Compressibility Studies of Binary Solutions Involving Water as a Solute in Nonaqueous Solvents at $T = 298.15$ K

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The experimental measurements of the speed of sound and density in binary solutions of MeOH, EtOH, *n*-PrOH, *n*-BuOH, acetonitrile (ACN), dimethylformamide (DMF), tetrahydrofuran (THF), and 1,4-dioxane as solvents and water as the solute in the concentration range of 0.02 mol·kg^{-1} to 1 mol·kg^{-1} at $T = 298.15$ K are reported. The data are used to obtain the isentropic compressibility of solution. The apparent molar volume (ϕ_V) and compressibility (ϕ_K) of water at different concentrations are evaluated. The data of limiting volume (ϕ_V^0) and compressibility (ϕ_K^0) and their concentration variation are examined to study the effect due to water−solvent and water−water interactions. It has been observed that there is loss of volume and compressibility of liquid water molecules in transferring them from the pure liquid state to a nonaqueous solvent. An attempt is made to explain the large negative value of ϕ_K^0 in alcohols due to H-bonding characteristics of water and alcohol and the effect of the presence of nonpolar groups. The possibilities of the presence of water-centered complexes or participation of water in a chain-like structure along with pressure effects are examined on the basis of concentration variation of the derived properties.

Introduction

The unusual solvent properties of water have been interpreted in terms of the structure of the liquid (i.e., the possibility of intermolecular association by means of H-bonding into three-dimensional structures).[1,2] It is known that only linear association is possible in pure monohydric alcohols, which does not lead to unusual properties.[3] It may be asked whether structural effects, similar to these in water, might occur in other simple organic liquids. Thermodynamic and spectroscopic properties of aqueous solutions of electrolytes and nonelectrolytes have been studied in great detail.[4,5] The interactions have been explained in terms of solute−solvent and solute−solute (hydrophobic) interactions in aqueous solutions especially for model compounds such as alcohols, hydrocarbons, alkali halides, tetra-alkylammonium halides. and surfactants.[6] The concepts of structure-making and structure-breaking solute have been found to be useful to explain the properties and effects due to salting-in and salting-out, especially in mixed aqueous solvent systems.[7] However, such studies for solutes including water in organic polar and organic nonpolar solvents are very much limited because of experimental difficulties and theoretical developments.[8]

The dilute solution of water in organic solvents is of great interest. In such solutions the long range structure of water, which is so important to the properties of dilute aqueous solution, is no longer in existence, and the only species of any importance are monomers, dimers, trimers, etc. A comprehensive review by Christian et al.[9] summarizes the earlier work carried out to elucidate the nature of specific solute−solvent or water-forming molecular complexes in addition to monomer−dimer self-associative equilibria. It is generally believed that water dissolves in aliphatic and aromatic hydrocarbons as monomers. In slightly polar solvents, vapor pressure and other nonthermodynamic evidence indicate that the water is associated to some extent.[10] Our recently reported dielectric and IR spectral properties of solutions of water in benzene solutions reveal that water molecules exist in cyclic trimer form having a low equilibrium constant.[11] The viscosity studies of water solutions in alcohols have been explained in terms of participation of water molecules in chain-like structure formation (linear H-bonding) and formation of water-centered complexes for butanol and higher alcohols.[12]

It is felt that knowledge regarding structural aspects of water dissolved in small amounts in organic solvents having varied dipole moments and dielectric constant properties may yield useful information to understand the role of water at interfaces and especially across cell membranes for transportation of ions and conformational changes involved in biological living systems. We have tried to look into the above-mentioned problem of structure of liquid water when dissolved in a series of alcohols, 1,4-dioxane, THF, DMF, and ACN. Although thermodynamics does not yield directly the structural aspects of the molecular interaction, one can derive meaningful inferences from thermodynamic properties such as partial volume, partial compressibility and free energy, and enthalpy function indirectly. We report in this paper, speed of sound and density measurements carried out for solutions (up to 1 mol·kg^{-1}) involving water as a solute at $T = 298.15$ K. The solvents chosen were MeOH, EtOH, *n*-PrOH, *n*-BuOH, THF, ACN, 1,4-dioxane, and DMF. The data are used to calculate isentropic compressibility, apparent molar volume (ϕ_V), and apparent molar isentropic compressibility (ϕ_K) of water as a function of the concentration of water. The appropriate determination of partial molal volume (ϕ_V) and compressibility (ϕ_K) of water at infinite dilution and its variation with concentration yield information about water−solvent and water−water interactions. These aspects are presented and discussed herein.

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Table 1. Density ρ, Sound Speed u, and Other Properties of the Various Solvents Studied at T = 298.15 K

	ρ/kg·m^{-3}		u_0/m·s^{-1}		$10^{11}\beta_S$	$10^6 V^0$		μ
solvent	exptl	lit.	exptl	lit.	Pa^{-1}	m^3·mol^{-1}	ϵ	D
MeOH	786.66	786.60[a]	1103.8	1103.0[d]	104.3	40.2	32.6[b]	1.66[b]
EtOH	785.21	785.06[b]	1142.1	1141.2[d]	97.6	58.7	24.3[b]	1.68[b]
n-PrOH	799.68	799.70[c]	1207.0	1205.4[d]	85.8	75.2	20.1[b]	1.66[b]
n-BuOH	806.02	806.00[c]	1241.6	1245.0[d]	80.5	92	17.1[b]	1.68[b]
ACN	776.39	776.60[c]	1281.3	1280.0[e]	78.5	52.9	36.0[f]	3.37[b]
THF	882.06	881.97[d]	1280.2	1280.4[d]	69.2	81.8		1.69[g]
DMF	944.08	944.07[a]	1460.2	1459.3[d]	49.7	77.4	36.7[f]	3.86[f]
1,4-dioxane	1028.34	1026.87[b]	1346.3	1346.0[d]	53.7	85.7	2.2[b]	0.45[b]

[a] Ref 13. [b] Ref 14. [c] Ref 15. [d] Ref 16. [e] Ref 17. [f] Ref 18. [g] Ref 19.

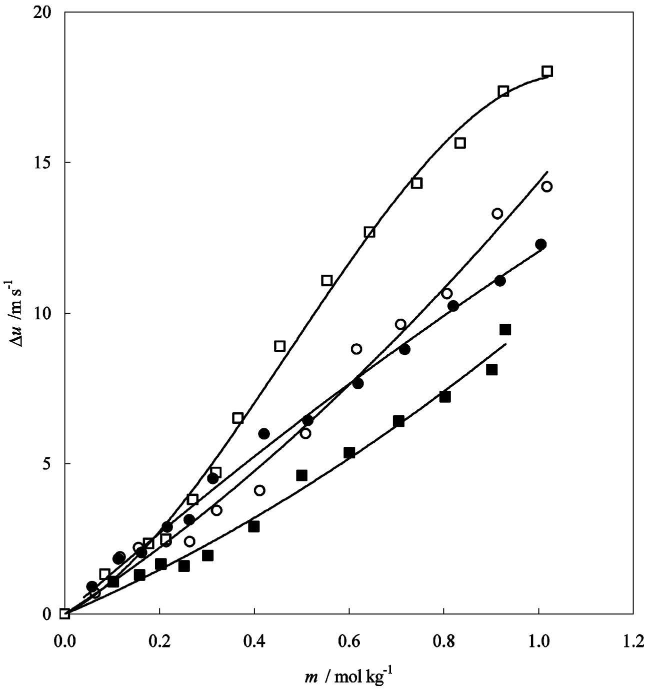

Figure 1. Variation of speed of sound parameter (Δu) as a function of molality of water (m) at T = 298.15 K: ○, H_2O + MeOH; □, H_2O + EtOH; ●, H_2O + *n*-PrOH; ■, H_2O + *n*-BuOH.

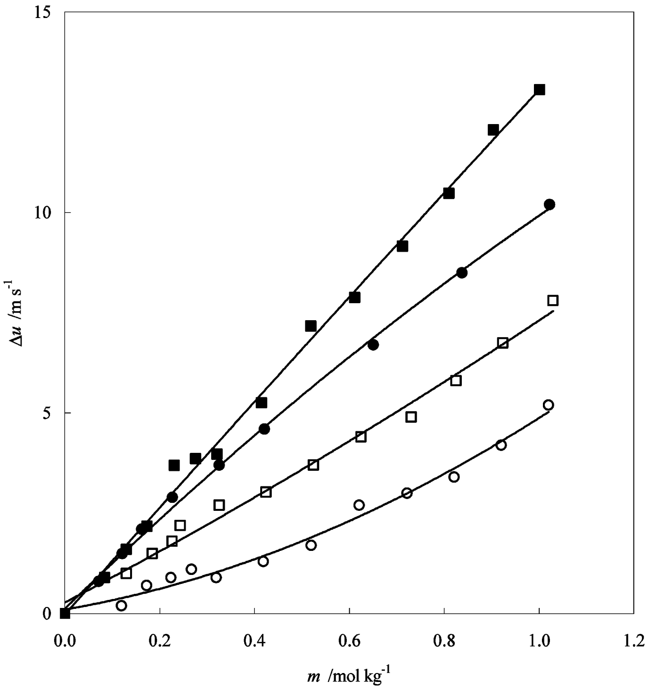

Figure 2. Variation of speed of sound parameter (Δu) as a function of molality of water (m) at T = 298.15 K: ○, H_2O + ACN; □, H_2O + THF; ●, H_2O + 1,4-dioxane; ■, H_2O + DMF.

Experimental Section

1,4-Dioxane, DMF, ACN, and MeOH were of spectroscopic grade procured from Thomas Baker. EtOH, *n*-PrOH, and *n*-BuOH were of AR grade procured from s.d. Fine Chemicals, while THF was procured from Merck.

1,4-Dioxane was treated with KOH, and the aqueous layer was removed. It was then allowed to stand over pellets of KOH for 1 day and dried over sodium for several hours. It was then redistilled over sodium and collected in an amber glass stoppard bottle. ACN was kept in the presence of $CaCl_2$ for 12 h and distilled, and the middle fraction was treated with molecular sieves for several hours. The distilled ACN was then refluxed over P_2O_5 and distilled. THF was simply distilled, and the middle fraction of the distillate was kept over molecular sieves for about 12 h and then redistilled. *n*-BuOH was treated with hot ignited CaO, and the aqueous layer was removed. It was then allowed to stand over CaO for 1 day, dried over sodium, and distilled; the middle fraction was collected in an amber glass stoppard bottle. The other solvents DMF, MeOH, EtOH, and *n*-PrOH were used without any further purification. In these solvents the water concentrations were determined using a microprocessor-based automatic Karl Fischer titrator, TKF-55, Chemito from the M/S Toshniwal Company. Pyridine-free Aquanil-5 Karl Fischer reagent of Thomas Baker was used for analysis. The reagent was standardized with a solution of water in MeOH. The instrument was able to detect water content of the order of ± 2 ppm in organic solvents. The water contents found for the solvents 1,4-dioxane, THF, DMF, ACN, MeOH, EtOH, *n*-PrOH, and *n*-BuOH were of the magnitude of 580, 433, 539, 282, 469, 1201, 258, and 1167 ppm, respectively.

Densities of all the purified liquids and solutions of water in organic solvents were determined using a high-precision Anton Paar DMA 60/602 digital densitometer at T = 298.15 K. The uncertainty in the density measurement was found to be of the order of $\pm 1 \times 10^{-2}$ kg·m^{-3}. The reliability of density data was checked by determining density values for the various solvents used. The values obtained for 1,4-dioxane, THF, DMF, ACN, MeOH, EtOH, *n*-PrOH, and *n*-BuOH were found to be in good agreement with literature data,[13−19] which are collected in Table 1. The minimum assays of water content were also considered, while preparing the solutions of water in organic solvents. The water used for the preparation of solutions was freshly prepared double quartz distilled deionized water. All the solutions were prepared on a molality basis.

Speed of sound measurements were carried out for solutions of water in organic solvents at T = 298.15 K using an ultrasound interferometer operated at 2 MHz frequency (M/S Mittle Enterprises). Good quality thermostating (temperature inside the cell ± 0.05 K) to maintain constant temperature was achieved by circulating water by means of a Julabo thermostat having an accuracy of ± 0.02 K around the cell. The reproducibilities in speed of sound measurements were found to be better than ± 0.5 $m \cdot s^{-1}$ in individual values. The values obtained for pure liquids (i.e., 1,4-dioxane, THF, DMF, ACN, MeOH, EtOH, *n*-PrOH, and *n*-BuOH) are in good agreement with the best literature data available and have also been collected in Table 1 along with other solvent properties such as dielectric constant, molar volume, and dipole moment of the solvents used.[13−19]

Results

The variations of the speed of sound parameter ($\Delta u = u_{\text{solution}} - u_{\text{solvent}}$) as a function of the molality of water in 1,4-dioxane, THF, DMF, ACN, MeOH, EtOH, *n*-PrOH, and *n*-BuOH are shown in Figures 1 and 2. Isentropic compressibility (β_S) of water was obtained using the Laplace equation $\beta_S = 1/(u^2\rho)$. The variations of β_S values with the molality of water are shown in Figures 3 and 4. The uncertainties in β_S values were obtained using

$$\Delta\beta_S = \beta_S\left[\left(\frac{2\Delta u}{u}\right) + \left(\frac{\Delta\rho}{\rho}\right)\right] \tag{1}$$

and were found to be of the order of $\pm\, 0.05 \times 10^{-11}$ Pa^{-1} for most of the solvents and in the worst cases were 0.1×10^{-11} Pa^{-1}.

The apparent molar volume (ϕ_V) and apparent isentropic compressibility (ϕ_{K_S}) of water in the above solvents as a function of the molality of water were calculated using

$$\phi_V = \left(\frac{M_2}{\rho}\right) + \left[\frac{n_1 M_1(\rho_0 - \rho)}{m\rho\rho_0}\right] \tag{2}$$

and

$$\phi_K = \left(\frac{M_2\beta_S}{\rho}\right) + \left[\frac{n_1 M_1(\beta_S\rho_0 - \beta_S^0\rho)}{m\rho\rho_0}\right] \tag{3}$$

where n_1 is number of moles of solvent in 1 kg, M_1 is molar mass of solvent, M_2 is molar mass of water, m is molality while β_S^0, ρ_0, β_S, and ρ are the isentropic compressibility and density of solvent and solution, respectively. The errors in ϕ_V and ϕ_K values were obtained using

$$\Delta\phi_V = -\left(\frac{n_1 M_1}{m^2}\right)\left(\frac{1}{\rho} - \frac{1}{\rho_0}\right)\delta m + \left[-\left(\frac{n_1 M_1}{c}\right)\left(\frac{1}{\rho}\right)\delta\rho\right] \tag{4}$$

and

$$(\Delta\phi_K)^2 = \left[-\left(\frac{\beta_S}{\rho^2}\right)\left(\frac{n_1 M_1}{m} + M_2\right)\right]^2(\delta\rho)^2 + \left[-\left(\frac{1}{\rho}\right)\left(\frac{n_1 M_1}{m} + M_2\right)\right]^2(\Delta\beta_S)^2 \tag{5}$$

and found to be of the order of $\pm\, 0.5 \times 10^{-6}$ $cm^3 \cdot mol^{-1}$ for ϕ_V and ± 5 to ± 10 $mm^3 \cdot MPa^{-1} \cdot mol^{-1}$ ϕ_K at a water concentration of 0.1 $mol \cdot kg^{-1}$. The data of ϕ_V and ϕ_K for water as a function of water molality are given in Figures 5 to 8, respectively, for various solvent systems at $T = 298.15$ K. The limiting infinite dilution values for ϕ_V and ϕ_K parameters and their concentration variation are estimated by treating the data of density and adiabatic compressibility of solutions in the following way. The basic data of speed of sound (u), density (ρ), apparent molar volume, and compressibility of water at different molalities of water in various solvents are presented in Tables 2 and 3, respectively.

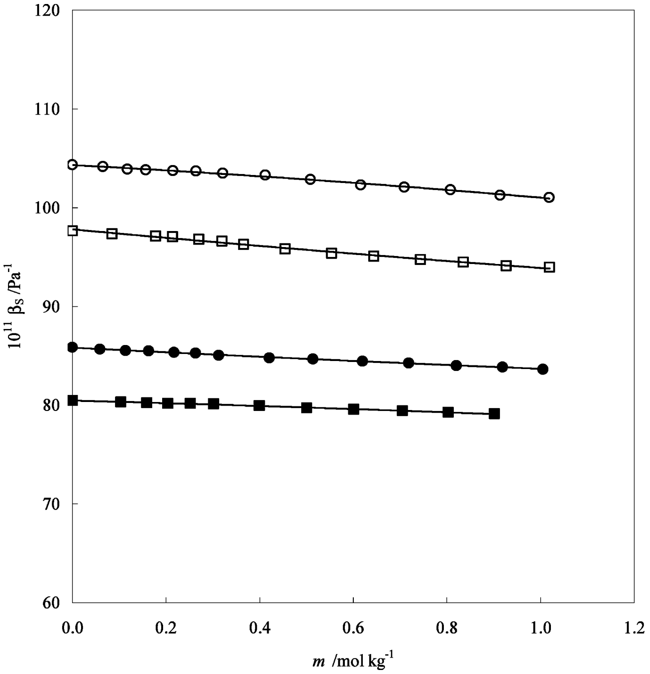

Figure 3. Isentropic compressibility (β_S) variation with molality of water (m) at $T = 298.15$ K: ○, H_2O + MeOH; □, H_2O + EtOH; ●, H_2O + *n*-PrOH; ■, H_2O + *n*-BuOH.

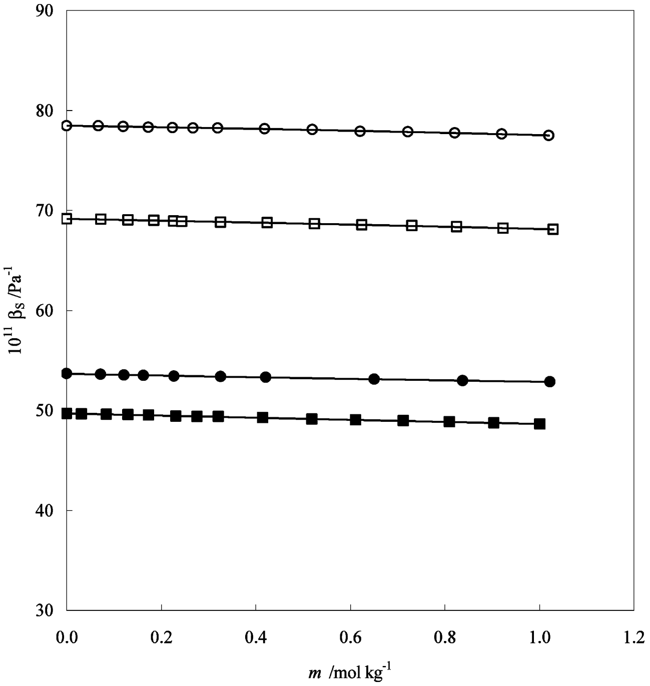

Figure 4. Isentropic compressibility (β_S) variation with molality of water (m) at $T = 298.15$ K: ○, H_2O + ACN; □, H_2O + THF; ●, H_2O + 1,4-dioxane; ■, H_2O + DMF.

The method suggested by Sakurai and Nakagawa[20] was adopted for treating the volumes. The apparent molar volume of water (ϕ_V) is given by

$$\phi_V = \frac{M_2}{\rho_0} - \left(\frac{\rho_0 - \rho}{\rho_0 c}\right) \tag{6}$$

In this expression c is the concentration of water expressed in molarity scale ($mol \cdot L^{-1}$) and M_2 is the molar mass of water.

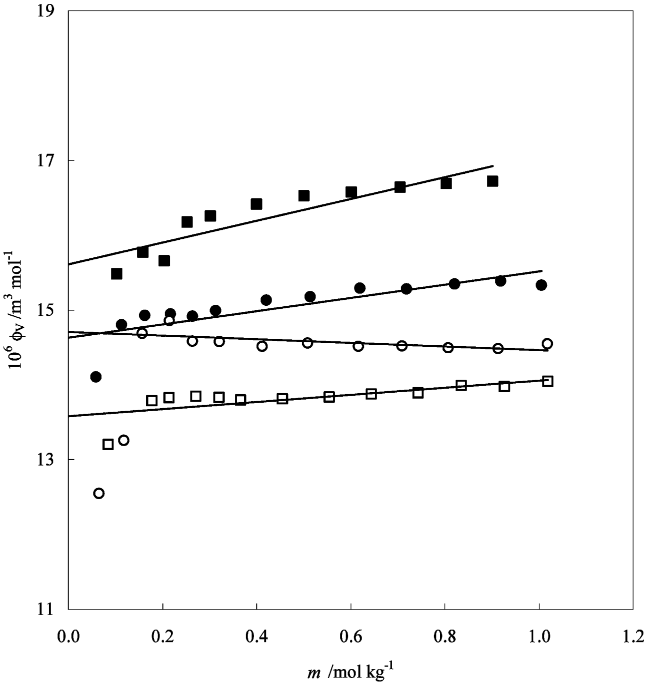

Figure 5. Dependence of apparent molar volume (ϕ_V) of water on molality of water (m) at T = 298.15 K: ○, H_2O + MeOH; □, H_2O + EtOH; ●, H_2O + *n*-PrOH; ■, H_2O + *n*-BuOH.

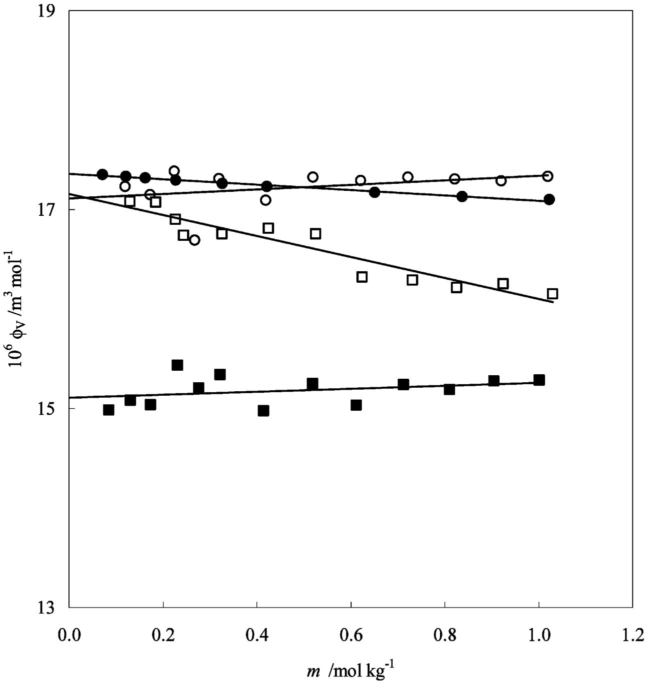

Figure 6. Dependence of apparent molar volume (ϕ_V) of water on molality of water (m) at T = 298.15 K: ○, H_2O + ACN; □, H_2O + THF; ●, H_2O + 1,4-dioxane; ■, H_2O + DMF.

For dilute solutions ϕ_V can be represented in the form:

$$\phi_V = \phi_V^0 + S_V c \tag{7}$$

where ϕ_V^0 is the partial molal volume of water at infinite dilution. From eqs 6 and 7, the density of solution is given by

$$\rho = \rho_0 + Ac + Bc^2 \tag{8}$$

where $A = (M_2 - \rho_0\phi_V^0)$ and $B = -\rho_0 S_V$. Values of A, B, ϕ_V^0, and S_V obtained from a least-squares analysis of each set of results are listed in Table 4. An analogous approach is developed for the apparent molar compressibility data by deriving the equations in the following way:

$$\phi_K = \frac{(\beta - \beta_0)}{c} + \beta_0\phi_V^0 + \beta_0 S_V c \tag{9}$$

and

$$\phi_K = \phi_K^0 + S_K c \tag{10}$$

Since the data of apparent isentropic compressibility of water (ϕ_{K_S}) is obtained from the adiabatic compressibility of solution (β_S), we write

$$\beta_S = \beta_0 + A'c + B'c^2 \tag{11}$$

where $A' = (\phi_K^0 - \beta_0\phi_V^0)$ and $B' = (S_K - \beta_0 S_V)$.

The least-squares fitting method was used to obtain the A' and B' values although there is a scattering of the data of ϕ_K using eq 9 with data having a concentration of water below 0.1 m (which are neglected). The data of limiting isentropic compressibility values for water ($\phi_{K_S}^0$) and their variation with concentration (S_K) based on eq 11 are summarized along with A' and B' values in Table 4.

Discussion

It is observed from Figures 1 and 2 that by addition of water the speed of sound increases in the order for alcoholic solvents as *n*-BuOH < *n*-PrOH < MeOH < EtOH. The rise in speed is much more in EtOH, which signifies comparatively more structural interaction with water. For other solvents, the rise in speed is in the order of ACN < THF < 1,4-dioxane < DMF (Figures 3 and 4). β_S values for all the systems decrease slightly with an increase in the concentration of water. For alcoholic solvents, the magnitude of β_S values is in the order MeOH > EtOH > *n*-PrOH > *n*-BuOH while for other solvents it is ACN > THF > 1,4-dioxane > DMF. These differences arise because of the individuality of the structure of solvents. When examined in terms of variation of the dielectric constant and dipole moment of solvent molecules, no definite correlations can be found. It is felt that in governing the studied properties, the electrostatic H-bonding as well as dipole−dipole interaction certainly contributes to the structural interactions.

The limiting apparent molar volume of water (ϕ_V^0) in all the studied systems is found to be less than the molar volume of pure water (18.068×10^{-6} m^3·mol^{-1} at T = 298.15 K) meaning a contraction in volume in transferring pure liquid water to organic solvents. The results are in good agreement with the data reported for water in alcohols by Sakurai and Nakagawa.[20] The apparent molar volume of water decreases slightly as a function of water concentration in MeOH (i.e., dϕ_V/dm parameter) while it increases in other alcoholic solvents, while the dϕ_V/dm parameters are (analogous to the S_V parameter) slightly positive for ACN and DMF and negative for 1,4-dioxane and THF, respectively. Thus on the basis of dϕ_V/dm we can distinguish two types of interactions (solute−solute and water−water) as in (i) *n*-BuOH, *n*-PrOH, EtOH, ACN, and DMF and the other in (ii) MeOH, THF, and 1,4-dioxane. Thus, solvation of water that takes place in MeOH, THF, and 1,4-dioxane may be due to dipole−dipole and H-bonding interactions, which are similar to those existing in water while the dϕ_V/dm is governed by solvophobic interaction (association) for the solvents of the first group (i.e., solvents containing more nonpolar groups). The S_V values for water in alcoholic solvents are in good agreement

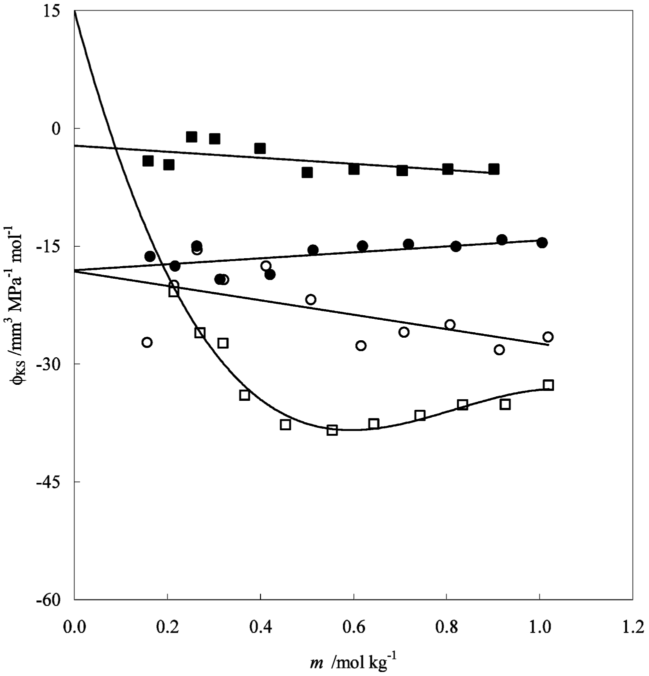

Figure 7. Dependence of apparent molar isentropic compressibility (ϕ_{K_S}) of water on molality of water (m) at T = 298.15 K: ○, H_2O + MeOH; □, H_2O + EtOH; ●, H_2O + n-PrOH; ■, H_2O + n-BuOH.

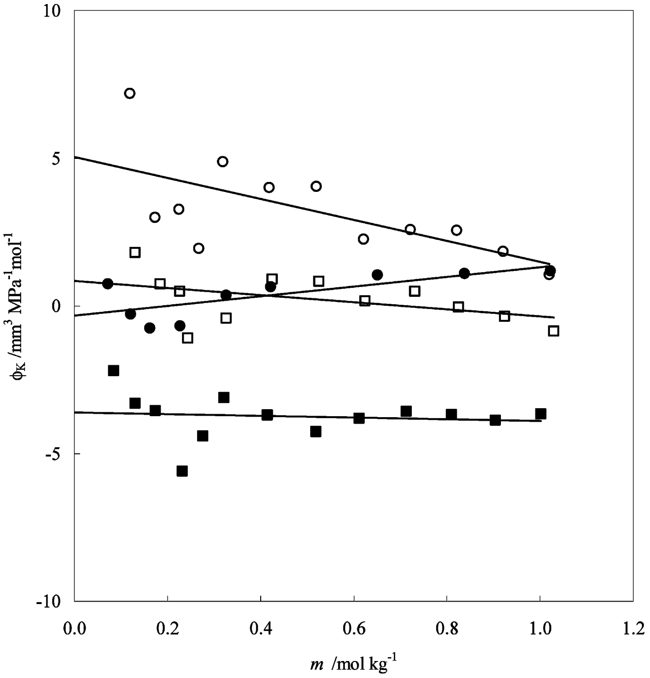

Figure 8. Dependence of apparent molar isentropic compressibility (ϕ_{K_S}) of water on molality of water (m) at T = 298.15 K: ○, H_2O + ACN; □, H_2O + THF; ●, H_2O + 1,4-dioxane; ■, H_2O + DMF.

Table 2. Density ρ, Sound Speed u, β_S, ϕ_V, and ϕ_{K_S} of Water in Alcohols at T = 298.15 K

m	ρ	u	$10^{11}\,\beta_S$	$10^6\,\phi_V$	ϕ_{K_S}	m	ρ	u	$10^{11}\,\beta_S$	$10^6\,\phi_V$	ϕ_{K_S}
$\mathrm{mol\cdot kg^{-1}}$	$\mathrm{kg\cdot m^{-3}}$	$\mathrm{m\cdot s^{-1}}$	$\mathrm{Pa^{-1}}$	$\mathrm{m^3\cdot mol^{-1}}$	$\mathrm{mm^3\cdot MPa^{-1}\cdot mol^{-1}}$	$\mathrm{mol\cdot kg^{-1}}$	$\mathrm{kg\cdot m^{-3}}$	$\mathrm{m\cdot s^{-1}}$	$\mathrm{Pa^{-1}}$	$\mathrm{m^3\cdot mol^{-1}}$	$\mathrm{mm^3\cdot MPa^{-1}\cdot mol^{-1}}$
					Water + MeOH						
0.00000	786.660	1103.8	104.3	13.9[a]	−18.2[a]	0.50853	789.270	1109.8	102.9	14.6	−21 ± 2
0.15659	787.454	1106.0	103.8	14.7	−27 ± 8	0.61591	789.834	1112.6	102.3	14.5	−27 ± 2
0.21426	787.724	1106.2	103.7	14.9	−20 ± 6	0.70890	790.308	1113.4	102.1	14.5	−25 ± 2
0.26413	788.016	1106.2	103.7	14.6	−15 ± 5	0.80742	790.823	1114.4	101.8	14.5	−25 ± 2
0.32112	788.308	1107.2	103.5	14.6	−19 ± 4	0.91358	791.368	1117.1	101.3	14.5	−28 ± 1
0.41209	788.789	1107.9	103.3	14.5	−17 ± 3	1.01803	791.860	1118.0	101.0	14.5	−26 ± 1
					Water + EtOH						
0.00000	785.207	1142.1	97.6	13.4[a]	14.9[a]	0.55413	788.300	1153.2	95.4	13.8	−38 ± 3
0.21398	786.407	1144.6	97.1	13.8	−21 ± 7	0.64373	788.782	1154.8	95.1	13.9	−38 ± 2
0.27050	786.720	1145.9	96.8	13.8	−26 ± 5	0.74300	789.321	1156.4	94.7	13.9	−37 ± 2
0.31985	786.998	1146.8	96.6	13.8	−27 ± 4	0.83492	789.775	1157.7	94.5	14.0	−35 ± 2
0.36588	787.262	1148.6	96.3	13.8	−34 ± 4	0.92645	790.279	1159.5	94.1	14.0	−35 ± 2
0.45432	787.753	1151.0	95.8	13.8	−38 ± 3	1.01891	790.734	1160.1	94.0	14.0	−33 ± 1
					Water + n-PrOH						
0.00000	799.683	1207.0	85.8	14.3[a]	−18.1[a]	0.51368	802.083	1213.4	84.7	15.2	−16 ± 2
0.16267	800.472	1209.0	85.5	14.9	−16 ± 6	0.61958	802.528	1214.7	84.5	15.3	−15 ± 1
0.21698	800.732	1209.9	85.3	14.9	−18 ± 4	0.71831	802.982	1215.8	84.3	15.3	−15 ± 1
0.26347	800.961	1210.1	85.3	14.9	−15 ± 3	0.82045	803.412	1217.2	84.0	15.3	−15 ± 1
0.31291	801.185	1211.5	85.0	15.0	−19 ± 3	0.91914	803.833	1218.1	83.8	15.4	−14 ± 1
0.42093	801.664	1213.0	84.8	15.1	−19 ± 2	1.00508	804.252	1219.3	83.6	15.3	−15 ± 1
					Water + n-BuOH						
0.00000	806.024	1241.6	80.46	15.1[a]	−2.2[a]	0.50072	807.906	1246.2	79.70	16.5	−6 ± 2
0.15880	806.701	1242.9	80.24	15.8	−4 ± 5	0.60115	808.262	1247.0	79.57	16.6	−5 ± 1
0.20344	806.906	1243.3	80.18	15.7	−5 ± 4	0.70503	808.615	1248.0	79.40	16.6	−5 ± 1
0.25259	807.034	1243.2	80.17	16.2	−1 ± 3	0.80321	808.946	1248.8	79.27	16.7	−5 ± 1
0.30192	807.215	1243.6	80.11	16.3	−1 ± 3	0.90166	809.283	1249.7	79.12	16.7	−5 ± 1
0.39984	807.558	1244.5	79.95	16.4	−3 ± 2						

[a] Extrapolated values at infinite dilution

with those reported in the literature[20] while the same data for other solvents are reported for the first time.

Alcohols are known to form linear one-dimensional H-bonded structures. When water is being added, H-bonding with alcoholic -OH is linked to account for the variation of thermodynamic and viscosity properties. Seen in this light in the extreme alcohol-rich concentrations, H-bonding interaction affects the ϕ_V^0 and dϕ_V/dm values showing individualistic differences. In hydrophobic n-BuOH, the lengthening of the alkyl chain seems to reduce the extent of H-bonding interaction showing comparative high dϕ_V/dm value signifying the stronger water−water interaction in addition to water−alcohol H-bonding interactions. It is also observed that DMF causes solute−solvent interaction to a large extent as compared to others while in its solutions the water−water interactions do not appear to be significant. The H-bonding interactions for ACN are not possible because

Table 3. Density ρ, Sound Speed u, β_S, ϕ_V and ϕ_{K_S} of Water in Organic Solvents at T = 298.15 K

m mol·kg^{-1}	ρ kg·m^{-3}	u m·s^{-1}	$10^{11}\,\beta_S$ Pa^{-1}	$10^6\,\phi_V$ m^3·mol^{-1}	ϕ_{K_S} mm^3·MPa^{-1}·mol^{-1}
Water + ACN					
0.00000	776.389	1281.3	78.5	17.1[a]	5.0[a]
0.11973	776.819	1281.5	78.4	17.2	7 ± 7
0.17293	777.019	1282.0	78.3	17.1	3 ± 5
0.22443	777.174	1282.2	78.3	17.4	3 ± 4
0.26743	777.435	1282.4	78.2	16.7	2 ± 3
0.31916	777.518	1282.2	78.2	17.3	5 ± 3
0.41884	777.923	1282.6	78.1	17.1	4 ± 2
0.51979	778.218	1283.0	78.1	17.3	4 ± 2
0.62105	778.584	1284.0	77.9	17.3	2 ± 1
0.72172	778.921	1284.3	77.8	17.3	3 ± 1
0.82122	779.276	1284.7	77.8	17.3	3 ± 1
0.92053	779.631	1285.5	77.6	17.3	2 ± 1
1.01978	779.949	1286.5	77.5	17.3	1 ± 1
Water + THF					
0.00000	882.056	1280.2	69.2	17.3[a]	0.9[a]
0.13015	882.394	1281.2	69.0	17.1	2 ± 5
0.18450	882.536	1281.7	69.0	17.1	1 ± 3
0.22627	882.674	1282.0	68.9	16.9	1 ± 3
0.24403	882.753	1282.4	68.9	16.7	−1 ± 3
0.32585	882.981	1282.9	68.8	16.8	0 ± 2
0.42467	883.242	1283.2	68.8	16.8	1 ± 2
0.52495	883.543	1283.9	68.7	16.8	1 ± 1
0.62450	884.032	1284.6	68.5	16.3	0 ± 1
0.73087	884.381	1285.1	68.5	16.3	0 ± 1
0.82535	884.726	1286.0	68.3	16.2	0 ± 1
0.92426	885.015	1287.0	68.2	16.3	0 ± 1
1.02938	885.427	1288.0	68.1	16.2	0 ± 1
Water + DMF					
0.00000	944.076	1460.2	49.7	15.1[a]	−3.6[a]
0.08457	944.384	1461.1	49.6	15.0	−2 ± 4
0.13044	944.540	1461.8	49.5	15.1	−3 ± 3
0.17378	944.701	1462.4	49.5	15.0	−4 ± 2
0.23154	944.826	1463.9	49.4	15.4	−6 ± 2
0.27625	945.027	1464.1	49.4	15.2	−4 ± 1
0.32149	945.143	1464.2	49.4	15.3	−3 ± 1
0.41462	945.584	1465.5	49.2	15.0	−4 ± 1
0.51892	945.835	1467.4	49.1	15.3	−4 ± 1
0.61146	946.263	1468.1	49.0	15.0	−4 ± 1
0.71233	946.490	1469.4	48.9	15.2	−4 ± 1
0.81000	946.853	1470.7	48.8	15.2	−4 ± 0.4
0.90439	947.103	1472.3	48.7	15.3	−4 ± 0.4
1.00129	947.417	1473.3	48.6	15.3	−4 ± 0.4
Water + Dioxane					
0.00000	1028.337	1346.3	53.7	17.4[a]	−0.3[a]
0.07165	1028.349	1347.1	53.6	17.4	1 ± 6
0.12140	1028.361	1347.8	53.5	17.3	0 ± 3
0.16250	1028.371	1348.4	53.5	17.3	0 ± 2
0.22720	1028.390	1349.2	53.4	17.3	0 ± 2
0.32620	1028.424	1350.0	53.4	17.3	0 ± 1
0.42140	1028.463	1350.9	53.3	17.2	1 ± 1
0.65120	1028.573	1353.0	53.1	17.2	1 ± 1
0.83750	1028.675	1354.8	53.0	17.1	1 ± 1
1.02220	1028.782	1356.5	52.8	17.1	1 ± 0.4

[a] Extrapolated values at infinite dilution

Table 4. Volumetric and Isentropic Compressibility Properties of Water at T = 298.15 K in Various Solvents Obtained from Equations 8 and 11

solvent	A g·mol^{-1}	B g·cm^3·mol^{-1}	$10^6\,\phi_V^0$ m^3·mol^{-1}	S_V cm^3·mol^{-2}	$10^{11}\,A'$ cm^3·Pa^{-1}·mol^{-1}	$10^{11}\,B'$ cm^6·Pa^{-1}·mol^{-2}	$\phi_{K_S}^0$ mm^3·MPa^{-1}·mol^{-1}	S_K mm^6·MPa^{-1}·mol^{-2}
MeOH	6.58	10.93	14.5	−13.9	−3288.71	−1251596.2	−18.2	−12.5
EtOH	7.29	−366.57	13.7	466.8	−5564.37	686327.4	14.9	7.3
n-PrOH	6.07	−464.15	14.9	580.4	−3049.90	412913.4	−18.1	4.6
n-BuOH	4.87	−326.32	16.3	404.9	−1500.43	−672641.6	−2.2	−6.4
ACN	4.49	22.87	17.4	−29.4	−844.10	−497358.7	5.0	−5.0
THF	2.94	948.33	17.1	−1075.1	−985.69	−197837.9	0.9	−2.7
DMF	3.79	−204.81	15.1	216.9	−1156.83	31604.7	−3.6	0.4
1,4-dioxane	0.21	223.01	17.3	−216.9	−900.22	112525.7	0.3	1.0

of its high dipole moment, but the dipole−dipole interaction can lead to a slight alteration in the ϕ_V^0 value and a marginal increase in H-bonding interactions among water molecules. In the systems 1,4-dioxane and THF (both being ethers), solute−solvent interactions appear to be of similar nature and extent; however, the water−water interactions are comparatively more in THF. It has been reported that 1,4-dioxane can form complexes with water. Assuming this is true, one can attribute the small variation in ϕ_V^0 and small negative $\mathrm{d}\phi_V/\mathrm{d}m$ to a similar type of interactions between H-bonded water and 1,4-dioxane clusters with each other.

The pressure derivative of apparent molar volume (ϕ_V) is apparent molar compressibility of solute (ϕ_K) that is, $\phi_K = \mathrm{d}\phi_V/\mathrm{d}P$. In turn, knowledge of ϕ_K behavior can be used to have some insight on the pressure effect on various equilibria and interactions. It is known that the ϕ_K^0 values of electrolytes are negative, meaning a loss in compressibility of water around the cations.[21] Similar effects are exhibited by carbohydrates having unique conformational interacting sites such as axial and equatorial substitutions (myoinositol $\phi_K^0 = -61.1$ mm^3·MPa^{-1}·mol^{-1} at $T = 278.15$ K).[22] Such values are attributed to strong dipole−dipole interactions.[22] We have also found that for 18-crown-6 and Bu_4NBr, the ϕ_K^0 values are negative but of small magnitude as compared to the electrolytes.[23,24] Mathieson and Conway have differentiated hydrophobic and hydrophilic ions on the basis of their ϕ_K^0 magnitudes.[25] The positive magnitude ϕ_K^0 has been observed for many nonelectrolytes[22,26−28] and for ions such as H^+, NH_4^+, and BF_4^+. [25] A clear distinction must be made between the soft structures promoted by H-bonding and the stiff structures promoted by hydrophobic interaction. Many type of solutes are differentiated in water as a structure maker or breaker on the basis of excess partial molar volumes ($\overline{V_2^E} = \overline{V_2^0} - V_2^0$ where V_2^0 is the molar volume). In this criterion, the standard state of solute is restricted to the solute as a pure liquid.[3,5] However, such a restriction is not needed in examining the ϕ_K^0 data of solutes.

Our analysis for $\phi_K{}^0$ of water and its variation with concentration in various organic solvents allows us to examine the status and interactions of water molecules. On the basis of compressibility and volume of pure water, we expect the ϕ_K^0 value for water as +8.12 mm^3·MPa^{-1}·mol^{-1} at T = 298.15 K.

It is very surprising that the ϕ_K^0 values of water in alcohols are negative except in EtOH and that the value depends much on the chain length of the alcoholic molecules. In MeOH, the ϕ_K^0 is most negative while in *n*-BuOH it is least negative (Figure 7). It is expected that in *n*-BuOH, instead of a straight chain elongation, some coiling may occur, resulting in less of a change in compressibility due to H-bonding interactions with water. Probably such interactions may result in the formation of water centered complexes as envisaged in viscosity studies.[12] For a smaller alcohol like MeOH, the H-bonding with water causes stiffening of structure, resulting in a loss of compressibility of water and may be thought of in terms of participation of water molecules in the chain-like structures of alcohols.

We observed almost zero values for $\phi_{K_S}^0$ in etheric solvents, meaning the presence of weak dipole−dipole interactions that are not sensitive to compressional effects. The small difference between the $\phi_{K_S}^0$ in ACN with that in pure water signifies that water mixes with this solvent causing interaction similar to those present in water (strong dipole−dipole correlations) without altering the properties of individual molecules significantly. Comparatively, DMF is a strong solvating solvent because of its basicity exhibiting a slightly negative $\phi_{K_S}^0$ (Figure 8).

On the basis of sign and magnitude of the S_V parameter, we expect a similar behavior for the calculated S_K parameter ($S_K = B' + \beta_0 S_V$) accounting for effect due to solute−solute interaction. Seen in this context, negative S_K values for MeOH, *n*-BuOH, ACN, and THF indicate stabilization of the structural entities against the pressure effect, while positive S_K values for *n*-PrOH may be due to breakdown of H-bonded clusters by application of pressure. The almost zero values of S_K for DMF and 1,4-dioxane indicate that the compressibilities of solvated water molecules due to weak H-bonding are not affected appreciably during application of pressure. When these calculated S_K values are compared with the experimental S_K behavior, the following observations are noted.

(i) The ϕ_K variation ($d\phi_K/dm$) for 1,4-dioxane is in accordance with the calculated S_K value. Similar results for MeOH, ACN, DMF, and THF signify stabilization due to dipole−dipole interaction against pressure.

(ii) In case of water dissolved in EtOH (Figure 7), it is observed that ϕ_K decreases up to ≈ 0.5 to 0.6 $\text{mol}\cdot\text{kg}^{-1}$ of water and increases slowly thereafter. Thus, the $\phi_{K_S}^0$ value is positive. Considering these trends, water in EtOH shows anomalous behavior and may be attributed to azeotrope formation. To understand this behavior clearly, further detailed studies are needed.

(iii) There is a good agreement between observed $d\phi_K/dm$ and calculated S_K values for *n*-PrOH and *n*-BuOH. However, the magnitudes are small, meaning that water−water interactions are not significantly affected by pressure.

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