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Effect of 1,4-Dioxane on the Structure of Aqueous *t*-Butyl Alcohol. Sound Velocity Studies

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The structure of aqueous *t*-butyl alcohol in the water rich region is known to be more structured than pure water. 1,4-dioxane is known to be a weakly hydrophobic solute. The effect of 1,4-dioxane on the structure of aqueous *t*-butyl alcohol has been studied by fixing the temperature of sound velocity maximum in the ternary solution from the experimentally determined ultrasonic velocity data at different temperatures. The structural contribution to the shift in the temperature of sound velocity maximum of the aqueous *t*-butyl alcohol solution due to the addition of 1,4-dioxane, $[\Delta T_{\mathrm{str.}}]_{\mathrm{exptl}}$, has been found to be positive having the nature of variation similar to that of the effect of 1,4-dioxane on pure water, when the concentration (X_s) of *t*-butyl alcohol is 0.0075. But, for aqueous *t*-butyl alcohol solutions having $X_s=0.0025$ and $X_s=0.0046$, $[\Delta T_{\mathrm{str.}}]_{\mathrm{exptl}}$, has been found to be negative reaching maximum values around $X_2=0.0045$ and there after decreasing with a tendency to become positive at higher concentrations of 1,4-dioxane. These results have been explained in the light of structure breaking and formation of dioxane complexes in the ternary solutions.

The hydrophobic nature of *t*-butyl alcohol has been established beyond doubt[1–16] whereas controversial views exist on the structural propensity of 1,4-dioxane.[17–27] Our earlier studies on the effect of *t*-butyl alcohol[28,29] and 1,4-dioxane[30] on the temperature of sound velocity maximum (TVM) and adiabatic compressibility minimum (TACM) indicated both the solutes to enhance the ordered structure of water when present in small amounts. In our earlier work,[31] we have carried out the TVM studies on ternary systems namely water+glycerol+1-butanol and water+pyridine+1-butanol and found to be useful in delineating the temperature dependence of structural propensity of 1-butanol. In continuation of TVM studies in probing the structure of ternary systems, we have taken up the studies on the effect of 1,4-dioxane on the temperature of sound velocity maximum of aqueous mixtures of *t*-butyl alcohol of different concentrations and the results are reported in this paper. Our interest in these studies is to see how a structure promoter (1,4-dioxane) influences the aqueous binary solution structure containing a structure promoter (*t*-butyl alcohol).

Experimental

Triple distilled degassed water was used to prepare stock solutions of aqueous *t*-butyl alcohol. This stock solution was used to prepare ternary solution of 1,4-dioxane of desired concentration. The concentration of 1,4-dioxane in the ternary solution was calculated by considering aqueous binary stock solution as a cosolvent of effective molecular weight M_{12} given by $X_wM_w+X_sM_s$ where M_w,M_s and X_w,X_s represent the molecular weights and mole fractions respectively of water and *t*-butyl alcohol. AR grade *t*-butyl alcohol and 1,4-dioxane were used after necessary purification following the procedure given by Weissberger.[32] Ultrasonic velocity in the solutions was determined using a single crystal variable path interferometer working at 3 MHz with an accuracy of ±0.003%, the details of which were discussed elsewhere.[28]

Results

Diffraction corrected ultrasonic velocity as a function of temperature at different concentrations of 1,4-dioxane in aqueous *t*-butyl alcohol ($M_{12}=18.1556$, $X_s=0.0025$; $M_{12}=18.2735$, $X=0.0046$, and $M_{12}=18.4884$, $X_s=0.0075$) are presented graphically in Figs. 1—3.

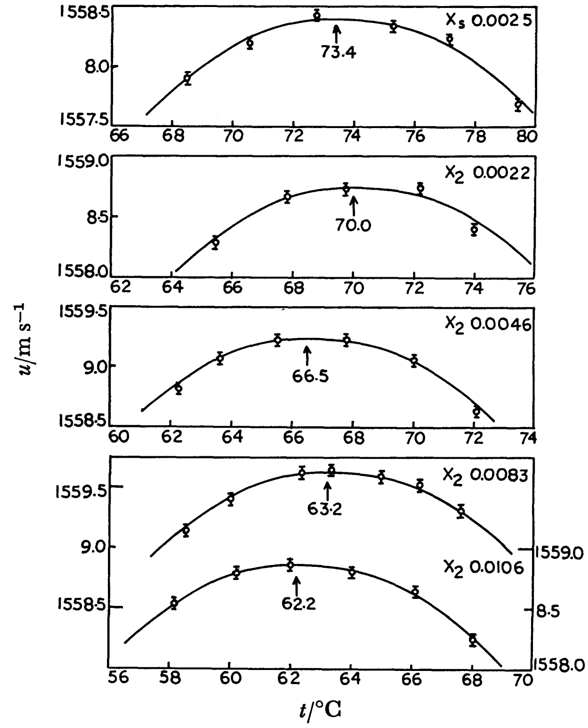

Fig. 1. Ultrasonic velocity *versus* temperature in aqueous solutions of *t*-butyl alcohol ($X_s=0.0025$) at different mole fractions of 1,4-dioxane.

The TVM in the ternary solution was fixed using the template of the velocity-temperature curve for pure water with an accuracy of ±0.2 °C as described earlier.[31]

Discussion

The shift in the temperature of sound velocity maximum of aqueous *t*-butyl alcohol due to the addition of 1,4-dioxane may be given by

$$\Delta T = (T_{\text{exptl}})_{\text{ternary soln}} - (T_{\text{exptl}})_{\text{binary soln}} \tag{1}$$

ΔT arises due to two effects namely dilution effect and structural effect which may be separated by considering the expressions representing the temperature dependence of velocity in aqueous *t*-butyl alcohol and 1,4-dioxane. The structural contribution to the shift in the temperature of sound velocity maximum in the ternary solution can be calculated using the following expressions that may be obtained on the same lines as that for pure water.[29]

$$[\Delta T_{\text{str.}}]_{\text{exptl}} = T_{\text{exptl}} - T_{\text{id.}} \tag{2}$$

where

$$T_{\text{id.}} = T_{\text{binary soln}} - \left(\frac{\phi_2}{\phi_{12}}\right)^2\left(\frac{W_{12}}{W_2}\right)\frac{2\beta}{\alpha}\left(\frac{u_{12}}{u_2}\right)^3. \tag{3}$$

In the above expression ϕ_{12}, ϕ_2 and W_{12}, W_2 represent the volume fractions and weight fractions of aqueous *t*-butyl alcohol and 1,4-dioxane respectively in the terary solution. α represents the temperature coefficient of sound velocity in 1,4-dioxane and u_{12} and u_2 the velocities in the aqueous *t*-butyl alcohol and 1,4-dioxane respectively. For 1,4-dioxane u_2 is given by

$$u_2 = u_2^0 - \alpha t, \tag{4}$$

where u_2^0 and α are 1452.42 ms^{-1} and 4.33 ms^{-1} °C^{-1} respectively and t represents the temperature in °C. u_{12} may be written as

$$u_{12} = u_{12}^0 - \beta(T-t)^2. \tag{5}$$

The values of u_{12}, β, and T for aqueous *t*-butyl alcohol for different X_s are given in Table 1.

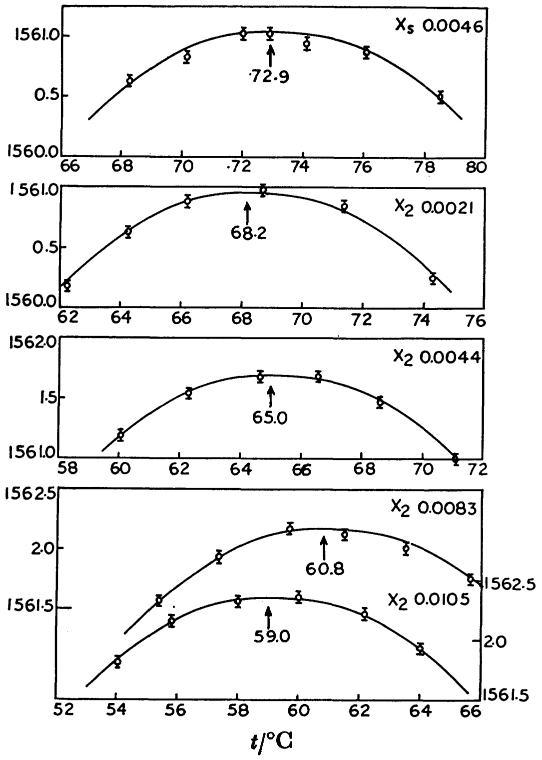

Fig. 2. Ultrasonic velocity *versus* temperature in aqueous solutions of *t*-butyl alcohol (X_s=0.0046) at different mole fractions of 1,4-dioxane.

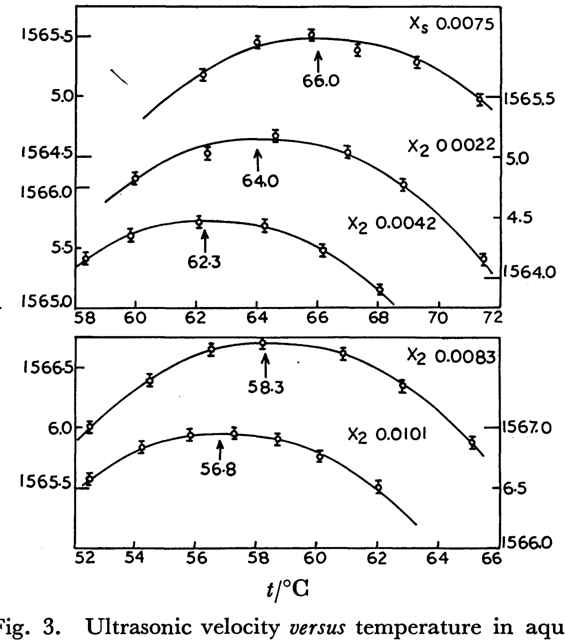

Fig. 3. Ultrasonic velocity *versus* temperature in aqueous solutions of *t*-butyl alcohol (X_s=0.0075) at different mole fractions of 1,4-dioxane.

Table 1. Values of u_{12}^0, β, and T for aqueous *t*-butyl alcohol

X_s	u_{12}^0 / ms^{-1}	β / ms^{-1} °C^{-2}	T / °C
0.0000	1557.00	0.0245	74.0
0.0025	1558.44	0.0217	73.6
0.0046	1561.02	0.0196	73.0
0.0075	1565.48	0.0190	66.1

Table 2. $T_{\text{id.}}$, T_{exptl}, and $[\Delta T_{\text{str.}}]_{\text{exptl}}$ at different mole fractions X_2 of 1,4-dioxane in binary aqueous mixtures of *t*-butyl alcohol

W_2	X_2	$T_{\text{id.}}$ / °C	T_{exptl} / °C	$[\Delta T_{\text{str.}}]_{\text{exptl}}$ / °C
		X_s=0.0025		
0.0106	0.0022	70.9	70.0	−0.9
0.0220	0.0046	68.1	66.5	−1.6
0.0392	0.0083	63.5	63.2	−0.3
0.0495	0.0106	62.0	62.2	+0.2
		X_s=0.0046		
0.0100	0.0021	70.3	68.2	−2.0
0.0210	0.0044	67.5	65.0	−2.4
0.0387	0.0083	63.0	60.8	−2.1
0.0485	0.0105	60.5	59.0	−1.5
		X_s=0.0075		
0.0104	0.0022	63.4	64.0	+0.6
0.0197	0.0042	61.0	62.3	+1.3
0.0385	0.0083	56.4	58.3	+1.9
0.0465	0.0101	54.5	56.8	+2.3

In all cases $T_{\text{id.}}$ was calculated using the method of successive approximations. Table 2 gives the values of T_{exptl}, $T_{\text{id.}}$, and $[\Delta T_{\text{str.}}]_{\text{exptl}}$ at different concentrations of 1,4-dioxane. The variation of $[\Delta T_{\text{str.}}]_{\text{exptl}}$ *versus* mole fraction X_2 of 1,4-dioxane in different aqueous *t*-butyl alcohol solutions are shown graphically in Fig. 4 along with the $[\Delta T_{\text{str.}}]_{\text{exptl}}$ *versus* X_2 of

1,4-dioxane in pure water taken from literature.[30] From the figure it is clear that the structural contribution to the shift in TVM of aqueous *t*-butyl alcohol is negative for the binary mixtures in which $X_s=$ 0.0025 and 0.0046 reaching maximum values around $X_2\simeq 0.0045$ and thereafter decreases with a tendency to become positive at higher concentrations of 1,4-dioxane. But, when the mole fraction of *t*-butyl alcohol in the aqueous *t*-butyl alcohol is 0.0075, $[\Delta T_{\text{str.}}]_{\text{exptl}}$ is positive increasing with increase in the concentration of 1,4-dioxane and is quite similar to the structural contribution to the shift in TVM of water, not only with respect to sign but even with respect to the magnitude of the structural shift. These results indicate that the structural propensity of 1,4-dioxane remains the same whether the solvent is pure water or aqueous *t*-butyl alcohol in which $X_s=0.0075$. But, the negative values of the structural shifts when $X_s=0.0025$ or 0.0046 point out the existence of a complex behavior. It is worthwhile to note here that the structural contribution to the shift in TVM of pure water due to the addition of *t*-butyl alcohol[29] reaches maximum around $X_s\simeq 0.0046$. Beyond this the structural shift decreases with increasing concentration of *t*-butyl alcohol. Hence it may be concluded that when $X_s\simeq 0.0046$ the rate of collapse of the hydrogen bonded clusters due to the addition of 1,4-dioxane may be more than the rate at which water molecules become organized into clusters around 1,4-dioxane molecules leading to the negative values of the structural shifts. But as the concentration of 1,4-dioxane increases, the rate of cluster formation around 1,4-dioxane molecules due to the hydrophobic nature of its methylene groups overtakes the rate of disintegration of the hydrogen bonded clusters. This situation is reflected in the tendency of $[\Delta T_{\text{str.}}]_{\text{exptl}}$ to become positive as the concentration of 1,4-dioxane increases. When $X_s=0.0075$, the time average of the structure of aqueous *t*-butyl alcohol resembles that of pure water and free water molecules try to form clusters around 1,4-dioxane and positive structural shifts may be thought of as due to the ordering of water structure owing to the formation of hydrates of dioxane as reported in literature.[18,19,33]

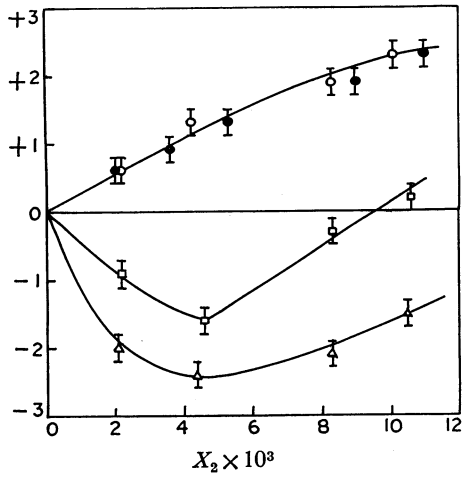

Fig. 4. $\Delta T_{\text{str. exptl}}$ *versus* mole fraction X_2 of 1,4-dioxane in different solvents.

□ : Aqueous *t*-butyl alcohol $X_s=0.0025$, TVM 73.6 °C, △ : Aqueous *t*-butyl alcohol $X_s=0.0046$, TVM 73.0 °C, ○ : Aqueous *t*-butyl alcohol $X_s=0.0075$, TVM 66.1 °C, ● : Pure water, TVM 74 °C.

TABLE 3. COMPARISON OF THE SHIFTS PRODUCED IN THE TVM OF WATER DUE TO THE ADDITION OF ORGANIC SOLUTES WITH THE OBSERVED SHIFT IN THE TERNARY SOLUTION, TREATING AQUEOUS BINARY SOLUTIONS AS AQUEOUS

X_D	X_B	$(\Delta T)_{X_D}$ / °C	$(\Delta T)_{X_B}$ / °C	$\Delta T_{\text{calcd}}=(\Delta T)_{X_D}+(\Delta T)_{X_B}$ / °C	$\Delta T_{\text{obsd}}=T_w-T_{T\,\text{soln}}$ / °C
		Water + *t*-Butyl alcohol + 1,4-Dioxane			
		$X_s=0.0025$			
0.0022	0.00247	1.75±0.4	0.65±0.4	2.40±0.8	4.0±0.4
0.0046	0.00246	3.65±0.4	0.65±0.4	4.30±0.8	7.5±0.4
0.0083	0.00245	6.60±0.4	0.65±0.4	7.25±0.8	10.8±0.4
0.0106	0.00245	8.40±0.4	9.05±0.8	9.05±0.8	11.8±0.4
		$X_s=0.0046$			
0.0021	0.00459	1.65±0.4	1.2±0.4	2.85±0.8	5.8±0.4
0.0044	0.00458	3.50±0.4	1.2±0.4	4.70±0.8	9.0±0.4
0.0083	0.00456	6.60±0.4	1.2±0.4	7.80±0.8	13.2±0.4
0.0105	0.00455	8.35±0.4	1.2±0.4	9.55±0.8	15.0±0.4
		$X_s=0.0075$			
0.0022	0.00748	1.75±0.4	8.00±0.4	9.75±0.8	10.0±0.4
0.0042	0.00747	3.35±0.4	7.95±0.4	11.30±0.8	11.7±0.4
0.0083	0.00743	6.60±0.4	7.90±0.4	14.50±0.8	15.7±0.4
0.0101	0.00742	8.05±0.4	7.85±0.4	15.90±0.8	17.2±0.4

X_D: Mole fraction of 1,4-dioxane when aqueous *t*-butyl alcohol is treated as cosolvent of effective molecular weight $M_{B,W}$. X_B: Mole fraction of *t*-butyl alcohol when aqueous 1,4-dioxane is treated as cosolvent of effective molecular weight $M_{D,W}$.

The structural shifts have been evaluated based on the assumption that aqueous *t*-butyl alcohol as seen by 1,4-dioxane is aqueous implying that the cosolvent (aqueous *t*-butyl alcohol) solute (1,4-dioxane) interactions are similar to that of pure solvent (water) and solute. This is true only if the interactions between 1,4-dioxane and *t*-butyl alcohol are negligible when compared with the interaction of 1,4-dioxane with aqueous nature of the solution structure. Even though the parabolic nature of velocity *versus* temperature profile of ternary solutions, as is evident from Figs. 1—3, support the validity of the above contention; we have calculated the shift in TVM of water due to the addition of the two organic solutes (independently) namely 1,4-dioxane and *t*-butyl alcohol to water, ΔT_{calcd}, and a comparison is made with the observed shift, ΔT_{obsd}, (74 °C-T_{exptl} in the ternary solution) to see whether the shift ΔT is additive with respect to them. Our earlier data[30,31] on TVM of aqueous 1,4-dioxane and *t*-butyl alcohol are taken for the evaluation of the shifts corresponding to the concentrations of these solutes in the ternary systems. The shift in TVM of water corresponding to the concentrations of the present study are obtained by least square fitting of the data.[30,31] As per the data presented in Table 3, the agreement between the calculated and observed shifts is quite good in the case of ternary system for which X_s=0.0075. But when X_s=0.0025 or 0.0046 the observed shifts and calculated shifts differ significantly. This disparity may be attributed to the hindrance caused by *t*-butyl alcohol molecules in the formation of hydrates of dioxane or to some enhancement in the structural propensity of both *t*-butyl alcohol and 1,4-dioxane due to the presence of each over the other in destabilizing the three dimensional structure of water. The agreement between the observed and calculated shifts when X_s= 0.0075 clearly indicates that the structure of aqueous *t*-butyl alcohol as seen by 1,4-dioxane is the same as that of pure water. In other words the structural propensity of 1,4-dioxane is unaffected by the presence of *t*-butyl alcohol when its mole fraction is 0.0075. This behavior may be due to the fact that for aqueous *t*-butyl alcohol in which X_s=0.0075, further addition of *t*-butyl alcohol or 1,4-dioxane destabilize the hydrogen bonded clusters and the monomers so formed take part readily in the formation of hydrates of dioxane leading to a positive sign for the structural shifts.

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