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Structure of Aqueous Isomeric Butyl Alcohols—Sound Velocity Studies

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The effect of isomeric butyl alcohols on the temperature of sound velocity maximum in water (TSVM) was studied using a variable path interferometer working at 3 MHz. The structural contribution to the shift in TSVM, $[\Delta T_{\mathrm{str}}]_{\mathrm{exp}}$, was evaluated for the butyl alcohols and the results are compared with those obtained from studies on the effect of these solutes on the temperature of adiabatic compressibility minimum and density maximum of water. The results indicate that the butyl alcohols enhance the hydrogen-bonded structure of water at low concentrations and at any given concentration, the order of increasing structural contribution to the shift in TSVM being *t*-butyl > *s*-butyl > isobutyl > butyl alcohols. The structural propensities of the butyl alcohols as revealed by TSVM studies are in line with the information obtained from the temperature of adiabatic compressibility minimum and density maximum studies. The results of the present study indicate that TSVM studies are useful in understanding the solution structure in aqueous mixtures.

Many studies have been reported on the solution structure of aqueous alcohols. They mainly deal with the observation of non-ideal thermodynamic behaviour of aqueous mixtures such as viscosity composition,[1] ultrasonic velocity,[2,3] and absorption[4,5] maxima as a function of concentration and negative partial molal volumes.[6,7] At any given temperature water can be considered to consist of essentially two species, one hydrogen bonded and the other non-hydrogen bonded, this being the most common of the many theories.[8] Water exhibits a density maximum at 3.98 °C, adiabatic compressibility minimum at 64 °C and sound velocity maximum at 74 °C. Any parameter which can affect the structural equilibrium of water will also influence the temperature at which the extrema are observed. Hence a study of the effect of non-electrolytes on these physical properties of water helps one to understand the structural propensities of these solutes in water. Wada and Umeda[9] studied the effect of isomeric butyl alcohols on the temperature of density maximum of water. In an earlier communication[10] we reported the effect of these solutes on the temperature corresponding to the adiabatic compressibility minimum of water. Both studies indicate that isomeric butyl alcohols hehave as structure promoters when added in small amounts to water.

According to Eyring and Kincaid[11] a sound wave in a liquid is supposed to travel with infinite velocity within a molecule and with gas kinetic velocity in the intermolecular space. On this assumption, the conversion of hydrogen-bonded into close-packed ones (due to rise in temperature) results in a positive temperature coefficient of sound velocity and the simultaneous volume expansion of both species gives rise to a negative temperature coefficient of velocity. The competition between these two opposing tendencies leads to the sound velocity maximum observed at 74 °C, where thermal expansion balances the effect due to the equilibrium shift. Above 74 °C the structural expansion plays a dominant role and the velocity decreases with increasing temperature.

Any parameter which can affect the structural equilibrium in water would also influence the temperature of sound velocity maximum (TSVM). Hence ultrasonic velocity measurements in aqueous solutions in the vicinity of TSVM are likely to throw some light on the structural effects of different molecules. However, ultrasonic velocity is not generally considered to be a primary thermodynamic quantity. It can be considered to be dependent on density and adiabatic compressibility. Density and adiabatic compressibility of aqueous solutions show a complex temperature dependence, each becoming maxima and minima, respectively, at certain temperatures which are not the same. Under these conditions, we are not certain whether the condition $(\mathrm{d}u/\mathrm{d}t)_{t=\mathrm{TSVM}}=0$ can be considered to be a criterion for structure breaking or structure promotion where u denotes ultrasonic velocity and t temperature. The present paper deals with the studies on the effect of isomeric butyl alcohols on the TSVM of water with a view to comparing the results with those obtained from density maximum[9] and adiabatic compressibility minimum[10] studies and thereby evaluate the usefulness of velocity measurements.

Experimental

A. R grade isomeric butyl alcohols were used after purification. Ultrasonic velocity in the pure components and aqueous mixtures was determined using a single crystal variable path interferometer working at 3 MHz with an accuracy of ±0.003 percent. The details of the experimental technique and the method of measurement of velocity and temperature of liquid were reported.[10]

Solutions of desired concentration were prepared by weighing the samples using triple distilled, degassed water. Ultrasonic velocity in the solutions were determined at $\simeq 2$ °C intervals over a range of 5 °C on either side of TSVM. The velocities were corrected for diffraction effects, following the procedure developed by Subrahmanyam *et al.*[12] At low concentrations of the organic solute, the temperature dependence of sound velocity in the aqueous solutions is parabolic and resembles that of pure water. Hence a transparent template of the curve for pure water was employed to fix TSVM. The accuracy in fixing TSVM is ± 0.2 °C.

Results

Diffraction corrected ultrasonic velocities in dilute aqueous solutions of isomeric butyl alcohols as a function of temperature at different concentrations are given in Table 1. Some typical results are shown in Fig. 1.

Table 1. Ultrasonic velocity in aqueous solutions of isomeric butyl alcohols at different temperatures

Temperature *t*(°C)	Velocity *u*(m/s)	Temperature *t*(°C)	Velocity *u*(m/s)
Water + *t*-butyl alcohol			
$X_2=0$		$X_2=0.0013$	
	1550+		1550+
68.05	4.60	68.50	6.37
69.60	4.84	69.20	6.52
71.10	5.06	70.20	6.80
72.20	5.19	71.95	7.03
73.55	5.27	72.65	6.95
75.05	5.26	74.60	6.92
76.15	5.21	76.35	6.79
77.55	5.10	78.35	6.56
78.60	4.86		
79.95	4.60		
$X_2=0.0025$		$X_2=0.0037$	
	1550+		1550+
68.50	7.90	68.25	9.27
70.55	8.19	69.55	9.49
72.75	8.43	71.35	9.69
75.30	8.34	73.15	9.67
77.15	8.23	74.85	9.58
79.40	7.67	77.50	9.33
$X_2=0.0046$		$X_2=0.0062$	
	1550+		1550+
68.25	10.62	64.60	12.90
70.15	10.82	66.70	13.15
72.00	11.02	68.55	13.40
72.90	11.03	70.00	13.41
74.10	10.94	72.05	13.23
76.05	10.87	74.20	12.97
78.50	10.50	76.65	12.19
$X_2=0.0075$			
	1550+		
62.20	15.17		
64.00	15.45		
65.80	15.51		
67.30	15.39		
69.25	15.29		
71.35	14.96		
Water + *s*-butyl alcohol			
$X_2=0.0014$		$X_2=0.0024$	
	1550+		1550+
68.10	5.64	66.60	7.01
70.30	6.00	68.80	7.44
72.65	6.05	70.95	7.49
74.60	5.89	73.35	7.44
75.95	5.71	76.10	7.12
78.30	5.30	78.10	6.71
$X_2=0.0048$		$X_2=0.0077$	
	1550+		1550+
61.30	9.02	59.20	12.90
63.60	9.53	61.45	13.32
66.55	9.89	64.00	13.38
68.75	9.96	66.40	13.41
71.30	9.72	68.60	13.06
73.40	9.37	70.00	12.86
$X_2=0.0107$			
	1550+		
55.10	16.13		
55.80	16.25		
57.05	16.46		
59.50	16.82		
61.75	16.78		
64.20	16.60		
66.00	16.24		
Water + isobutyl alcohol			
$X_2=0.0017$		$X_2=0.0037$	
	1550+		1550+
68.05	5.72	65.95	7.14
70.60	5.98	68.30	7.53
72.85	6.03	70.35	7.49
75.15	5.86	72.00	7.49
77.20	5.50	74.50	7.14
79.10	5.02	76.00	6.84
$X_2=0.0056$		$X_2=0.0082$	
	1550+		1550+
62.60	9.28	57.30	11.16
64.55	9.64	59.85	11.50
67.15	9.65	62.35	11.73
69.35	9.58	65.20	11.61
71.35	9.30	61.75	11.24
74.00	8.80	69.65	10.94
Water + butyl alcohol			
$X_2=0.0014$		$X_2=0.0028$	
	1550+		1550+
68.35	3.87	64.50	4.45
70.15	4.12	66.40	4.65
72.50	4.20	68.55	4.87
74.35	4.27	70.40	5.02
75.85	4.02	72.15	4.96
77.70	3.72	74.15	4.72
		75.95	4.36
$X_2=0.0038$		$X_2=0.0064$	
	1550+		1550+
63.15	5.75	59.05	7.75
65.00	6.10	61.55	8.26
67.25	6.35	63.70	8.47
69.20	6.38	65.75	8.51
71.05	6.27	67.90	8.41
73.15	6.00	70.55	8.00
$X_2=0.0080$		$X_2=0.0098$	
	1550+		1550+
56.45	9.80	54.60	11.63
58.10	10.10	57.20	11.90
60.25	10.28	59.55	11.95
62.65	10.19	61.55	11.80
64.92	9.94	63.55	11.44
67.35	9.58	65.10	11.20

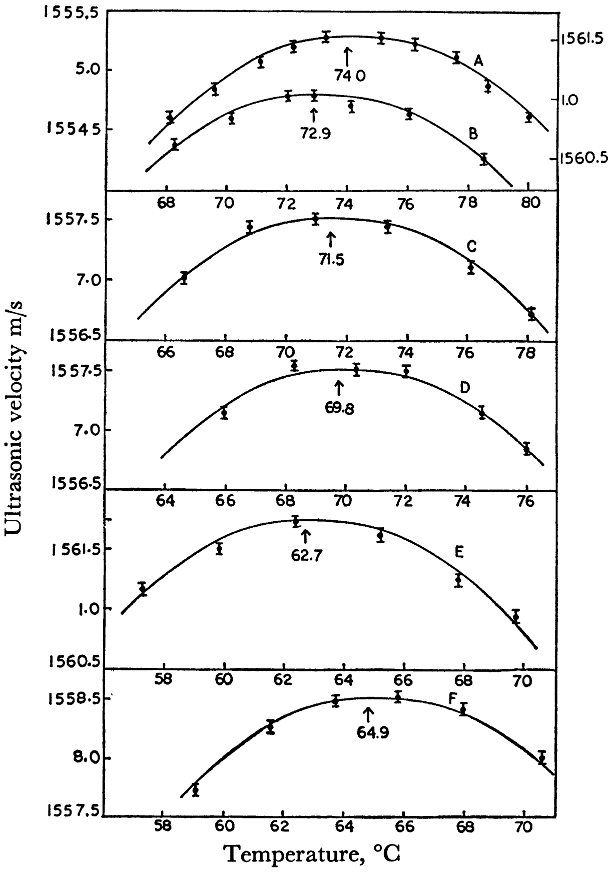

Fig. 1. Ultrasonic velocity in dilute aqueous solutions of isomeric butyl alcohols at different temperatures. A: Pure water. B: water+*t*-butyl alcohol, $X_2=0.0046$, C: water+*s*-butyl alcohol, $X_2=0.0024$, D, E: water+isobutyl alcohol, $X_2=0.0037$, 0.0082, F: water+butyl alcohol, $X_2=0.0064$.

Discussion

In order to understand the structural propensities of solutes in aqueous mixtures from TSVM studies, it is necessary to obtain an expression for the TSVM of the solution in terms of known quantities. For this purpose it is neccessary to express the sound velocity in the mixture in terms of the velocities in the pure components. Since there is no agreed view regarding the method of evaluation of sound velocity in an ideal mixture, we have taken up the additivity of adiabatic compressibility on volume fractions. The adiabatic compressibility of an aqueous solution can be represented by

$$\beta = \phi_1\beta_1 + \phi_2\beta_2 + \beta^{\mathrm{E}}, \tag{1}$$

where β_1, β_2, and ϕ_1, ϕ_2 refer to the adiabatic compressibilities and volume fractions of water and the organic solute, respectively, and β^{E} represents the excess adiabatic compressibility. Since

$$\beta = \frac{1}{u^2\rho}, \tag{2}$$

where u is the ultrasonic velocity and ρ density, we can rewrite Eq. 1 as

$$\frac{1}{u^2\rho} = \frac{\phi_1}{u_1^2\rho_1} + \frac{\phi_2}{u_2^2\rho_2} + \beta^{\mathrm{E}}. \tag{3}$$

It is not necessary to use $\rho=\phi_1\rho_1+\phi_2\rho_2+\rho^{\mathrm{E}}$ in the above equation since the effect of ρ^{E}, the excess density, on the velocity of the solution is negligibly small. Hence we can rewrite Eq. 3 as

$$\frac{1}{u^2} = \frac{\phi_1^2}{w_1u_1^2} + \frac{\phi_2^2}{w_2u_2^2} + \rho\beta^{\mathrm{E}}, \tag{4}$$

where w_1 and w_2 refer to the weight fractions of water and the organic solute, respectively, in the solution.

According to Willard[13] the velocity in pure water conforms to the relation

$$u_1 = 1557 - 0.0245(74-t)^2, \tag{5}$$

where t is the temperature in °C. Over a small range of temperature the sound velocity in the organic solute is given by

$$u_2 = u_2^{\circ} - \alpha_{\mathrm{u}}t, \tag{6}$$

where α_{u} is the temperature coefficient of sound velocity in the solute and u_2° is the velocity at 0 °C.

By substitution of Eqs. 5 and 6 in Eq. 4, differentiation with respect to temperature, and use of the conditions $(\mathrm{d}u/\mathrm{d}t)_{t=\mathrm{TSVM}}=0$, we obtain the following expression for TSVM in the solution:

$$\begin{aligned} T = 74 &- \left(\frac{\phi_2}{\phi_1}\right)^2\left(\frac{w_1}{w_2}\right)\left(\frac{\alpha_{\mathrm{u}}}{0.049}\right)\left(\frac{u_1^3}{u_2^3}\right) \\ &- \left(\frac{w_1}{\phi_1^2}\right)\left(\frac{u_1^3}{0.098}\right)\left[\rho\frac{\mathrm{d}\beta^{\mathrm{E}}}{\mathrm{d}t}+\beta^{\mathrm{E}}\frac{\mathrm{d}\rho}{\mathrm{d}t}\right]. \end{aligned} \tag{7}$$

The shift produced in the TSVM of water due to the presence of the organic solute, ΔT_{obsd}, is given by

$$\begin{aligned} \Delta T_{\mathrm{obsd}} = &- \left(\frac{\phi_2}{\phi_1}\right)^2\left(\frac{w_1}{w_2}\right)\left(\frac{\alpha_{\mathrm{u}}}{0.049}\right)\left(\frac{u_1}{u_2}\right)^3 \\ &- \left(\frac{w_1}{\phi_1^2}\right)\left(\frac{u_1^3}{0.098}\right)\left[\rho\frac{\mathrm{d}\beta^{\mathrm{E}}}{\mathrm{d}t}+\beta^{\mathrm{E}}\frac{\mathrm{d}\rho}{\mathrm{d}t}\right]. \end{aligned} \tag{8}$$

ΔT_{obsd} can be thought of as being due to two effects; structural effects caused by interaction of the two molecules and dilution. The effect of dilution is always to lower the TSVM. The first term on the right hand side of Eq. 8 represents the shift which can be called the ideal shift ΔT_{id}. If there is no interaction between the two types of molecules, we have $\Delta T_{\mathrm{obsd}}=\Delta T_{\mathrm{id}}$. The second term refers to the structural contribution to the shift in TSVM, ΔT_{str}, which can be evaluated either from the values of $\mathrm{d}\beta^{\mathrm{E}}/\mathrm{d}t$ and $\mathrm{d}\rho/\mathrm{d}t$ of the solution or by means of the relation

$$[\Delta T_{\mathrm{str}}]_{\mathrm{exp}} = T_{\mathrm{exp}} - T_{\mathrm{id}}, \tag{9}$$

where

$$T_{\mathrm{id}} = 74 - \left(\frac{\phi_2}{\phi_1}\right)^2\left(\frac{w_1}{w_2}\right)\left(\frac{\alpha_{\mathrm{u}}}{0.049}\right)\left(\frac{u_1}{u_2}\right)^3. \tag{10}$$

T_{id} can be evaluated using α_{u}, u_1, and u_2 and following the method of successive approximations. The values of u_2° and α_{u} for the isomeric butyl alcohols evaluated from a study of temperature dependence of ultrasonic velocity are given in Table 2. Since the temperature dependence of ϕ_1 and ϕ_2 is very small, ϕ_1 and ϕ_2 used for determining T_{id} were evaluated at the TSVM of the solution found experimentally.

The values of T_{exp}, T_{id}, and $[\Delta T_{\mathrm{str}}]_{\mathrm{exp}}$ at different concentrations for the isomeric butyl alcohols are given in Table 3. The variation of T_{exp} with mole fraction

Table 2. Ultrasonic velocity at 0 °C, $u_2°$, and temperature coefficient of sound velocity, α_u, for isomeric butyl alcohols

Solute	$u_2°$(m/s)	α(m/s °C)
t-Butyl alcohol	1227.20	−4.21
s-Butyl alcohol	1306.45	−3.75
Isobutyl alcohol	1271.95	−3.35
Butyl alcohol	1323.58	−3.36

Table 3. $T_{\rm exp}$, $T_{\rm id}$, and $[\Delta T_{\rm str}]_{\rm exp}$ at different mole fractions X_2 for isomeric butyl alcohols

Mole fraction X_2	$T_{\rm exp}$ (°C)	$T_{\rm id}$ (°C)	$[\Delta T_{\rm str}]_{\rm exp}$ (°C)
	t-Butyl alcohol		
0.0013	73.6	70.2	+3.4±0.2
0.0025	73.4	67.0	+6.4±0.2
0.0037	73.0	64.1	+8.9±0.2
0.0046	72.9	61.9	+11.0±0.2
0.0062	69.0	58.5	+10.5±0.2
0.0075	66.0	56.2	+9.8±0.2
	s-Butyl alcohol		
0.0014	72.3	71.6	+0.7±0.2
0.0024	71.5	69.8	+1.7±0.2
0.0048	68.0	66.1	+1.9±0.2
0.0077	64.2	62.0	+2.2±0.2
0.0107	60.5	58.5	+2.0±0.2
	isobutyl alcohol		
0.0017	71.9	71.2	+0.7±0.2
0.0037	69.8	68.2	+1.6±0.2
0.0056	67.1	65.6	+1.5±0.2
0.0082	62.7	62.2	+0.5±0.2
	Butyl alcohol		
0.0014	72.4	72.1	+0.3±0.2
0.0028	70.2	70.3	+0.1±0.2
0.0038	68.5	69.1	−0.6±0.2
0.0064	64.9	65.9	−1.0±0.2
0.0080	61.0	64.0	−3.0±0.2
0.0098	58.5	62.1	−3.6±0.2

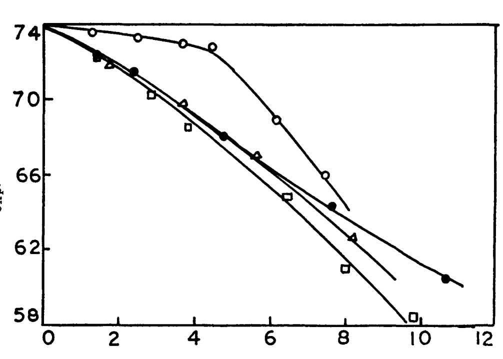

Fig. 2. Variation of $T_{\rm exp}$ with mole fraction X_2 of isomeric butyl alcohols.

○: *t*-Butyl alcohol, △: isobutyl alcohol, ●: *s*-butyl-alcohol, □: butyl alcohols.

X_2 for the butyl alcohols is shown graphically in Fig. 2.

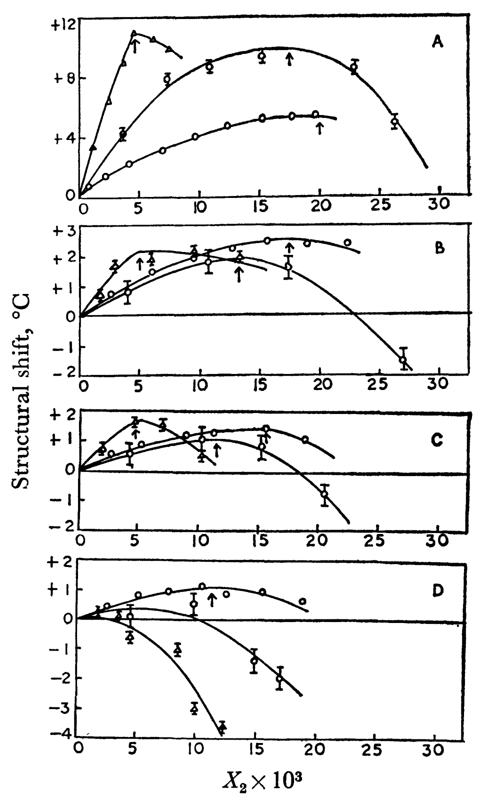

Fig. 3. Structural shifts versus molefraction X_2 of isomeric butanols.

⌶: $[\Delta T_{\rm str}]_{\rm exp}$, ⧲: $[\Delta T_{\beta \rm str}]_{\rm exp}$, ○: $[\Delta T'_{\rm str}]_{\rm exp}$.

A: Water+*t*-butyl alcohol, B: water+*s*-butyl alcohol, C: water+isobutyl alcohol, D: water+butyl alcohol.

Plots of $[\Delta T_{\rm str}]_{\rm exp}$ *versus* X_2 for the butyl alcohols are shown in Figs. 3A—3D. Also included in these figures are the variation of $[\Delta T'_{\rm str}]_{\rm exp}$ (structural contribution to the shift in the temperature of maximum density of water) and $[\Delta T_{\beta\ \rm str}]_{\rm exp}$ (structural contribution to the shift in the temperature of adiabatic compressibility minimum of water) taken from literature[9,10] to facilitate a comparison of the different studies.

$[\Delta T_{\rm str}]_{\rm exp}$ is positive at low concentrations for *t*-butyl, *s*-butyl, and isobutyl alcohols indicating stabilization of the hydrogen-bonded structure of water. $[\Delta T_{\beta\ \rm str}]_{\rm exp}$ and $[\Delta T'_{\rm str}]_{\rm exp}$ are also positive for these solutes. $[\Delta T_{\rm str}]_{\rm exp}$ and $[\Delta T_{\beta\ \rm str}]_{\rm exp}$ are positive for butyl alcohol though small in magnitude, in the very low concentration range, becoming negative at high concentrations. It is quite possible that the structure stabilizing propensity of this molecule becomes weak at high temperatures. At any given concentration, the structure enhancing efficiency of the butyl alcohols found from TSVM studies is in the order, *t*-butyl>*s*-butyl>isobutyl>butyl alcohol. The same order is found in studies on the effect of these butyl alcohols on the temperature density maximum[9] and adiabatic compressibility minimum[10] of water.

For the butyl alcohols, the optimum concentration at which the quantities $[\Delta T_{\rm str}]_{\rm exp}$, $[\Delta T_{\beta\ \rm str}]_{\rm exp}$, and $[\Delta T'_{\rm str}]_{\rm exp}$ become maxima are not the same (Figs. 3A—3D and Table 4). $T_{\rm exp}$, $T_{\beta\ \rm exp}$, and $T'_{\rm exp}$ (temperature of maximum density of the solution) for the aqueous isometric butyl alcohols at the optimum concentrations evaluated from the graphs (Fig. 2 and

TABLE 4 $(X_2)_{\mathrm{opt}}$ FOR DIFFERENT SOLUTES

Solute	$[\Delta T_{\mathrm{str}}]_{\mathrm{exp}}$		$[\Delta T_{\beta\ \mathrm{str}}]_{\mathrm{exp}}$		$[\Delta T_{\mathrm{str}}]_{\mathrm{exp}}$	
	$(X_2)_{\mathrm{opt}}$	T_{exp} (°C)	$(X_2)_{\mathrm{opt}}$	$T_{\beta\ \mathrm{exp}}$ (°C)	$(X_2)_{\mathrm{opt}}$	T' (°C)
t-Butyl alcohol	0.0047	72.4	0.0175	43.5	0.0200	0.87
s-Butyl alcohol	0.0040	69.0	0.0106	52.0	0.0140	2.36
Isobutyl alcohol	0.0038	69.8	0.0092	53.2	0.0124	1.65
Butyl alcohol	0.0027	71.2	0.0090	50.6	0.0090	2.48

literature[9,10]) are also given in Table 4.

The results indicate that the structural effects as revealed from density and adiabatic compressibility measurements have similar concentration dependence. In all cases $[\Delta T_{\mathrm{str}}]_{\mathrm{exp}}$ becomes maximum at much lower X_2 than either that of $[\Delta T_{\beta\ \mathrm{str}}]_{\mathrm{exp}}$ or $[\Delta T_{\mathrm{str}}]_{\mathrm{exp}}$. Even though the concentration at which $[\Delta T_{\beta\ \mathrm{str}}]_{\mathrm{exp}}$ becomes maximum is less than that at which $[\Delta T_{\mathrm{str}}]_{\mathrm{exp}}$ becomes maximum, for a given solute, they are close to each other. This indicates that there is a close similarity between the temperature of density maximum and adiabatic compressibility minimum in revealing the structural propensities of solutes in water. However, there is a large difference with respect to the concentration dependence of structural effects as revealed from TSVM studies. This is because $[\Delta T_{\mathrm{str}}]_{\mathrm{exp}}$ becomes maximum at a lower X_2 as compared to $[\Delta T_{\beta\ \mathrm{str}}]_{\mathrm{exp}}$ or $[\Delta T'_{\mathrm{str}}]_{\mathrm{exp}}$ for a given solute. It is difficult to interpret this behaviour from the fact that each study was confined to different temperature (TSVM studies around 74 °C, adiabatic compressibility minimum studies around 64 °C, and density maximum studies around 4 °C). The $(X_2)_{\mathrm{opt}}$ of each study is not commensurate to the temperature differences as is clear from Table 4. The occurrance of the maximum in $[\Delta T_{\mathrm{str}}]_{\mathrm{exp}}$ *versus* X_2 at very low X_2 values as compared to the other two studies may very likely be due to the dependent nature of ultrasonic velocity on density and adiabatic compressibility. However, the TSVM studies, in general, indicate correctly whether a solute behaves as a structure promoter or disrupter.

It is clear that even though ultrasonic velocity is not a primary thermodynamic quantity, TSVM studies could be used to classify the solutes as structure makers or breakers.

References

1) W. Herz and E. Lorentz, *Z. Phys. Chem.*, **A140**, 406 (1929).

2) Ch. Burton, *J. Acoust. Soc. Am.*, **20**, 186 (1948).

3) E. K. Baumgartner and G. Atkinson, *J. Phys. Chem.*, **75**, 2337 (1971).

4) H. Endo and O. Nomoto, *Bull. Chem. Soc. Jpn.*, **46**, 3004 (1973).

5) M. J. Blandamer, D. E. Carke, N. J. Hidden, and M. C. R. Symons, *Chem. Commun*, **1968**, 342.

6) V. S. Griffiths, *J. Chem. Soc.*, **1952**, 860.

7) G. N. Malcolm and J. S. Rowlinson, *Trans. Faraday Soc.*, **53**, 921 (1957).

8) F. Franks and D. J. G. Ives, *Quart. Rev.*, **20**, 1 (1966).

9) G. Wada and S. Umeda, *Bull. Chem. Soc. Jpn.*, **35**, 1797 (1962).

10) S. V. Subrahmanyam and N. Manohara Murthy, *J. Sol. Chem.*, **4**, 347 (1975).

11) H. Eyring and J. F. Kincaid, *J. Chem. Phys.*, **5**, 587 (1937).

12) S. V. Subrahmanyam, V. Hyder Khan, and C. V. Raghavan, *J. Acoust. Soc. Am.*, **46**, 272 (1969).

13) G. Willard, *J. Acoust. Soc. Am.*, **19**, 236 (1947).