

# APPENDIX

## PUBLICATIONS

## LIST OF PUBLICATIONS

S. No.	Title of the paper	Journal
1	Ultrasonic studies in dilute solutions of water and nonelectrolytes	Indian Journal of Pure & Applied Physics, <b>38</b> (2000) 10.
2	Studies on the effect of sulphates of lithium, sodium, potassium, ammonium and magnesium on the temperature of sound velocity maximum of water.	Acoustics Letters (Communicated)
3	Studies on the effect of mixed electrolytes on the temperature of sound velocity maximum of water	Acustica united with Acta Acustica (Communicated)
4	Studies on the effect of ammonium halides on the temperature of sound velocity maximum of water	Indian Journal of Pure & Applied Physics (Communicated).
5	Ultrasonic studies in dilute solutions of water and glycols	Indian Journal of Chemistry (Communicated)

## Ultrasonic studies in dilute solutions of water and nonelectrolytes

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Ultrasonic velocities in dilute solutions of water in n-propanol, isopropanol, glycerol, formamide, N-methyl formamide, dimethyl formamide, tetrahydrofuran and propylene glycol have been determined at 298.15 K using single crystal variable path interferometer working at 3 Mhz. Excess sound velocities have been evaluated using the formula which is thermodynamically valid. Both the ultrasonic velocity and excess ultrasonic velocity have been found to vary nonlinearly with concentration in the high dilution range of water in nonelectrolytes studied. The results are explained by considering the existence of water molecules as monomers up to certain optimum concentration  $(X_2)_{opt}$  of water and the nonlinear behaviour observed beyond  $(X_2)_{opt}$  has been explained in the light of water-water and water- nonelectrolyte interactions leading to the formation of islands of water-nonelectrolyte complexes.

### 1 Introduction

Ultrasonic velocity measurements have been carried out<sup>1-12</sup> throughout the composition range in completely miscible systems of water and nonelectrolytes. However, the measurements have been quite extensive in the water-rich region, because of the peculiarities exhibited in this region. In the organic-rich region the number of measurements are fewer and do not extend to infinite dilution of water. Most of the data simply show a linear variation in the mole-fraction range 0.9 to 1.0 of the organic solute in water.

Recently, density and partial molar volume measurements have been made of water in organic liquids as infinite dilution<sup>13</sup> with a view to understanding the structure and molecular interactions between the water and organic solute molecules. The literature survey indicates that ultrasonic velocity measurements in the organic rich region are scanty. An initial attempt<sup>14</sup> has been made in these laboratories to understand the structure of dilute solutions of water in a few nonelectrolytes from measurements of ultrasonic velocity and evaluation of excess sound velocity. The present paper deals with further studies carried out on ultrasonic behaviour of dilute solution of water in a few other nonelectrolytes.

### 2 Experimental Details

AR grade n-propanol, isopropanol, glycerol, formamide, N-methyl formamide, dimethyl formamide, tetrahydrofuran and propylene glycol used in the present study were purified as per standard procedures<sup>15</sup>. The densities of the pure liquids, determined using a bicapil-

lary type pycnometer with an accuracy of 2 parts in  $10^5$  were 799.65 kg m<sup>-3</sup>, 781.05 kg m<sup>-3</sup>, 1258.35 kg m<sup>-3</sup>, 1129.19 kg m<sup>-3</sup>, 998.24 kg m<sup>-3</sup>, 944.20 kg m<sup>-3</sup>, 881.97 kg m<sup>-3</sup> and 1032.76 kg m<sup>-3</sup> for n-propanol, isopropanol, glycerol, formamide, N-methyl formamide, dimethyl formamide, tetrahydrofuran and propylene glycol, at 298.15 K. These values are in good agreement with literature values.

Ultrasonic velocity in pure liquids and in solutions were determined at 298.15K using a single-crystal variable-path interferometer working at 3 Mhz with an accuracy of 0.01%. The temperature of the liquid was maintained constant to better than 0.005K by immersing the interferometer in a water thermostat whose temperature was maintained at any desired temperature using permanent heaters and switched low wattage heaters. The temperature of the liquid was measured using a bead type thermistor and a constant current Wheatstone bridge with a chopper-stabilized operational amplifier as null detector. The thermostat and electronic circuitry were housed in an air-conditioned room maintained at  $20 \pm 1^\circ\text{C}$ . This resulted in improved stability of the oscillator and efficient temperature control. Solutions of desired concentration were prepared by weight using triple-distilled de-gassed water.

### 3 Results and Discussion

Ultrasonic velocities in dilute solutions of water in n-propanol, isopropanol, glycerol, formamide, N-methyl formamide, Dimethyl formamide and tetrahy-

drofuran and propylene glycol are shown as a function of water concentration in Fig. 1. Excess sound velocities were determined using the following relations.<sup>24</sup> :

$$u^E = u_{\text{exp}} - u_{\text{id}} \quad \dots(1)$$

$$\text{where } u_{\text{id}} = \frac{1}{\rho_{\text{id}} \beta_{\text{id}}} \quad \dots(2)$$

$$\text{and } \beta_{\text{id}} = K_{\text{id}} - \frac{T v_{\text{id}} (\alpha_{\text{id}})^2}{C p_{\text{id}}} \quad \dots(3)$$

$$\text{here } \rho_{\text{id}} = \phi_1 \rho_1 + \phi_2 \rho_2 \quad \dots(4)$$

$$K_{\text{id}} = \phi_1 K_1 + \phi_2 K_2 \quad \dots(5)$$

$$V_{\text{id}} = X_1 V_1 + X_2 V_2 \quad \dots(6)$$

$$\alpha_{\text{id}} = \phi_1 \alpha_1 + \phi_2 \alpha_2 \quad \dots(7)$$

$$C p_{\text{id}} = X_1 C p_1 + X_2 C p_2 \quad \dots(8)$$

$\beta$ ,  $k$ ,  $\rho$ ,  $\alpha$ ,  $V$  and  $C_p$  represent the adiabatic compressibility, isothermal compressibility, density, thermal expansion coefficient, molar volume and molar specific heat at constant pressure respectively. The suffix 1 refers to the organic solvent and suffix 2 refers to pure water, suffix id represents the ideal value of the parameter in the solution. The pure liquid parameters required for calculating  $u^E$  are given in Table 1.

The variation of excess sound velocity with mole fraction  $X_2$  of water in n-propanol, isopropanol, glycerol, propylene glycol, formamide, NMF, DMF and THF are presented in Fig.2.

An examination of the data presented in Fig. 1 indicates that ultrasonic velocity varies nonlinearly with concentration of water in all the systems except at very

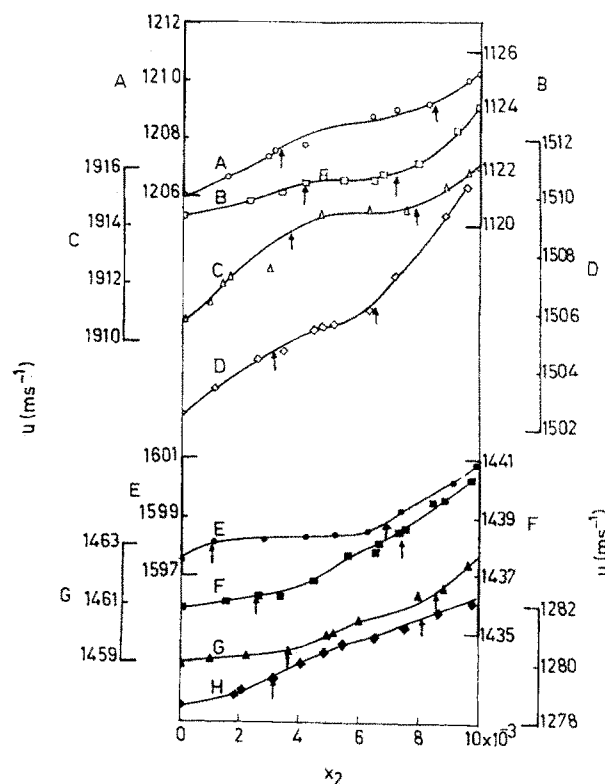


Fig. 1 — Ultrasonic velocity  $u$  versus molefraction  $X_2$  of water in dilute solutions of water in nonelectrolytes

A – n-propanol, B – isopropanol, C – glycerol, D – Propylene glycol. E – formamide, F – N-methyl formamide, G – dimethyl formamide and H – tetra hydrofuran

Table 1 —  $u$ ,  $\rho$ ,  $C_p$ ,  $\alpha$ ,  $\beta$  and  $K$  of pure liquids at 298.15K

Liquid	$u$ ( $\text{m s}^{-1}$ )	$\rho$ ( $\text{kg m}^{-3}$ )	$C_p$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )	$\alpha \times 10^4$ ( $\text{K}^{-1}$ )	$\beta \times 10^{11}$ ( $\text{N}^{-1} \text{m}^2$ )	$K \times 10^{11}$ ( $\text{N}^{-1} \text{m}^2$ )	Ref
Water	1496.7	997.07	75.30	2.59	44.77	45.25	3
n-Propanol	1206.0	799.65	149.00	9.80	86.10	100.54	3
Iso Propanol	1140.3	782.40	153.40	10.10	102.10	117.33	25
Glycerol	1910.8	1258.35	221.90	4.96	21.86	24.26	3
Formamide	1597.5	1129.19	107.8	7.75	34.63	41.26	26
N-methyl formamide	1436.0	998.24	125.1	8.76	48.89	59.70	27
Dimethyl formamide	1459.0	944.20	150.8	9.99	49.79	69.24	27
Tetrahydrofuran	1278.6	881.97	123.56	12.43	69.48	99.87	27
Propylene glycol	1502.5	1032.76	177.06	6.95	42.89	48.88	28

low concentrations. The optimum concentrations  $(X_2)_{opt}$  up to which linearity is observed in  $u$  versus  $X_2$  are presented in Table 2. Beyond these optimum concentrations  $u$  versus  $X_2$  is nonlinear for all the systems. This behaviour is well reflected in the excess ultrasonic velocity versus  $X_2$  as shown in Fig. 2. The values  $(X_2)_{opt}$  in  $u^E$  versus  $X_2$  are also given in Table 2.

In the water rich region, n-propanol is known to enhance the hydrogen bonded structure of water as revealed from temperature of density maximum<sup>25</sup> (TDM) and sound velocity maximum<sup>29</sup> (TSVM) and adiabatic compressibility minimum<sup>30</sup> (TACM) studies. Isopropanol is also known to stabilize the three dimensional structure of water when present in small amounts from temperature of density maximum studies<sup>25</sup>. The structural contribution to the shift in the TDM is positive at low concentrations of isopropanol. Glycerol is known to destabilize the hydrogen bonded structure of water even when present in small amount as revealed from the negative values of the structural contribution to the shifts in TDM, TSVM and TACM. The low positive values of excess molar heat capacity for (water + glycerol) system<sup>3</sup> also reflect the structure breaking nature of glycerol. Formamide, N-methyl formamide and dimethyl formamide are known to form 3:1 and or 2:1 water amide complexes due to strong inter-component association as reflected from the extreme observed in various excess thermodynamic functions as a function of concentration of the amides<sup>24,26,27</sup>.

Studies on excess volumes, enthalpies and thermal expansivities<sup>31,32</sup> suggest that the THF molecule promotes water structure in the water rich region. The excess heat capacity and compressibility data<sup>33</sup> also support the possibility of strong hydrophobic hydration in the water rich region of (water + THF) mixtures.

In the water rich region propylene glycol is known to enhance the hydrogen bonded structure of water as is reflected from the positive values of the structural shifts in TMD studies<sup>25</sup>. However at high temperatures this molecule loses its structure stabilizing character as is reflected from TSVM and TACM studies<sup>34</sup>.

In the very high dilution region of water in nonelectrolytes, it is how the water molecules exist as clusters or monomers that decide the ultrasonic behaviour as is reflected from Figs. 1 and 2. According to Eucken<sup>35</sup> water may be considered to be composed of four distinct monomers,  $(H_2O)$ , dimers  $(H_2O)_2$ , quadrumers  $(H_2O)_4$  and Octomers  $(H_2O)_8$ . If water exists as monomers then ultrasonic velocity must vary linearly with concentra-

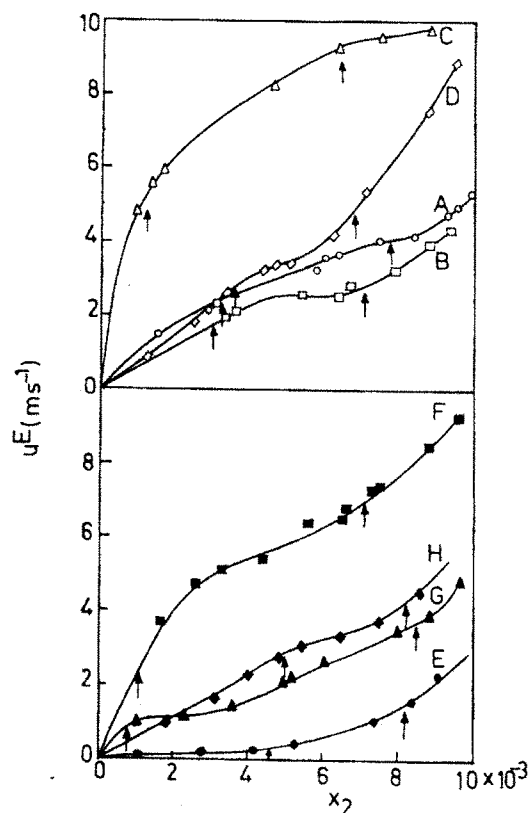


Fig. 2 — Excess ultrasonic velocity  $u^E$  versus molefraction  $X_2$  of water in dilute solutions of water in nonelectrolytes

A – n-propanol, B – isopropanol, C – glycerol, D – Propylene glycol, E – formamide, F – N-methyl formamide, G – dimethyl formamide and H – tetra hydrofuran

Table 2 — Optimum concentration of water  $(X_2)_{opt}$  up to which  $u$  versus  $X_2$  and  $u^E$  versus  $X_2$  are linear

System	$(X_2)_{opt}$	
	$u$ versus $X_2$	$u^E$ versus $X_2$
n-Propanol + Water	0.0032	0.0032
Iso propanol + Water	0.0040	0.0030
Glycerol Water	0.0035	0.0012
Formamide + Water	0.0010	0.0045
N-methyl formamide + Water	0.0025	0.0010
Dimethyl formamide + Water	0.0035	0.0008
Tetrahydro furan + Water	0.0030	0.0050
Propylene glycol + Water	0.0030	0.0034

tion in dilute solutions of water in nonelectrolytes. The linearity in  $u$  versus  $X_2$  and  $u^E$  versus  $X_2$  up to  $(X_2)_{opt}$  may be explained as due to the water molecules existing as monomers, that is, as isolated molecules dispersed uniformly in the non electrolyte.

Beyond  $(X_2)_{opt}$   $u$  versus  $X_2$  is nonlinear and this nonlinear behaviour can be seen more markedly in  $u^E$  versus  $X_2$  curves for all the systems. This nonlinear variation indicates that in dilute solutions of water in non electrolytes water molecules exist as polymeric molecules. This behaviour favours the interpretation of water as distorted ice like structure with bonds constantly breaking and reforming and the associations extending throughout the whole liquid. As per this view, when water is present in very small amounts in a nonelectrolyte liquid, one may consider the existence of water molecules dispersed homogeneously throughout the bulk of the solution with the possibility of formation of water-water or water-non electrolyte associations.

The possible dissociation reaction schemes<sup>36</sup> that may exist when water is dissolved in the nonelectrolyte

are illustrated in Fig. 3. The observed nonlinear and non-ideal behaviour in  $u$  versus  $X_2$  and  $u^E$  versus  $X_2$  may be attributed to the existence of hypothetical particles in the solution with the possibility of bond formation with either water molecules or nonelectrolytes. The formation of islands of water, nonelectrolyte complexes in dilute solutions may be responsible for the observed ultrasonic behaviour.

It may be mentioned here that Sakurai and Nakagawa<sup>13</sup> from the study of densities of dilute solutions of water in n-alkanols, observed the limiting partial molar volumes  $V_w$  of water for solutions of lower alkanols to be smaller than the molar volume of pure water and this behaviour has been attributed to the strong hydrogen bond formation between water and alkanol molecules. In a similar way the observed ultrasonic behaviour of water in n-propanol, isopropanol, F, NMF, DMF, THF and PG beyond  $(X_2)_{opt}$  may be attributed to the hydrogen bond formation between hypothetical particle and nonelectrolyte molecules in the concentration range where  $u$  versus  $X_2$  and  $u^E$  versus  $X_2$  show flat profiles

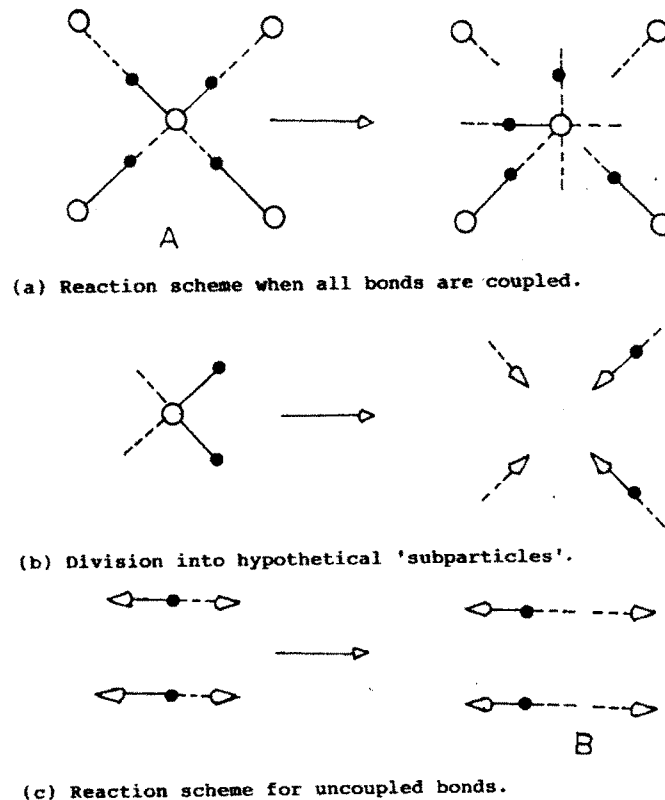


Fig. 3 — Dissociation reaction schemes of water. O — oxygen, • — hydrogen ----- hydrogen bond or possibility of bond formation <->- hypothetical 'sub-particle' (has one bond possibility), A — the four places available for bond formation in water molecule are occupied by neighbours (hydrogen bonded cluster structure). B — normal close packed liquid (monomer water molecules)

between the arrows marked in the Figs 1 and 2. In the case of (glycerol + water) system  $u$  versus  $X_2$  and  $u^E$  versus  $X_2$  are rather smooth which reflect the existence of water more as monomers or dimers than as trimers or octomers or complexes with glycerine molecules. It is worthwhile to note here that in the case of (THF + water) system, when water is added to pure THF, water-water hydrogen bonds are broken and water-THF hydrogen bonds are formed. The positive values of partial molar excess enthalpies of water observed<sup>31</sup> at low  $X_2$  suggest that the mixed bonding is weaker than the bonding in pure water. When water is added to pure isopropanol, the apparent molar volume of the alkanol decreases by up to 10 percent. The negative excess volume of the mixture in the organic rich region has been attributed to the packing of small water molecules in void volumes between organic molecules<sup>37,38</sup>. This behaviour supports proposed view of formation of islands of water molecules in the solution to explain the ultrasonic behaviour.

At higher concentrations beyond the second arrow shown in the Figs 1 and 2  $u$  versus  $X_2$  and  $u^E$  versus  $X_2$  show a linear or gradual increase with  $X_2$ . This behaviour might be due to collapse of water-nonelectrolytes clusters and formation of free water molecules as monomers, dimers, quadrumers or octomers distributed uniformly throughout the solution.

In the concentration region between the two arrows marked in the Figs 1 and 2 there appears to be formation of islands of clusters of water molecules dispersed uniformly throughout the solution. The rate of change of velocity with concentration is either low or remains unchanged indicating that there is no much change in the intermolecular space as a result of addition of water to the nonelectrolyte.

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