzene at 303 K.

X2	U ms ⁻¹	ρ kgm ⁻³	$\eta \times 10^3$ Nsm ⁻²	$\beta \times 10^{10}$ N ⁻¹ m ²	$L_f \times 10^{11}$ M	$V_f \times 10^8$ m ³ mol ⁻¹	$\pi_i \times 10^5$ Nm ⁻²	$R \times 10^{-3}$ m ^{10/3} s ^{-1/3} mol ⁻¹	W m ³ /mole (N/m ²) ^{1/7}	Zx10 kgm ⁻² s ⁻¹
Water+dioxane (1)										
0.0193	1547	0.9972	1.1347	4.1668	4.0729	0.0477	8.9914	0.2222	0.4203	1.5427
0.0423	1566	1.0022	1.2556	4.0867	4.0336	0.0463	8.6969	0.2379	0.4496	1.5694
0.0697	1571	1.0044	1.3162	4.0696	4.0252	0.0487	8.1382	0.2567	0.4848	1.5779
0.0997	1573	1.0149	1.6916	4.1017	4.0410	0.0376	8.4765	0.2748	0.5182	1.5964
0.1377	1579	1.0208	1.7717	4.0943	4.0374	0.0404	7.8181	0.2996	0.5643	1.6118
Water+acetone (2)										
0.0128	1549	0.9817	1.1059	4.0916	4.0361	0.0472	9.1366	0.2182	0.4136	1.5207
0.0271	1557	0.9713	1.2839	4.0065	3.9939	0.0398	9.4084	0.2278	0.4323	1.5123
0.443	1564	0.9618	1.2824	3.9321	3.9566	0.0423	8.9428	0.2387	0.4536	1.5043
0.0646	1572	0.9529	1.4677	3.8561	3.9182	0.0370	9.0477	0.2512	0.4780	1.4980
0.0867	1581	0.9418	1.4614	3.7677	3.8730	0.0400	8.5036	0.2657	0.5062	1.4889

Ultrasonic velocity (U), Density (ρ) Viscosity (η) Calculated adiabatic compressibility (β), Free length (L_f), Free volume (V_f), Internal pressure (π_i), Rao's constant (R), Wada's constant (W) and Specific acoustic impedance (Z)

Conclusion

The ultrasonic velocity, density, viscosity and other related parameters were calculated. The observed increase of ultrasonic velocity indicates the solute-solvent interaction. The existence of type of molecular interaction is solute-solvent is favored in system 1 and 2, confirmed from the Z, U and η etc., the existence of solute-solvent interaction is in the order: Acetone > 1, 4-dioxane.

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