[Vol-1, Issue-4, January-March 2024]
International Journal of Science and Social Science Research [IJSSSR] ISSN: 2583-7877

Thermodynamic studies in ternary mixtures containing water, formamide and t- butanol at 298.15 K

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Abstract— At 298.15 K, ultrasonic speeds and the isentropic compressibilities of aqueous solutions containing formamide (F) + t-butanol have been measured. As the concentration of formamide in the cosolvent (aqueous formamide) increases, it is observed that the concentrations of t-butanol at which isentropic compressibility becomes minimum and ultrasonic speed becomes maximum decrease. This behavior suggests that compared to aqueous t-butanol, aqueous ternary solutions are less structured. The concentration dependence of excess isentropic compressibility and excess ultrasonic speed very nicely reflects this behavior. This behavior is explained by the fact that the presence of formamide reduces t-butanol's capacity to form clathrate hydrates. Isentropic compressibility rises with concentration and ultrasonic speed falls when formamide concentration in the cosolvent (x_F) > 0.2.

Keywords: Ternary solution; ultrasonic speed; isentropic compressibility ;clathrate hydrates; hydrophobic hydration.

I. INTRODUCTION

The knowledge of thermodynamic properties of the mixture is required for efficient designing of separation processes and transport equipment. Intermolecular interactions are critical in ternary and binary liquid mixtures. They alter the compatibility and alignment of the molecules in a solution. The degree of connection in the liquid mixtures was qualitatively assessed using the ultrasonic velocity of the mixtures. Binding forces between atoms or molecules are essentially related to a liquid's ultrasonic velocity. Understanding the nature of molecular interactions in binary and ternary liquid mixtures has made good use of these qualities. 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. 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. Numerous studies have been conducted on the ultrasonic speed and compressibility behavior of binary and ternary mixtures comprising water and nonelectrolytes, especially at extremely low concentrations of nonelectrolytes
[1–14]. The nonelectrolyte's stability of the three-dimensional hydrogen-bonded structure of water has been attributed to the peak in ultrasonic speed observed in relation to its concentration in the water + nonelectrolyte mixture. The ultrasonic behaviour of aqueous t-butanol in the water rich region has been studied extensively in view of highly hydrophobic propensity of t-butanol. The maximum enhancement in the hydrogen structure of water due to the hydrophobic interactions between t-butanol percent of t-butanol as evidenced by the existence of extrema in many of the physical properties. Baumgartner and Atkinson[2] proposed the formation of clathrate hydrates well characterized by 17 hydrate structures from the observation of ultrasonic speed peak at 0.0556 molefraction of t-butanol. The hydroxyl-proton chemical shift that Atkinson and Symons [9] and Bowron et al. [10] observed as a function of temperature in aqueous t-butanol solutions, as well as neutron diffraction investigations, indicate that the strength of the hydrophobic interaction of t-butanol is likewise temperature-sensitive.

It would be interesting to study how the hydrophobic hydration in aqueous t-butanol in the water rich region gets influenced by the presence of small amounts of another completely miscible nonelectrolyte. The authors have studied the ultrasonic behaviour of ternary mixtures of water + t-butanol + 2-ethoxyethanol [20] and water + t-butanol + dimethylformamide [21] and found to be useful in understanding the molecular interactions.The studies on the ultrasonic behaviour of water + t-butanol + formamide are presented and discussed in this paper.

II. EXPERIMENTAL

II.I. MATERIALS

Analytical reagent grade formamide (F) and t-butanol were purified according to the standard procedures[15]. At 298.15 K, the densities of the pure liquids for t-butanol and formamide, respectively, were measured using a bicapillary type pycnometer with an accuracy of 2 parts in 10^5, and 780.92 kg m^{-3}. These findings agree well with values found in the literature [3,13,16, 17].

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

II.II. MEASUREMENTS

A single crystal variable path interferometer that we designed and built in our lab was used to measure ultrasonic speeds in pure liquids, aqueous binary (water + F), and ternary (water + F + t-butanol) solutions at 298.15 K. 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 ±0.01ºC 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 was discovered to be controlled to within by employing a chopper-stabilized operational amplifier as the null detector and a bead type thermistor, which forms one arm of the constant current Wheatstone bridge with an accuracy of ± 0.005ºC. The thermostat and the electronic assembly were housed in the air-conditioned room whose temperature was maintained at 20 ±1º 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 ±0.05 m s^{-1}. Additionally, a bicapillary type pycnometer was used to determine the densities of the solutions with an accuracy of 2 in 10^5.

III. RESULTS AND DISCUSSION

Ultrasonic speeds (u_{ts}) in aqueous formamide at different concentrations of t-butanol are presented graphically in Fig.1. The densities (ρ_{ts}) of aqueous formamide at different concentrations of t-butanol are presented in Table 1. The pure liquid parameters used to evaluate $(\beta_{ts})_{id}$ and hence $(u_{ts})_{id}$ are presented in Table 2. The isentropic compressibility (β_{ts}) of the solutions have been evaluated using the standard relation $\beta_{ts} = [u_{ts}^2\rho_{ts}]^{-1}$. where u_{ts}, and ρ_{ts} represents ultrasonic speed and density of the ternary solution respectively.

The excess isentropic compressibilities of the ternary solutions ($\beta_{ts}^{E)}$ have been evaluated using the relation

$$\beta_{ts}^{E} = \beta_{ts} - [\Phi_{t\text{-}B}\beta_{t\text{-}B} + \Phi_{cs}\beta_{cs}] \tag{1}$$

Where β_{ts} represents the compressibility of the ternary solution and $\beta_{t\text{-}B}$, β_{cs} represent the compressibilities of t-butanol and cosolvent (aqueous F) respectively.$\Phi_{t\text{-}B}$ and Φ_{cs} represent the volume fractions of t-butanol and cosolvent respectively in the ternary solution where

$$\Phi_{t\text{-}B}+\Phi_{cs}=1 \tag{2}$$

The excess ultrasonic speeds in the ternary solutions have been determined using the following expressions [18]

$$u_{ts}^{E}=(u_{ts})_{exp}-(u_{ts})_{id} \tag{3}$$

where

$$(u_{ts})_{id}= [[(\beta_{ts})_{id}(\rho_{ts})_{id}]^{-1}]^{1/2} \tag{4}$$

and

$$(\beta_{ts})_{id} = (K_{ts})_{id} - [\, T\,(V_{ts})_{id}\,(\alpha_{ts})_{id}^2 / ((C_P)_{ts})_{id})\,] \tag{5}$$

here

$$(\rho_{ts})_{id} = \Phi_{t\text{-}B}\rho_{t\text{-}B} + \Phi_{cs}\rho_{cs} \tag{6}$$

$$(K_{ts})_{id}=\Phi_{t\text{-}B}K_{t\text{-}B} + \Phi_{cs}\,K_{cs} \tag{7}$$

$$(V_{ts})_{id} = X_{t\text{-}B}V_{t\text{-}B} + X_{cs}\,V_{cs} \tag{8}$$

$$(\alpha_{ts})_{id} = \Phi_{t\text{-}B}\,\alpha_{t\text{-}B} + \Phi_{cs}\,\alpha_{cs} \tag{9}$$

$$[(C_P)_{ts}]_{id} = X_{t\text{-}B}(C_P)_{t\text{-}B} + X_{cs}\,(C_P)_{cs} \tag{10}$$

where ρ, α, C_P, β, K,V and stand for the corresponding values of the following: density, thermal expansion coefficient, molar heat capacity at constant pressure, isentropic compressibility, isothermal compressibility, and molar volume. 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 Formamide have been taken from the experimental data available in literature [14,19] and are presented in Table 2.

The variation of isentropic compressibility (β_{ts}), excess sound speed (u_{ts}^E) and excess isentropic compressibility (β_{ts}^E) with molefraction of t-butanol[19] in the ternary solution (Water + F + t-butanol) at different concentrations of F in the cosolvent (water + F) are presented graphically in Figs. 2- 4 respectively.

An examination of the data presented in Fig.1 indicates that the concentration of t-butanol at which ultrasonic speed reaches maximum, then decreases with increase in concentration of formamide. This behavior indicates that the ternary system is less structured than the aqueous t-butanol. At a concentration $x_F > 0.2$, ultrasonic speed decreases with increase in the concentration of t-butanol in the ternary solution. This behaviour indicates that the hydrophobic interactions between water and t-butanol molecules leading to clathrate hydrate structure as proposed [2,3,6,7]or the hydrophobic hydration induced local density nhancement in the solvent water by t-butanol as proposed by Bowron et al [10] are influenced by the presence of formamide in the ternary solution. Since formamide is hydrophilic in nature. When t-butanol is added to water + formamide binary system, the clathrate hydrate formation of aqueous t-butanol is destroyed by the formamide. As the concentration of formamide increases more than 0.2 the ternary system behaves like a normal liquid.

An Examination of the data presented in Fig. 2 shows that isentropic compressibility decreases with t-butanol concentration up to certain concentration $(x_{t\text{-}B})_{opt}$ and then increases. When the concentration of $x_F > 0.2$ the isentropic compressibility of the ternary system increases linearly with increasing concentration of t-butanol.

As seen from the Fig. 3 the excess ultrasonic speed reaches a maximum up to a particular concentration of $x_{t\text{-}B}$ and then remains almost constant with increase in $x_{t\text{-}B.}$

Fig. 4 indicates that excess isentropic compressibility decreases linearly up to a particular concentration of $x_{t\text{-}B}$ and then takes a change in slope in the curve for the higher concentrations of $x_{t\text{-}B}$. However, a similar trend is observed when the concentration of $x_F > 0.2$the β_{ts}^E linearly decreases.

The cosolvent observed in u_{ts}, β_{ts} and u_{ts}^E versus $(x_{t\text{-}B})_{opt}$ for the ternary system of water + formamide + t-butanol is shown in Table 3 as $(x_{t\text{-}B})_{opt}$ versus x_F. An examination of the data presented in Table 2 indicates that when x_F in the cosolvent exceeds 0.2, At this point, adding more t-butanol causes the hydrogen bonded structure of water to become unstable, which prevents t-butanol from forming clathrate hydrates in aqueous solutions.

These observations show that formamide interacts with aqueous t-butanol disrupting the clathrate hydrate formation of t-butanol and further increase of concentration it forms amide complexes around 1:3 ($x_F \geq 0.3114$).

IV. CONCLUSIONS

As Formamide concentration in the ternary solution rises, the ultrasonic speed maximum and isentropic compressibility minimum move towards lower t-butanol concentrations. The solution exhibits standard solution behavior when the concentration of F in the cosolvent is greater than 0.2 molefraction, resulting in a linear decrease in ultrasonic speed and an increase in isentropic compressibility with concentration of t-butanol. The concentration dependences of excess ultrasonic speed and excess isentropic compressibility also reflect this behaviour of the ternary solution. When $x_F > 0.2$ both $u^E$and β^E vary linearly with molefraction of t-butanol may be due to the fact that formamide interacts with aqueous t-butanol disrupting the clathrate hydrate formation of t-butanol and further increase of concentration it forms amide complexes around 1:3 ($x_F \geq 0.3114$).

FIGURE LEGENDS

Fig.1. Variation of Ultrasonic speed (u_{ts}) with mole fraction of t-Butanol ($x_{t\text{-}B}$) in the ternary system (water + formamide+ t-Butanol) at different concentrations of formamide (x_F) in the cosolvent (water + formamide)

x_F = A : 0.0000, B: 0.0132, C : 0.0398, D : 0.0682,
E : 0.01106, F : 0.2032, G : 0.3114

Fig.2. Variation of isentropic compressibility (β_{ts}) with mole fraction of t-Butanol ($x_{t\text{-}B}$) in the ternary system (water + formamide + t-Butanol) at different concentrations of formamide (x_F) in the cosolvent (water + formamide)

x_F = A : 0.0000, B: 0.0132, C : 0.0398, D : 0.0682,
E : 0.01106, F : 0.2032, G : 0.3114

Fig.3. Variation of excess ultrasonic speed (u_{ts}^E) with mole fraction of t-Butanol ($x_{t\text{-}B}$) in the ternary system (water + formamide + t-Butanol) at different concentrations of formamide (x_F) in the cosolvent (water + formamide)

x_F = A : 0.0000, B: 0.0132, C : 0.0398, D : 0.0682,
E : 0.01106, F : 0.2032, G : 0.3114

Fig.4. Variation of excess isentropic compressibility (β_{ts}^E) with mole fraction of t-Butanol ($x_{t\text{-}B}$) in the ternary system (water + formamide + t-Butanol) at different concentrations of formamide (x_F) in the cosolvent (water + formamide)

x_F = A : 0.0000, B: 0.0132, C : 0.0398, D : 0.0682,
E : 0.01106, F : 0.2032, G : 0.3114

Table 1 - u_{ts}, ρ_{ts}, β_{ts}, $(u_{ts})_{id}$, $(\beta_{ts})_{id}$ and u_{ts}^E, β_{ts}^E versus mole fraction of t-butanol (X_{t-B}) in the cosolvent (water + 2-methoxyethanol) at 298.15 K

X_{t-B}	u_{ts}	ρ_{ts}	β_{ts}	$(\beta_{ts})_{id}$	β_{ts}^E	$(u_{ts})_{id}$	u_{ts}^E
			$X_F = 0.0132$				
0.0000	1509.3	1021.41	43.0	-	-	-	-
0.0076	1530.8	1008.84	42.3	47.4	-5.1	1457.8	73.0
0.0162	1551.4	996.36	41.7	50.3	-8.6	1421.6	129.8
0.0274	1565.6	987.84	41.3	53.8	-12.5	1382.7	182.9
0.0435	1574.2	984.22	41.0	58.2	-17.2	1338.9	235.3
0.0593	1572.8	981.19	41.2	62.0	-20.8	1305.6	267.2
0.0727	1558.4	980.37	42.0	64.8	-22.8	1282.8	275.6
0.0805	1543.2	976.53	43.0	66.4	-23.4	1271.3	271.9
0.0893	1524.6	966.78	44.5	68.0	-23.5	1259.7	264.9
			$X_F = 0.0398$				
0.0000	1526.2	1038.34	41.3	-	-	-	-
0.0068	1541.2	1031.86	40.8	46.7	-5.9	1462.8	78.4
0.0154	1563.6	1014.94	40.3	49.9	-9.6	1427.0	136.6
0.0253	1578.4	1003.47	40.0	52.9	-12.9	1392.5	185.9
0.0382	1585.7	996.74	39.9	56.4	-16.5	1355.7	230.0
0.0523	1580.2	988.82	40.5	59.9	-19.4	1323.3	256.9
0.0624	1567.5	980.70	41.5	62.2	-20.7	1304.0	263.5
0.0684	1554.3	969.39	42.7	63.4	-20.7	1293.7	260.6
0.0753	1540.6	951.07	44.3	64.8	-20.5	1282.8	257.8
			$X_F = 0.0682$				
0.0000	1540.8	1046.45	40.3	-	-	-	-
0.0054	1555.3	1038.69	39.8	45.8	-6.0	1470.7	84.6
0.0128	1570.6	1029.02	39.4	48.2	-8.8	1439.2	131.3
0.0206	1586.4	1016.24	39.1	50.6	-11.5	1410.5	175.9
0.0298	1591.5	1012.33	39.0	53.2	-14.2	1381.5	210.0
0.0403	1585.4	1007.22	39.5	55.9	-16.4	1353.4	232.0
0.0484	1576.8	993.09	40.5	57.9	-17.4	1334.7	242.1
0.0601	1560.6	972.98	42.2	60.6	-18.4	1311.4	249.2
0.0691	1545.4	960.35	43.6	62.5	-18.9	1295.9	249.5

X_{t-B}	u_{ts}	ρ_{ts}	β_{ts}	$(\beta_{ts})_{id}$	β_{ts}^E	$(u_{ts})_{id}$	u_{ts}^E

			$X_F = 0.1106$				
0.0000	1557.4	1056.62	39.0	-	-	-	-
0.0064	1570.8	1047.24	38.7	45.5	-6.8	1459.0	101.8
0.0153	1577.4	1043.89	38.5	48.2	-9.7	1433.5	143.9
0.0271	1574.8	1031.27	39.1	51.6	-12.5	1394.4	180.4
0.0331	1566.5	1026.47	39.7	53.1	-13.4	1377.4	189.1
0.0402	1553.4	1015.71	40.8	54.9	-14.1	1359.1	194.3
0.0451	1541.3	1002.25	42.0	56.1	-14.1	1347.7	193.6
0.0512	1529.8	989.11	43.2	57.5	-14.3	1334.5	195.3
			$X_F = 0.2032$				
0.0000	1580.1	1068.05	37.5	-	-	-	-
0.0054	1588.3	1065.73	37.2	43.9	-6.7	1480.8	107.5
0.0103	1591.4	1058.61	37.3	45.3	-8.0	1461.4	130.0
0.0192	1585.6	1041.23	38.2	47.7	-9.5	1430.1	155.5
0.0283	1577.4	1012.33	39.7	50.0	-10.3	1402.5	174.9
0.0363	1568.5	996.25	40.8	52.0	-11.2	1381.2	187.3
0.0431	1561.9	975.98	42.0	53.5	-11.5	1365.0	196.9
0.0512	1548.8	962.76	43.3	55.3	-12.0	1347.5	201.3
			$X_F = 0.3114$				
0.0000	1590.6	1075.81	36.7	-	-	-	-
0.0048	1580.5	1070.38	37.4	42.3	-4.9	1494.0	86.5
0.0108	1569.5	1059.93	38.3	43.9	-5.6	1471.6	97.9
0.0173	1560.3	1045.18	39.3	45.5	-6.2	1449.7	110.6
0.0263	1551.8	1032.98	40.2	47.7	-7.5	1422.6	129.2
0.0384	1544.9	1016.95	41.2	50.4	-9.2	1391.4	153.5
0.0412	1539.6	1014.12	41.6	51.0	-9.4	1384.8	154.8
0.0522	1537.4	1002.56	42.2	53.2	-11.0	1361.3	176.1

Table 2. u, ρ, V, C_P, 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 10^4 (K^{-1})	β$x10^{11}$ ($N^{-1}m^2$)	K$x10^{11}$ ($N^{-1}m^2$)	Ref.
Water	1496.7	997.07	18.08	75.30	2.59	44.77	45.25	4
t-butanol	1123.2	780.95	94.91	224.9	12.68	101.50	121.72	4
formamide	1599.0	1129.19	39.80	107.8	7.75	34.63	41.26	14

Table 3. $(x_{t\text{-}B})_{opt}$ versus X_F in the cosolvent observed in u, β,u^E and β^E versus $(x_{t\text{-}B})$ in the ternary solutions of water + Formamide + t-butanol

X_F	$(X_{t\text{-}B})_{opt}$		
	$\mathbf{u_{ts}}$	$\boldsymbol{\beta_{ts}}$	$\mathbf{U_{ts}^E}$
0.0000	0.051	0.048	0.065
0.0132	0.049	0.046	0.068
0.0398	0.040	0.040	0.061
0.0682	0.029	0.031	0.054
0.1106	0.016	0.016	0.035
0.2032	0.009	0.011	0.021
0.3114	-	-	0.012

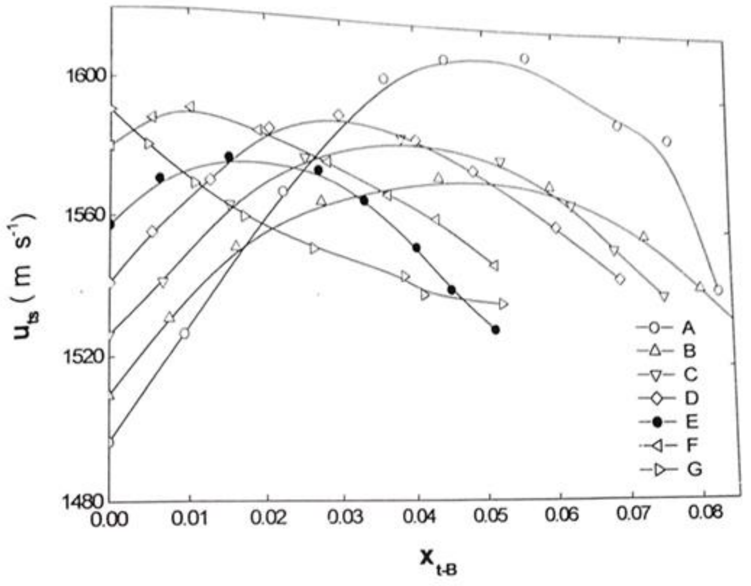

Fig. 1

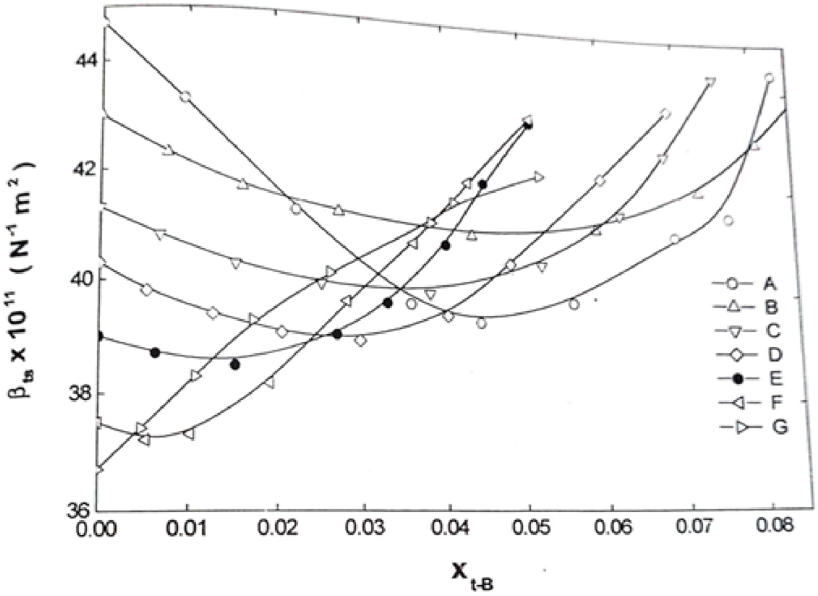
β_{ts} x 10^{11} (N^{-1} m^{2})
44
42
40
38
36
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
X_{t-B}
A
B
C
D
E
F
G

Fig. 2

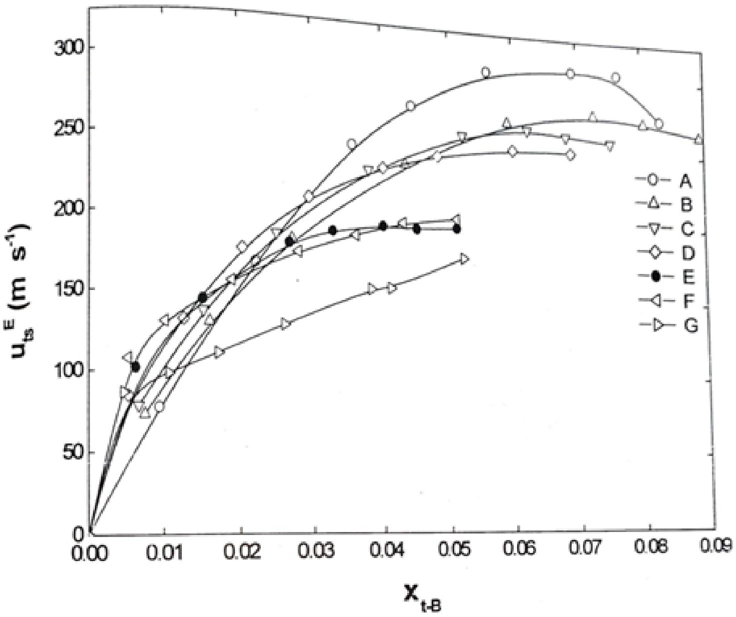
u_{ts}^{E} (m s^{-1})
300
250
200
150
100
50
0
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
X_{t-B}
A
B
C
D
E
F
G

Fig. 3

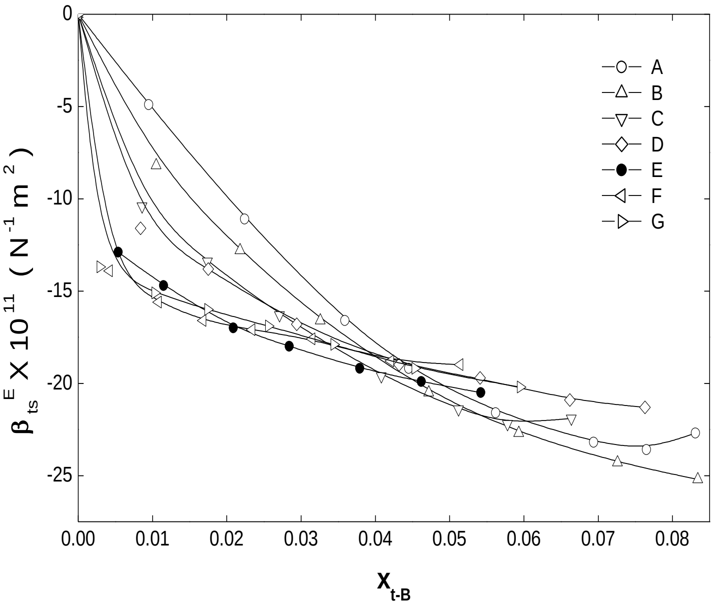

Fig. 4

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