

Ultrasonic Studies of Molecular Interactions in Ternary Mixtures Containing Water, Acetonitrile and T-Butanol

Dr. V. Siva Prasad^{1*}, Dr. Raja Sekhara Reddy K.²

¹Department of Physics, Govt. Firstgrade College, Channapatna-562 160, Karnataka, India

²Department of Mathematics, Govt. Firstgrade College, Gauribidanur-561208, Karnataka, India

*Corresponding Author Email Address: varakuti[at]gmail.com

Abstract: *Ultrasonic speeds in and isentropic compressibilities of a liquid is fundamentally related to binding forces between the atoms or molecules. The measurements of ultrasonic velocity have been adequately employed in understanding the nature of molecular interaction in pure liquids, binary and ternary mixtures. In this research paper we have studied the effect of aqueous solutions of Water + acetonitrile (AN) + t-butanol at 298.15 K. The concentrations of t-butanol at which ultrasonic speed becomes maximum and isentropic compressibility becomes minimum are found to decrease with increase in the concentration of acetonitrile in the cosolvent (Aqueous acetonitrile). This behaviour indicates that the aqueous ternary solutions are less structured than aqueous t-butanol. This behaviour is explained as due to a decrease in the ability of t-butanol to form clathrate hydrates owing to the presence of acetonitrile. When the concentration of acetonitrile in the cosolvent (x_{AN}) > 0.1015, ultrasonic speed decreases and isentropic compressibility increases with concentration of t-butanol indicating that the ternary solution behaving as normal solution. Further addition of acetonitrile or t-butanol leads to destabilization of the hydrogen bonded structure of water and t-butanol loses its ability to form clathrate hydrates in aqueous solutions.*

Keywords: Ternary mixture, ultrasonic speed, compressibility, clathrate hydrates, hydrogen bond, nonelectrolytes

1. Introduction

The measurement of ultrasonic velocity enables the accurate determination of some useful acoustic and thermodynamic parameters, their excess functions, which are highly sensitive to molecular interactions, thus, provide qualitative information about the physical nature and strength of intermolecular interactions in liquid mixtures. In recent years, there has been considerable advancement in the experimental investigation of excess thermodynamic properties of liquid mixtures. These properties have been adequately employed in understanding the nature of molecular interactions in binary and ternary liquid mixtures. In chemical industry, knowledge of the thermodynamic properties of non-electrolyte solutions is essential in the design involving chemical separation, heat transfer, mass transfer and fluid flow. Ultrasonic speed and compressibility behaviour of binary and ternary mixtures containing water and nonelectrolytes have been studied extensively, particularly at very low concentration of nonelectrolytes [1-15]. The peak observed in ultrasonic speed versus concentration of nonelectrolyte in water + nonelectrolyte mixture has been attributed to stabilization of the three dimensional hydrogen bonded structure of water by the nonelectrolyte leading to formation of clathrate hydrates. The ultrasonic speed peak observed at $x_{t-B} \approx 0.05$ of t-butanol in water + t-butanol binary mixture [10, 13, 14] has been attributed to clathrate hydrate formation. It would be interesting to study how the structure of ternary systems would be, containing water and completely miscible nonelectrolytes when present in small amounts, that is, at very low concentrations. It is from this angle we have taken up the study of ultrasonic speed and isentropic compressibility of water + acetonitrile + t-butanol mixtures to see how the clathrate hydrate

structure of aqueous t-butanol would get influenced by the presence of increasing amounts of acetonitrile. The results are reported here.

2. Experimental

Materials

Analytical reagent grade acetonitrile and t-butanol were purified according to the standard procedures [16]. The densities of the pure liquids determined using a bicapillary type pycnometer with an accuracy of 2 parts in 1^5 are 780.92 kg^{-3} and 776.54 kg^{-3} for t-butanol and acetonitrile 0 mm respectively at 298.15 K. These values are in good agreement with literature values [17, 18, 19].

Triple distilled degassed water was used to prepare stock solutions (varied concentrations) of aqueous acetonitrile. This stock solution was used to prepare ternary solution of t-butanol of desired concentration. The concentration of t-butanol in the ternary solution was calculated by considering aqueous acetonitrile binary stock solution as a cosolvent of effective molecular weight M_{12} given by $x_w M_w + x_s M_s$ where M_w , M_s and x_w , x_s represent the molecular weights and mole fractions of water and acetonitrile respectively. All solutions were prepared by weight with an accuracy of 0.1 mg. The buoyancy corrected weights were used for calculating the mole fractions. The error involved in the estimation of mole fractions of the samples is of the order of 1×10^{-4} .

Measurements

Ultrasonic speeds in pure liquids and aqueous binary (water + acetonitrile) and ternary (water + acetonitrile + t-

butanol) solutions at 298.15 K were determined using a single crystal variable path interferometer designed and fabricated in our laboratory. A tri-tet crystal controlled oscillator with frequency stability of ± 1 Hz was used to excite the quartz transducer. The quartz transducer whose fundamental frequency is 1 MHz was excited at its third harmonic. The frequency was measured with a digital frequency meter with an accuracy of one part per million. The voltage variations across the transducer were observed using a difference amplifier followed by an electronic voltmeter.

The mechanical assembly of the interferometer was immersed in a thermostatic water bath whose temperature can be controlled to $\pm 0.01^\circ\text{C}$ using suitable permanent heaters followed by "On and Off" low wattage heaters. The temperature gradients inside the experimental liquid were minimized by stirring it periodically. The temperature of the interferometric liquid measured using a bead type thermistor, which forms one arm of the constant current Wheatstone bridge followed by chopper-stabilized operational amplifier as null detector, was found to be controlled to within $\pm 0.005^\circ\text{C}$. The thermostat and the electronic assembly were housed in the air-conditioned room whose temperature was maintained at $20 \pm 1^\circ\text{C}$. The path length was measured for 50 dips. For each solution six to eight measurements were made and the average was chosen as the ultrasonic speed which was found to be accurate to $\pm 0.05 \text{ m}^{-1}$. The densities of the solutions were also determined using a bicapillary type pycnometer with an accuracy of 2 in 10^5 .

The ultrasonic speeds (u), densities (ρ), molar volumes (V), molar heat capacities at constant pressure (C_p), thermal expansion coefficient (α), isentropic compressibilities (β) and isothermal compressibilities (K) of pure liquids are presented in Table 1. The data are taken from literature [17, 18, 19].

3. Results and Discussion

Ultrasonic speeds (u_{ts}) in and densities (ρ_{ts}) of aqueous acetonitrile at different concentrations of t-butanol are presented in Table 2. The isentropic compressibility (β_{ts}) of the ternary solutions have been evaluated using the standard relation $\beta_{ts} = [u_{ts} \rho_{ts}]$.

The excess ultrasonic speeds in the ternary solutions have been determined using the following expressions [20].

where and

$$u_{ts} \text{ exp } ts \text{ id}$$

$$(u_{ts})_{id} = [(\beta_{ts})_{id} (\rho_{ts})_{id}]^{-1/2} \quad (2)$$

$$(\beta_{ts})_{id} = (K_{ts})_{id} - [T (V_{ts})_{id} (\alpha_{ts})_{id} / ((C_p)_{ts})_{id}] \quad (3)$$

In the above equations

$$(\rho_{ts})_{id} = \Phi_{t-B} \rho_{t-B} + \Phi_{cs} \rho_{cs} \quad (4)$$

$$(K_{ts})_{id} = \Phi_{t-B} K_{t-B} + \Phi_{cs} K_{cs} \quad (5)$$

$$(V_{ts})_{id} = x_{t-B} V_{t-B} + x_{cs} V_{cs} \quad (6)$$

$$(\alpha_{ts})_{id} = \Phi_{t-B} \alpha_{t-B} + \Phi_{cs} \alpha_{cs} \quad (7) \quad [(C_p)_{ts}]_{id} = x_{t-B}$$

$$(C_p)_{t-B} + x_{cs} (C_p)_{cs} \quad (8)$$

where Φ , x , β , K , ρ , α , V and C_p represent the Volume fraction, mole fraction, isentropic compressibility, isothermal compressibility, density, thermal expansion coefficient, molar volume and molar heat capacity at constant pressure respectively. The suffixes ts , $t-B$ and cs refer to ternary solution, t-Butanol and cosolvent respectively. The K_{cs} , α_{cs} , $(C_p)_{cs}$ of cosolvent of different concentrations of acetonitrile have been taken from the experimental data available in literature [21, 22].

The data presented in Table 2 are used to evaluate $(\beta_{ts})_{id}$ and hence $(u_{ts})_{id}$. The excess isentropic compressibilities $(\beta_{ts})^E$ in the ternary solutions were evaluated using the relation.

$$\beta_{ts} \text{ ts Exp } ts \text{ id}$$

The excess sound speeds and excess isentropic compressibilities are also presented in Table 3. The variation of isentropic compressibility (β_{ts}), excess sound speed (u_{tsE}) and excess isentropic compressibility (β_{tsE}) with molefraction of t-butanol [23] in the ternary solution (Water + acetonitrile + t-butanol) at different concentrations of acetonitrile in the cosolvent (water + acetonitrile) are presented graphically in Figs. 2-4 respectively.

An examination of the data presented in Figure 1 indicate that as the concentration of t-butanol increases, the speed of the ternary system increases and decreases on further increase of concentration of t-butanol. Whereas for concentration $x_{AN} = 0.1031$, the behaviour of the curve changes viz. as the concentration of t-butanol increases there is decrease in speed of the ternary system. The concentration of t-butanol at which ultrasonic speed reaches a maximum decreases with increase in concentration of acetonitrile (x_{AN}). In addition at concentration $x_{AN} = 0.0115$ the curve giving $(x_{t-B})_{opt}$ values of 0.053 which is more than 0.050 of water + t-butanol binary system. This indicates the ternary system of $x_{AN} = 0.0115$ is more structured than water + t-butanol at 0.05. Tamura et. al. [24] interpreted that acetonitrile acting as structure maker. In the water rich region acetonitrile prefers to interact with the free water molecule through weak hydrogen bonding rather than accommodated within the water structures and in the water rich region, $x_w \geq 0.9$ from the volumetric properties of water + acetonitrile mixture indicate that acetonitrile behaves as a structure maker.

Handa et. al. [25] explained the maxima in excess thermal expansion versus mole fraction through the collective effect of acetonitrile and of thermal energy to water. The deviation from the normal behaviour in the ultrasonic speed curves at about $x_{AN} = 0.1031$ may be interpreted that

the mixture is behaving like a structure breaker. Below this concentration the net effect is playing a predominant part in making the solution as structure maker.

An examination of the data presented in Figure 2 indicates that isentropic compressibility decreases with increase in concentration of t-butanol up to a particular concentration $(x_{t-B})_{opt}$ and on further increase, the isentropic compressibility increases. However, for the concentration $x_{AN} = 0.1031$ the isentropic compressibility increases abruptly up to $x_{t-B} = 0.005$ and thereafter linearly with concentration. This is similar to the behaviour observed in ultrasonic speed studies.

As seen from Figure 3, the u^E of this ternary solution increases abruptly with the concentration of t-butanol (x_{t-B}) , up to a particular concentration $(x_{t-B})_{opt}$ and then the variation is almost constant.

As seen from Figure 4, the β_{ts}^E decreases with increase in concentration of x_{t-B} . All these results indicate a behaviour similar to ultrasonic speed variation as shown in Figure 1.

In Table 3 are presented $(x_{t-B})_{opt}$ versus x_{AN} in the cosolvent observed E in u_{ts} , β_{ts} and u_{ts} versus x_{t-B} for the ternary system of water + acetonitrile + t-butanol. An examination of the data presented in Table 2 indicates that when x_{AN} in the cosolvent exceeds 0.1015, any further addition of t-butanol leads to destabilization of the hydrogen bonded structure of water and t-butanol loses its ability to form clathrate hydrates in aqueous solutions.

4. Conclusions

The ultrasonic speed maximum and isentropic compressibility minimum shift towards lower concentrations of t-butanol as the concentration of acetonitrile increases in the ternary solution. In lower concentrations the ternary system is more structured than the binary system particularly at $x_{AN} = 0.0115$ the curve giving $(x_{t-B})_{opt}$ values of 0.053 which is more than 0.050 of water + t-butanol binary system. This indicates the ternary system of $x_{AN} = 0.0115$ is more structured than water + t-butanol at 0.05. When the concentration of acetonitrile in the cosolvent is more than 0.1015 molefraction, the ultrasonic speed decreases linearly and isentropic compressibility increases linearly with concentration of t-butanol, the solution exhibiting the behaviour of a normal solution. The concentration dependences of excess ultrasonic speed and excess isentropic compressibility also reflect this behaviour of the ternary solution. When $x_{AN} > 0.1015$ both u^E and β^E vary linearly with molefraction of t-butanol and a β t-butanol loses its ability to form clathrate hydrates in aqueous solutions.

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Table 1: u, ρ, V, Cp, α, β and K of pure liquids at 298.15 K

Liquid	U (m s ⁻¹)	ρ (Kg m ⁻³)	V x 10 ⁶ (m ³ mol ⁻¹)	C _p (J mol ⁻¹ K ⁻¹)	α x 10 ⁶ (K ⁻¹)	βx10 ¹¹ (N ⁻¹ m ²)	Kx10 ¹¹ (N ⁻¹ m ²)	Ref.
Water	1496.	997.0	18.08	75.3	2.59	44.77	45.25	9
	7	7		0				
t-butanol	1123.	780.9	94.91	224.	12.6	101.5	121.72	9
	2	2		9	8	0		
Acetonitrile	1278.	776.5	91.0	13.7	78.8	111.4	41.26	17,1
	0	4		2	4	3		8

Table 2: u_{ts}, ρ_{ts}, β_{ts}, (u_{ts})_{id}, (β_{ts})_{id} and u_{ts}^E, β_{ts}^E versus mole fraction of t-butanol (x t-B) in the cosolvent (water + acetonitrile) at 298.15 K

x _{t-B}	u _{ts}	ρ _{ts}	β _{ts}	(β _{ts}) _{id}	β _{ts} ^E	(u _{ts}) _{id}	u _{ts} ^E
x _{AN} = 0.0115							
0.0000	1525.4	1015.92	42.3	-	-	-	-
0.0082	1540.6	1005.52	41.9	49.7	-7.8	1431.9	108.7
0.0214	1558.3	997.12	41.3	53.9	-12.6	1384.4	173.9
0.0326	1569.5	992.55	40.9	57.0	-16.1	1352.2	217.3
0.0453	1576.4	986.29	40.8	60.3	-19.5	1322.4	254.0
0.0604	1570.6	974.78	41.6	63.7	-22.1	1293.6	277.0
0.0693	1554.8	971.04	42.6	65.6	-23.0	1279.4	275.4
0.0754	1537.3	969.38	43.7	66.7	-23.0	1270.5	266.8
0.0825	1519.4	966.89	44.8	68.1	-23.3	1261.1	258.3
x _{AN} = 0.0326							
0.0000	1539.4	1029.23	41.0	-	-	-	-
0.0081	1555.2	1018.36	40.6	52.8	-12.2	1397.0	158.2
0.0138	1561.5	1017.67	40.3	54.5	-14.2	1378.9	182.6
0.0254	1583.4	997.14	40.0	57.7	-17.7	1347.3	236.1
0.0361	1587.9	993.98	39.9	60.4	-20.5	1323.0	264.9
0.0472	1582.6	985.83	40.5	62.9	-22.4	1301.7	280.9
0.0576	1570.5	981.68	41.3	65.1	-23.8	1284.5	286.0
0.0634	1558.3	980.50	42.0	66.2	-24.2	1275.9	282.4
0.0712	1541.7	973.91	43.2	67.6	-24.4	1265.3	276.4

$x_{AN} = 0.0508$							
0.0000	1550.4	1038.81	40.0	-	-	-	-
0.0061	1565.6	1030.25	39.6	54.8	-15.2	1377.5	188.1
0.0124	1578.2	1021.60	39.3	56.5	-17.2	1360	218.2
0.0183	1589.4	1012.41	39.1	58.0	-18.9	1345.3	244.1
0.0274	1593.1	1007.71	39.1	60.3	-21.2	1325.0	268.1
0.0393	1587.3	1004.81	39.5	62.9	-23.4	1302.3	285.0
0.0482	1577.6	987.21	40.7	64.8	-24.1	1287.7	289.9
0.0554	1565.4	976.27	41.8	66.2	-24.4	1277.0	288.4
0.0615	1551.5	963.87	43.1	67.3	-24.2	1268.8	282.7

$X_{i,B}$	u_{is}	ρ_{is}	β_{is}	$(\beta_{is})_{id}$	β_{is}^E	$(u_{is})_{id}$	u_{is}^E
$x_{AN} = 0.0714$							
0.0000	1539.4	1029.23	41.0	-	-	-	-
0.0081	1555.2	1018.36	40.6	52.8	-12.2	1397.0	158.2
0.0138	1561.5	1017.67	40.3	54.5	-14.2	1378.9	182.6
0.0254	1583.4	997.14	40.0	57.7	-17.7	1347.3	236.1
0.0361	1587.9	993.98	39.9	60.4	-20.5	1323.0	264.9
0.0472	1582.6	985.83	40.5	62.9	-22.4	1301.7	280.9
0.0576	1570.5	981.68	41.3	65.1	-23.8	1284.5	286.0
0.0634	1558.3	980.50	42.0	66.2	-24.2	1275.9	282.4
0.0712	1541.7	973.91	43.2	67.6	-24.4	1265.3	276.4

$x_{AN} = 0.0894$							
0.0000	1548.4	1076.28	38.8	-	-	-	-
0.0056	1560.2	1075.41	38.2	59.6	-21.4	1334.2	226.0
0.0136	1555.3	1073.76	38.5	61.5	-23.0	1316.7	238.6
0.0203	1547.5	1070.71	39.0	63.1	-24.1	1303.7	243.8
0.0264	1538.4	1061.64	39.8	64.4	-24.6	1292.9	245.5
0.0353	1530.7	1040.96	41.0	66.3	-25.3	1278.8	251.9
0.0424	1519.8	1025.92	42.2	67.7	-25.5	1268.8	251.0
0.0515	1511.4	1011.01	43.3	69.3	-26.0	1257.2	254.2

$x_{AN} = 0.1031$							
0.0000	1542.6	1110.78	37.8	-	-	-	-
0.0023	1536.6	1078.12	39.3	60.2	-20.9	1329.0	207.6
0.0051	1532.4	1076.26	39.6	60.9	-21.3	1322.8	209.6
0.0104	1528.8	1073.71	39.8	62.2	-22.4	1311.9	216.9
0.0206	1524.6	1071.73	40.1	64.5	-24.4	1293.3	231.3
0.0314	1522.3	1069.74	40.3	66.7	-26.4	1276.4	245.9
0.0451	1520.3	1065.46	40.6	69.3	-28.7	1258.2	262.1
0.0602	1517.8	1062.21	40.9	71.8	-30.9	1241.6	276.2

Table 3: (x t-B) opt versus x AN in the cosolvent observed in u, β , u E and β E versus (x t-B) in the ternary solutions of water + acetonitrile + t-butanol

X_{AN}	$(X_{t-B})_{opt}$		
	u_{ts}	β_{ts}	U_{ts}^E
0.0000	0.051	0.048	0.065
0.0115	0.053	0.045	0.062
0.0326	0.038	0.035	0.051
0.0508	0.030	0.029	0.048
0.0714	0.020	0.016	0.035
0.0894	0.011	0.007	0.025
0.1031	-	-	-

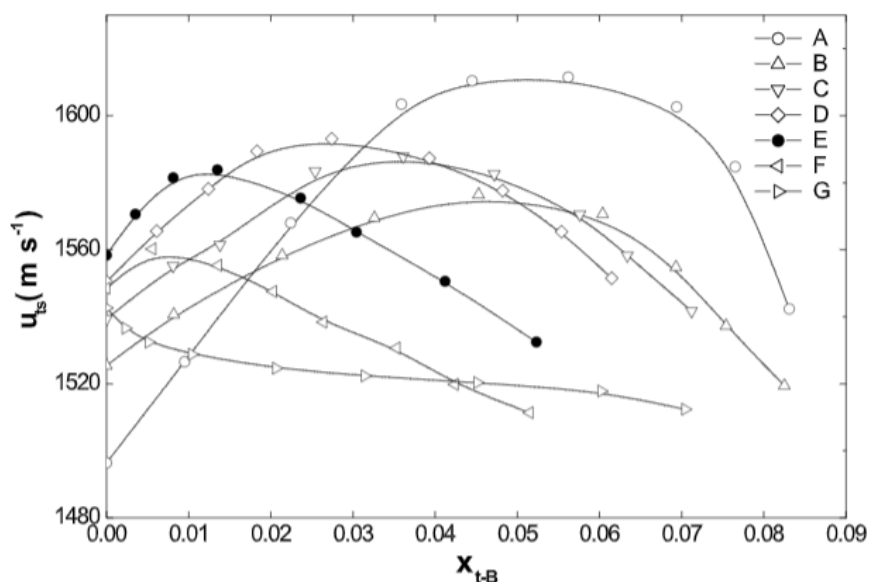


Figure 1

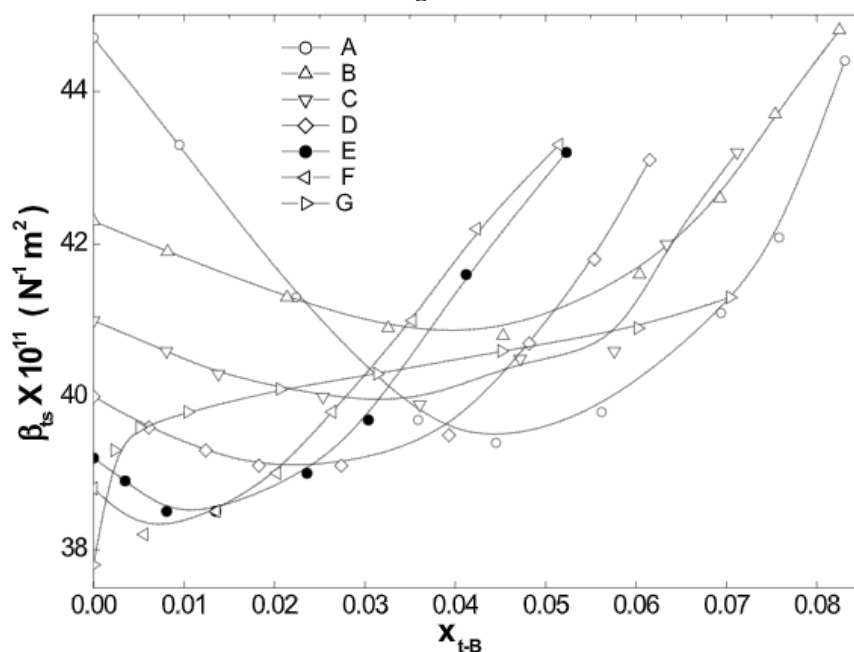


Figure 2

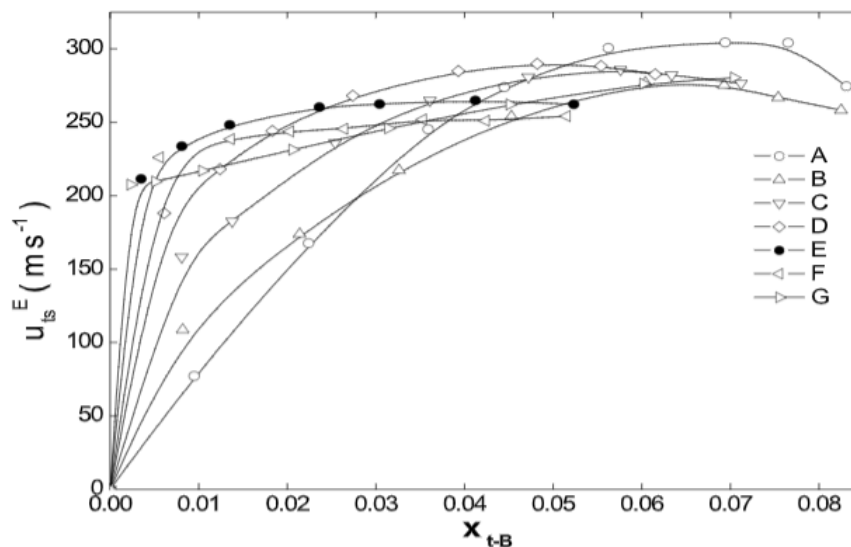


Figure 3

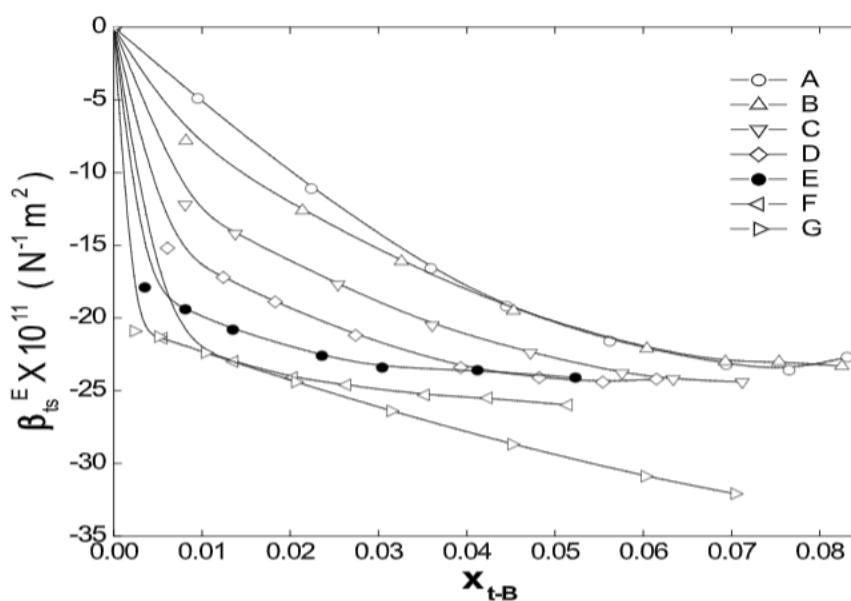


Figure 4

Figure Legends

Figure 1: Variation of Ultrasonic velocity (u_{ts}) with mole fraction of t-Butanol (x_{t-B}) in the ternary system (water + Acetonitrile + t-Butanol) at different concentrations of Acetonitrile (x_{AN}) in the cosolvent (water + Acetonitrile) $x_{AN} = A: 0.0000, B:0.0115, C: 0.0326, D: 0.0508, E: 0.0714, F: 0.0894, G: 0.1031$

Figure 2: Variation of adiabatic compressibility (β_{ts}) with mole fraction of t-Butanol (x_{t-B}) in the ternary system (water + Acetonitrile + t-Butanol) at different concentrations of Acetonitrile (x_{AN}) in the co-solvent (water + Acetonitrile) $x_{AN} = A: 0.0000, B:0.0115, C: 0.0326, D: 0.0508, E: 0.0714, F: 0.0894, G: 0.1031$

Figure 3: Variation of excess ultrasonic velocity (u_{ts}^E) with mole fraction of t-Butanol (x_{t-B}) in the ternary system (water + Acetonitrile + t-Butanol) at different concentrations of Acetonitrile (x_{AN}) in the cosolvent (water + Acetonitrile) $x_{AN} = A: 0.0000, B:0.0115, C: 0.0326, D: 0.0508, E: 0.0714, F: 0.0894, G: 0.1031$

Figure 4: Variation of excess adiabatic compressibility (β_{ts}^E) with mole fraction of t-Butanol (x_{t-B}) in the ternary system (water + Acetonitrile + t-Butanol) at different concentrations of Acetonitrile (x_{AN}) in the co-solvent (water + Acetonitrile) $x_{AN} = A: 0.0000, B:0.0115, C: 0.0326, D: 0.0508, E: 0.0714, F: 0.0894, G: 0.1031$