Temperature Dependence of Structural Propensity of 1-Butanol in Water

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The temperature dependence of structural propensity of 1-butanol has been studied by investigating its effect on the temperature of sound velocity maximum (TVM) in aqueous mixtures of glycerol and pyridine. The structural contribution to the shift in TVM of binary solution, $[\Delta T_{str}]_{exp}$ was found to be positive at low concentrations of 1-butanol for aqueous pyridine solutions whose TVM are 37.6 °C and 23.7 °C. For aqueous glycerol solutions whose TVM is 43.3 °C, $[\Delta T_{str}]_{exp}$ values, in the entire concentration range of 1-butanol studied, are found to be negative. The results indicate that below 40 °C 1-butanol behaves as a structure promoter while above 40 °C it behaves as a structure breaker.

The effect of solutes (electrolytes or nonelectrolytes) in promoting the hydrogen bonded structure of water is a function of temperature. Structure makers at low temperatures are known to behave as structure breakers at high temperatures.[1-4] Our earlier studies[5,6] on the effect of 1-butanol on the temperature of adiabatic compressibility minimum and sound velocity maximum of water indicate structure breaking property at high temperatures (around 60 and 75 °C) where as the density maximum studies by Wada and Umeda[7] (around 4 °C) indicate structure making propensity for this solute.

To understand the temperature dependence of structural propensity of 1-butanol, we have taken up a study of the effect of 1-butanol on the temperature corresponding to the sound velocity maximum of aqueous mixtures of glycerol (TVM=43.3 °C) and pyridine (TVM 37.6 and 23.7 °C) and the results are presented in this paper. Glycerol and pyridine which are known to be effective structure breakers[8] were chosen simply to lower TVM of water to any desired value at which the effect of 1-butanol could be studied to delineate its temperature dependence of structural propensity.

Experimental

Triple distilled degassed water was used to prepare stock solutions of aqueous glycerol and pyridine. These solutions were used to prepare ternary solutions of 1-butanol of desired concentration. The concentration of 1-butanol in the ternary solution was calculated by considering the aqueous binary stock solution as a solvent 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 glycerol and or pyridine. Ultrasonic velocity in binary solutions of aqueous glycerol and pyridine and in the ternary solutions with 1-butanol as the third component was determined using a single crystal variable path interferometer working at 3 MHz with an accuracy of ±0.003%. The details of the experimental technique and the method of measurement of velocity and temperature of the experimental liquid were discussed elsewhere.[5] The velocity measurements were confined to a temperature range of ≃5 °C on either side of TVM at intervals of ≃2 °C. AR grade glycerol, pyridine, and 1-butanol were used in the present study after necessary purification following the procedure given by Weissberger.[9]

Results

Diffraction corrected ultrasonic velocity as a function of temperature at different concentrations of 1-butanol in aqueous glycerol (M_{12}=24.7455, X_s=0.0909) and in aqueous pyridine solutions (M_{12}=20.5599, X_s=0.0416 and M_{12}=21.7209, X_s=0.0606) are presented graphically in Figs. 1 to 3. In all the solutions since the shape of the velocity temperature curves are similar to that of pure water, the template of the velocity-temperature curve for pure water was used to fix TVM and the accuracy in fixing TVM is ±0.2 °C.

Discussion

The shift in the temperature corresponding to the sound velocity maximum in the binary solutions of aqueous glycerol or pyridine due to the addition of 1-butanol may be given by

$$\Delta T = (T_{exp})_{ternary\ sol} - (T_{exp})_{binary\ sol.} \quad (1)$$

ΔT may be thought of as arising due to two effects namely dilution effect and structural effect. The dilution effect is always to lower TVM but the structural effect may be positive or negative depending on whether the nonelectrolyte promotes or disrupts the binary solution structure. These two effects may be separated by considering the expressions representing the temperature dependence of velocity in aqueous glycerol

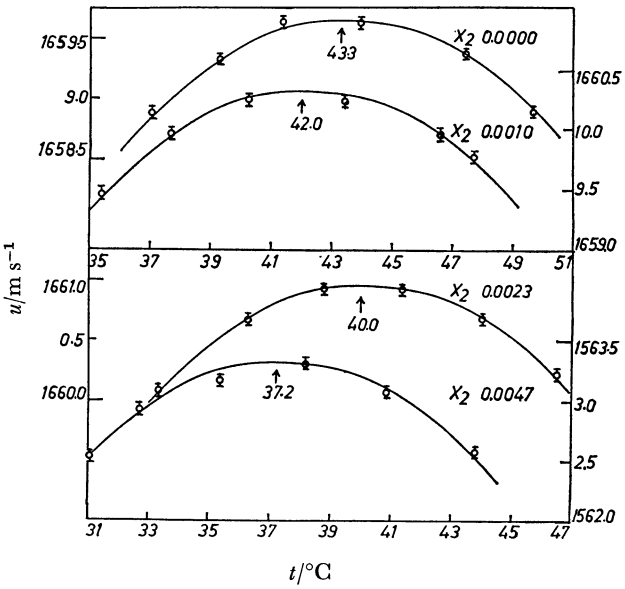

Fig. 1. Ultrasonic velocity *versus* temperature in aqueous solutions of glycerol at different molefractions of 1-butanol.

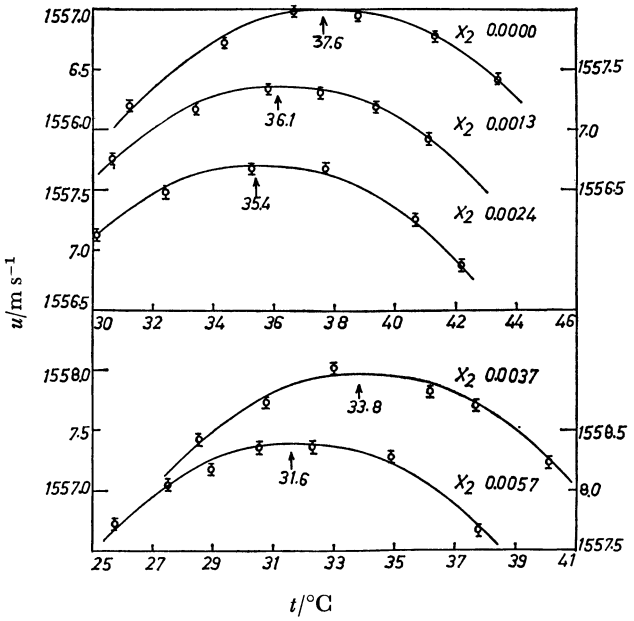

Fig. 2. Ultrasonic velocity *versus* temperature in aqueous solutions of pyridine at different molefractions of 1-butanol.

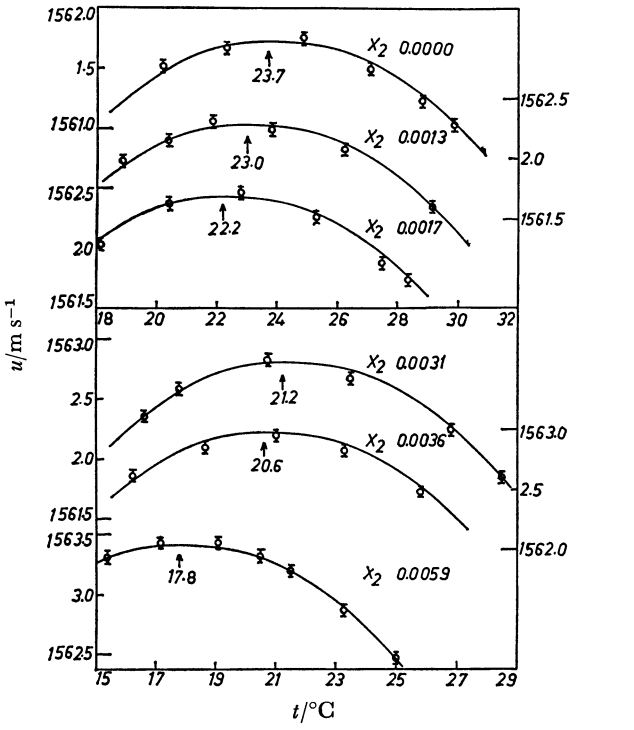

Fig. 3. Ultrasonic velocity *versus* temperature in aqueous solutions of pyridine at different molefractions of 1-butanol.

or pyridine and the nonelectrolyte.

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.[6]

$$[\Delta T_{str}]_{exp} = T_{exp} - T_{id}, \quad (2)$$

where

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

where ϕ_{12}, ϕ_2 and W_{12}, W_2 represent the volume fractions and weight fractions of binary aqueous solution and 1-butanol respectively in the ternary solution. α represents the temperature coefficient of sound velocity in 1-butanol and u_{12} and u_2 the velocities in the aqueous binary solution and solute respectively. For 1-butanol u_2 is given by

$$u_2 = u_2^\circ - \alpha t, \quad (4)$$

where u_2° and α are 1323.58 m s^{-1} and 3.3644 m s^{-1} °C^{-1} respectively and t represents the temperature in °C. u_{12} may be written as

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

The values of u_{12}°, β, and T for stock solutions of aqueous glycerol and pyridine are given in Table 1.

Table 1. Values of u_{12}°, β, and T for aqueous binary solutions

Solvent	X_s	u_{12}° / m s^{-1}	β / m s^{-1} °C^{-2}	T / °C
Aqueous glycerol	0.0909	1559.67	0.0204	43.3
Aqueous pyridine	0.0416	1556.99	0.0204	37.6
	0.0606	1561.72	0.0184	23.7

In all cases T_{id} was calculated using the method of successive approximations. Table 2 gives the values of T_{exp}, T_{id}, ΔT, and $[\Delta T_{str}]_{exp}$ at different concentrations of 1-butanol. The variation of $[\Delta T_{str}]_{exp}$ *versus* molefraction X_2 of 1-butanol in different aqueous binary solutions are shown graphically in Fig. 4 along with the $[\Delta T_{str}]_{exp}$ *versus* X_2 of 1-butanol in pure water taken from literature.[6] From the figure it is clear that below 40 °C 1-butanol behaves as a structure maker since $[\Delta T_{str}]_{exp}$ values are positive for solutions in which the TVM are 37.6 and 23.7 °C. $[\Delta T_{str}]_{exp}$

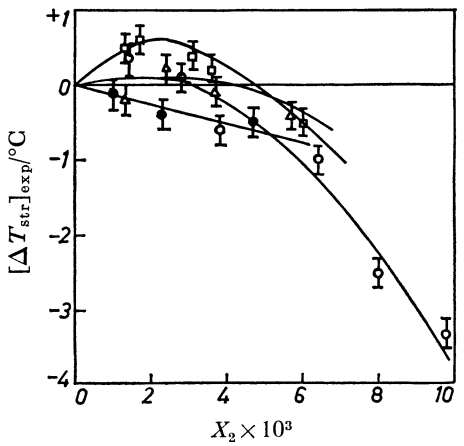

Fig. 4. $[\Delta T_{str}]_{exp}$ *versus* molefraction X_2 of 1-butanol in different solvents.
○: Pure water TVM 74 °C,
●: aqueous glycerol TVM 43.3 °C,
△: aqueous pyridine TVM 37.6 °C,
□: aqueous pyridine TVM 23.7 °C.

Table 2. T_{exp}, T_{id}, ΔT, and $[\Delta T_{str}]_{exp}$ at different molefractions X_2 of 1-butanol in binary aqueous mixtures

Solvent	X_2	T_{exp} / °C	T_{id} / °C	ΔT / °C	$[\Delta T_{str}]_{exp}$ / °C
Aqueous glycerol of TVM 43.3 °C	0.0010	42.0	42.1	−1.3	−0.01
	0.0023	40.0	40.4	−3.3	−0.4
	0.0047	37.2	37.7	−6.1	−0.5
Aqueous pyridine of TVM 37.6 °C	0.0013	36.1	36.3	−1.5	−0.2
	0.0024	35.4	35.2	−2.2	+0.2
	0.0037	33.8	33.9	−3.8	−0.1
	0.0057	31.6	32.0	−6.0	−0.4
Aqueous pyridine of TVM 23.7 °C	0.0013	23.0	22.5	−0.7	+0.5
	0.0017	22.2	21.6	−1.5	+0.6
	0.0031	21.2	20.8	−2.5	+0.4
	0.0036	20.6	20.4	−3.1	+0.2
	0.0059	17.8	18.3	−5.9	−0.5

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_B	X_G/X_P	$(\Delta T)_{X_B}$ / °C	$(\Delta T)_{X_G/X_P}$ / °C	$\Delta T_{calcd} = (\Delta T)_{X_B} + (\Delta T)_{X_G/X_P}$ / °C	$\Delta T_{obsd} = T_w - T_{t\,sol}$ / °C
		Water + Glycerol + 1-Butanol			
0.0010	0.0908	1.3±0.4	30.7±0.4	32.0±0.8	32.0±0.4
0.0023	0.0907	3.1+0.4	30.6±0.4	33.7±0.8	34.0±0.4
0.0047	0.0905	6.6±0.4	30.5±0.4	37.1±0.8	36.8±0.4
		Water + Pyridine + 1-Butanol			
0.0013	0.0416	1.7±0.4	36.4±0.4	38.1±0.8	37.3±0.4
0.0024	0.0415	3.2±0.4	36.3±0.4	39.5±0.8	38.6±0.4
0.0037	0.0415	5.1±0.4	36.3±0.4	41.4±0.8	40.2±0.4
0.0057	0.0414	8.1±0.4	36.2±0.4	44.3±0.8	42.4±0.4
0.0013	0.0605	1.7±0.4	50.1±0.4	51.8±0.8	51.0±0.4
0.0017	0.0605	2.2±0.4	50.1±0.4	52.3±0.8	51.8±0.4
0.0031	0.0604	4.3±0.4	50.0±0.4	54.3±0.8	52.8±0.4
0.0036	0.0604	5.0±0.4	50.0±0.4	55.0±0.8	53.4±0.4
0.0059	0.0602	8.4±0.4	49.9±0.4	58.3±0.8	56.2±0.4

X_B: Molefraction of 1-butanol when aqueous glycerol or aqueous pyridine is treated as cosolvents of effective molecular weights $M_{G,W}$ or $M_{P,W}$. X_G/X_P: Molefraction of glycerol/pyridine when aqueous 1-butanol is treated as cosolvent of effective molecular weight $M_{B,W}$.

values are negative for solutions in which the values of TVM are 43.3 and 74 °C indicating that above 40 °C 1-butanol behaves as a structure breaker. The behaviour of 1-butanol above 40 °C as a structure breaker was also confirmed from the studies on volumetric behaviour of aqueous isomeric butyl alcohols.[10] Hence the results of the present study indicate that as temperature increases the structure making efficiency of 1-butanol decreases and at temperatures above 40 °C it behaves as a structure breaker.

It is necessary to note that the assignment of structure making or breaking nature to 1-butanol as a function of temperature is valid only when 1-butanol has little interaction with glycerol or pyridine in the ternary system and interacts only with the water. Our results are based on the assumption that the aqeuous glycerol or pyridine as seen by 1-butanol is aqueous and the interactions between 1-butanol and glycerol or pyridine in the presence of water are negligible when compared with the interaction of 1-butanol with the aqueous nature of the solution structure. To know whether this is the actual situation prevailing in the ternary system, we have calculated the shift in TVM of water due to the addition of the two organic solutes (independently) namely glycerol or pyridine and 1-butanol to water, ΔT_{calcd}, and a comparison is made with the observed shift, ΔT_{obsd}, (74 °C − T_{exp} in the ternary solution) to see whether the shift ΔT is additive with respect to them. Our earlier data[6,8] on TVM of aqueous glycerol, pyridine, and 1-butanol are taken for the evaluation of the shifts corresponding to the concentrations of these solutes in the ternary systems. The shifts in the TVM of water corresponding to the concentrations of the present study are obtained

by least square fitting of the data.[6,8] As per the data presented in Table 3, the agreement between the calculated and observed shifts is quite good in the case of the ternary system water+glycerol+1-butanol. In the case of the ternary system water+pyridine+1-butanol, except when the concentrations of 1-butanol and pyridine are 0.0057 and 0.0414 and 0.0059 and 0.0602, the agreement between the calculated and experimental shifts is quite good. These observations indicate that ΔT is additive with respect to each solute and the effect of 1-butanol, glycerol, and pyridine on TVM of pure water is respectively independent of each other coexisting solute. However, the difference between the calculated and observed shifts for the ternary systems in which $X_B=0.0057$, $X_P=0.0414$ and $X_B=0.0059$, $X_P=0.0602$; which is about 2%, in our view, is due to the effect of temperature on the structure making or breaking power of the solutes being different in aqueous solution and in the ternary system and may not be considered as due to the influence of pyridine on 1-butanol or *vise versa* in their efficiency to shift the TVM of the solution. We would like to mention at this juncture that this point needs extensive study of ternary systems containing the two organic solutes which are both either structure breakers or structure makers. Further experimentation in this direction is in progress.

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