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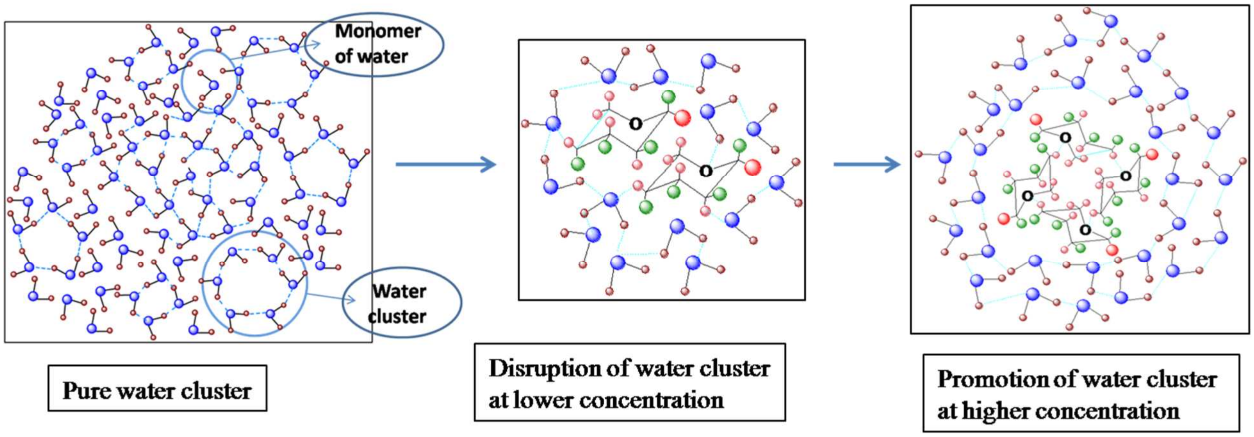
Graphical Abstract



Pure water cluster

Disruption of water cluster at lower concentration

Promotion of water cluster at higher concentration

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Temperature Perturbed Water Structure Modification by *D(-)*-Fructose at Different Concentrations

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ABSTRACT:

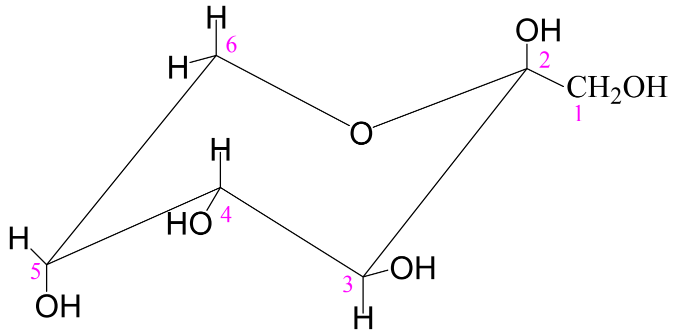
Temperature dependence of water structure modification has been studied at different *D*(-)-fructose concentrations by near-infrared (NIR) spectroscopy. The temperature susceptibility of different structural components of water with varying hydrogen bond strength in presence of *D*(-)-fructose has also been investigated as a function of temperature by 2D correlation spectroscopy from the characteristic spectral variation in water absorption peaks. Apparent molar volume, limiting partial molar volume, free energy change of activation, activation enthalpy change and entropy change for viscous flow, and other thermodynamic parameters for aqueous solution of *D*(-)-fructose at different temperatures and concentrations correlate very well with the water structure modification and ordering in presence of *D*(-)-fructose inferred from the results of NIR spectroscopy. A comprehensive analysis indicates that hydrogen bonding capability of the axial and equatorial OH groups in *D*(-)-fructose varies to a large extent and is mainly responsible for water-fructose interactions with water clusters of different size and geometry such as, dimer, trimer, and cyclic chains at different *D*(-)-fructose concentrations. *D*(-)-fructose has been found to act as water structure-breaker at lower concentrations whereas at higher concentrations it promotes water structure as a structure-maker additive.

1. Introduction

Life exists on the earth because of the abundance of liquid water. The structure of water molecules in the pure liquid state has therefore been subject of extensive research for several decades.[1-7] The structure is described by a combination of parameters, which inter alia includes: the numbers, energies, lengths and orientations of hydrogen bonds; a change in any of these means that the structure or the thermodynamic state of water is altered. There are mysteries and questions still remain unanswered; no single model has been found capable of explaining all the anomalies of water structure.

Hydrogen bonding of different degrees among water molecules is considered to be the origin of different water clusters,[8] which may be varied by different additives. Addition of solutes has profound influence on modifications of water structure similar to that due to changing temperature.[9-10] But a clearer understanding of the origin of modification of water structure with added substances still remains a elusive goal. Despite the challenges, there is intense interest in developing a picture of the local water structure in presence of additives due to fundamental importance of water-additive interaction in many fields of chemistry.[11]

A carbohydrate molecule is one of the most interesting additives that influence the water structure with their accumulation of hydroxyl groups at concentrations higher than any other biomolecules. Numerous studies concern the properties of aqueous solutions of carbohydrates,[12-13] since they are not only biochemically important compounds but also typical non-electrolytes with hydrophilic hydroxyl groups, which are capable of hydrogen bonding.[14] Research to date includes numerous studies which analyze various thermodynamic[15-17] and spectroscopic[18-19] behavior to infer that the hydration of carbohydrates depends on the number of hydroxyl groups,[19-20] the potential hydrogen bonding sites and relative positions of the next nearest neighbor hydroxyl groups within the carbohydrate molecules.[21] *D*(-)-fructose has proved itself as an important monosaccharide which acts as both water-structure breaker and water structure maker at different concentrations.[22] In solution, *D*(-)-fructose exists as an equilibrium mixture of 70% *β-D*-fructopyranose (Scheme 1) and about 23% *β-D*-fructofuranose, as well as of a small amount of the three other forms, including the acyclic structure.[23] In β-*D*-fructopyranose OH-2 and OH-5 are in axial position and the $–CH_2–$ group at position 6 is specified as the hydrophobic-lipophilic 'γ' site which strengthens the hydrogen bonds of the molecules in the bulk water due to repulsion on water.[24-25] In our earlier work we have also explained the importance of orientation of axial and equatorial OH groups in *D*(-)-fructose on water structure modification.[26] Despite progresses, a systematic study on the effect of temperature and concentration of *D*(-)-fructose on water structure modification has not been reported as it shows an ambivalent character towards water .



β-*D*-fructopyranose

Scheme 1. Most stable conformation of **β**-D-fructose

The present work provides new experimental information on the effect of temperature and concentration of *D*(-)-fructose on water structure modification by FT-NIR spectroscopy and the analysis of experimental results by 2D correlation approach. The results have also been correlated with the density and viscometric results which also provided useful information regarding thermodynamic states of the system.

2. Experimental

Materials

D(-)-fructose was received from E. Merck and used without further purifications. All of the aqueous solutions were prepared with deionized water (specific conductivity = 0.055 μS cm^{-1}, BOECOpure, Model: BOE – 8082060, Germany) prepared from distilled water (BOECO, Model: BOE – 8704000, Germany).

Methodology and instrumentation

FT-NIR spectra were recorded at a resolution 4.0 cm^{-1} on PerkinElmer, USA, Frontier FT-IR/NIR in absorbance mode with 32 scans for each sample in the range 4000-12000 cm^{-1}. The measurements were carried out by a high sensitive heatable liquid sampling cell in which rectangular CaF_2 windows with curved edges (Specac Model No.: GS20522) of path length 0.1 mm were used for measurements. The temperature was controlled by an electrical heating jacket (Specac Model No.: GS20730). The densities of the solutions were measured with Anton Paar (Model No.: DMA 4500) vibrating tube density meter. The viscosities of the solutions were measured with Lovis 2000 M/ME microviscometer which measures viscosity by rolling ball principle with an accuracy of $\pm 10^{-6}$ mPa s.

The spectra were corrected for the density change with temperature prior to 2D correlation analysis. The dynamic spectrum was obtained by subtraction of mean normalized reference spectrum from an ordered series of experimental spectra. The synchronous intensity was determined as cross-product of dynamic intensity at two different wavenumbers and the asynchronous intensity was computed using Hilbert transform.[27] The 2D correlation spectra were computed using MATLAB 13 (The Math Works Inc.) software.

3. Results and discussion

NIR spectra of pure water

NIR spectroscopy has an excellent ability to examine the features of hydrogen bonds and it is particularly useful for exploration of the hydrogen-bonded systems.[28-30] Moreover, several computational methods are also available to explain this hydrogen bonded system.[28-31] In the overtone region, the bands due to monomer and various associated species are better separated than in the IR region. Besides, the less-associated species are better identified in the NIR spectrum. For example, the absorption of free OH groups in the fundamental region is very weak, whereas it clearly appears in the NIR region. Finally, because of small molar absorptivities in the overtone region, one can employ more convenient cell path lengths. In contrast to sharp absorption peaks in the MIR region NIR spectra show less intensity and broad bands and reflection intensity in the NIR region is higher than in mid-infrared spectroscopy.

For isolated water molecules the excited vibrational frequencies are: 3651.7 cm^{-1} (υ_1), 1595.0 cm^{-1} (υ_2), 3755.8 cm^{-1} (υ_3). Combinational bands of the bending and stretching modes and overtones are excited at higher frequencies and can be measured in the NIR region.[32] Raw infrared spectra of water for the NIR (7500-4500 cm^{-1}) region were recorded at temperautures from 20 to 75^{o}C with a step of 5 ^{o}C. The present analysis spanned from 5700 to 4500 cm^{-1} where the strong absorption results from the second order combination transition between the asymmetric stretching and bending vibration of OH. From **Fig. 1** in the range of 5400-4600 cm^{-1} it is evident that the absorption maximum decreases with increasing temperature. Quite opposite changes are observed in the high frequency side where the absorption increases with the temperature rise. A closer examination of the crossing points between the two sub-ranges reveals that there is a spectral isosbestic point, which indicates the presence of different interactions in the components of water molecules in equilibrium to each other.

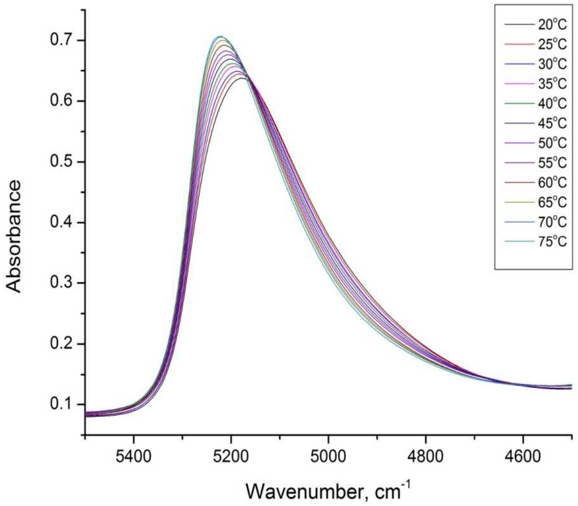


Fig. 1 NIR spectra of water in the range 5400-4600 cm^{-1} at different temperatures.

Effect of temperature and concentration on NIR spectra of water in presence of *D*(-)-fructose

NIR spectra of water in presence of *D*(-)-fructose were recorded at different temperatures and concentrations. Change of absorption maximum in the range of 6000-4600 cm^{-1} is apparent in the NIR spectra. At different concentrations of *D*(-)-fructose this band of water shifts from 5177 cm^{-1} to 5223 cm^{-1} with increase in temperature from 20 to 75 ^{o}C. It is clear from **Fig. 2** that the absorption maximum increases with increasing temperature and the band shifts to higher frequency side with the temperature rise. The increase in the band intensity with the rise of temperature is due to an increase in number of free OH groups. Moreover, the shifting of band to higher frequency indicates that higher energy is required to vibrate the molecules as the bond length decreases with increasing temperature. The concentration dependence of *D*(-)-fructose on the absorption band of water was also monitored at different temperatures. **Fig. 2** represents the absorbance as a function of concentrations of *D*(-)-fructose in the range of 6000-4600 cm^{-1} at 25 ^{o}C. The absorbance increases initially with increasing concentration of *D*(-)-fructose, which may be due to the decrease of the stability of the cluster due to an increase in the number of free OH group. This mechanism is valid up to the concentration of 0.50 M, above which the absorbance decreases with increasing concentration. Therefore, it can be inferred that after this point the *D*(-)-fructose molecules may tend to participate in hydrogen bonding surrounding the water cluster and the water structure is becoming more organized.

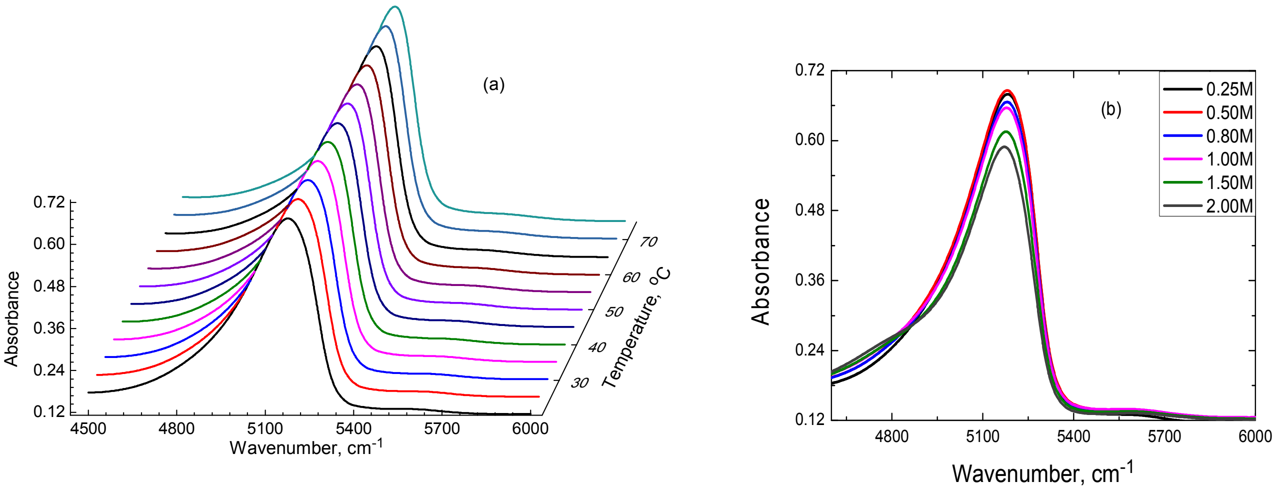


Fig. 2 (a) NIR spectra of water in presence of 0.25 M *D*(-)-fructose at different temperatures and (b) absorbance as a function of concentrations of *D*(-)-fructose in the range of 6000-4600 cm^{-1} at 25^{o}C.

Fig. 3 (a) and (b) show the synchronous and asynchronous maps, respectively, of the 2D variable-variable correlation analysis of aqueous solution of *D*(-)-fructose in the spectral region 4500-5600 cm^{-1}. The synchronous map shows autopeaks at 5050 and 5254 cm^{-1}, indicating that the spectral features at these positions vary in phase with each other. The diminishing component most strongly contributes to the intensity changes at 5050 cm^{-1} while the second peak at 5254 cm^{-1} was found to increase with increase in temperature.

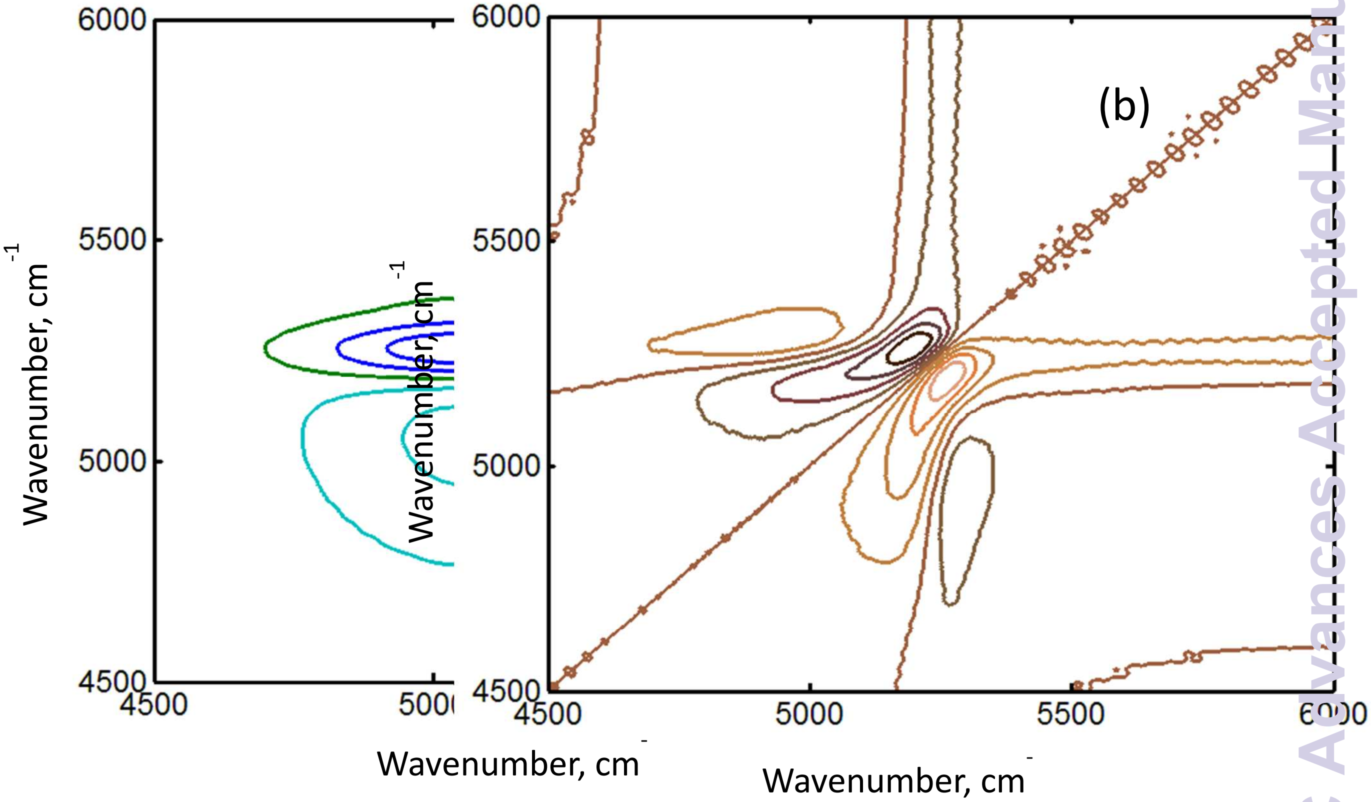


Fig. 3 (a) Synchronous and (b) asynchronous 2D NIR correlation spectrum calculated from the temperature dependent spectral changes of 0.25 M *D*(-)-fructose in water.

The appearance of negative cross-peaks between the auto-peaks and their signs reveals that the changes are correlated and occur in opposite directions. The asynchronous map shows two features with maximum and minimum values at 5254 and 5162 cm^{-1}, indicating that out-of-phase spectral changes occur at these wavelengths and that the change at 5254 cm^{-1} occurs before that at 5162 cm^{-1}.

The power spectra of aqueous solutions of *D*(-)-fructose in the temperature range 20-75 ^{o}C are shown in **Fig. 4**.The power spectrum is a diagonal of the synchronous spectrum which represents the overall extent of intensity changes with increasing temperature at a particular wavenumber.

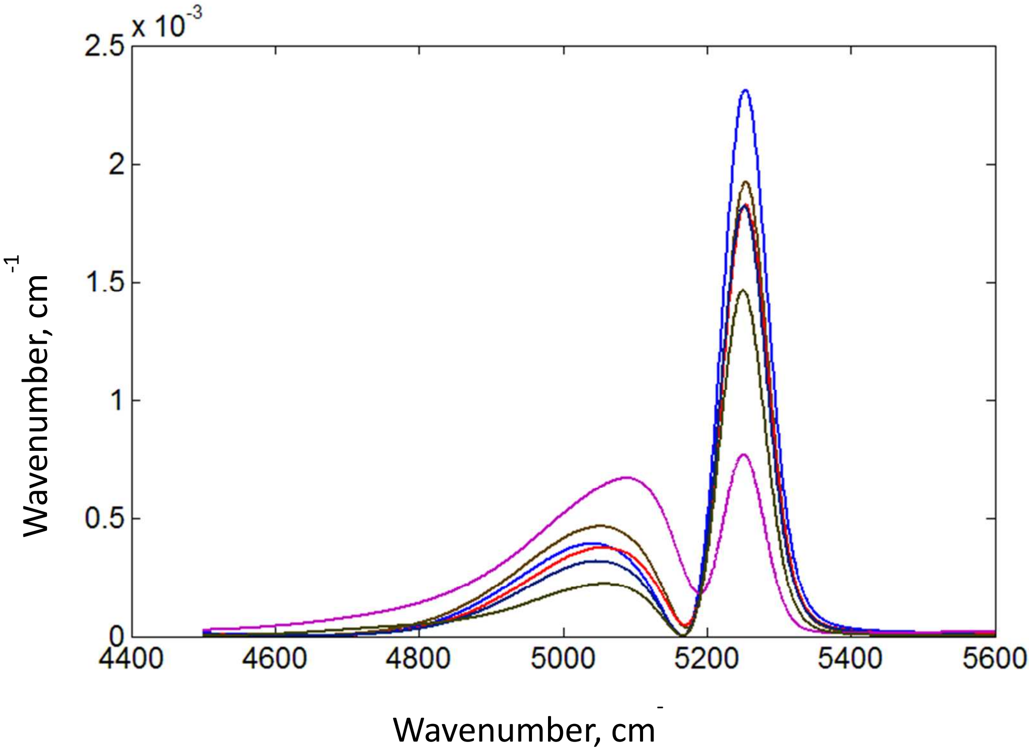


Fig.4 Power spectra of aqueous solutions of *D*(-)-fructoseat different concentrations as a function of temperature.

As can be seen, the weaker hydrogen bonds at higher frequency region are more temperature susceptible whereas the stronger hydrogen bonds at lower frequency region are less. *D*(-)-fructose at lower concentrations is more temperature susceptible than at higher concentrations. This may be due to the less water-fructose interactions at lower concentrations and *vice versa.*

Density and viscometric analysis of D(-)-fructose in water

The density and viscosity of *D*(-)-fructose solutions at different concentrations and temperatures (from 20 to 75°C) have been measured. The density of *D*(-)-fructose in water decreases gradually with increasing temperature in the concentration range studied. Moreover, the density of fructose at different concentrations also increases from 20 to 75°C. On the other hand, the viscosity of *D*(-)-fructose in water decreases sharply with the rise of temperature. In contrast, the viscosity of *D*(-)-fructose in water increases with increasing concentration at all temperatures of investigation. The experimental data of densities and viscosities of *D*(-)-fructose in water at different temperatures have been interpreted to explain the interactions of fructose-water, fructose-fructose and water-water in soluions. Thermodynamic parameters like energy of activation, Gibbs free energy change and entropy change of viscous flow may thus be determined.

To investigate the nature of solute-solvent, solute-solute interactions, the apparent molar volume of water-fructose system at different temperatures and concentrations was calculated from the density data of solutions by the following equation.

$$\Phi_V = \frac{M}{\rho} - \frac{1000(\rho - \rho_0)}{m\rho_0\rho} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

where, M is the molar mass of sugar in gmol^{-1}, m is the molal concentration of *D*(-)-fructose in mol kg^{-1}, ρ and ρ_o are densities of solution and solvent, respectively.

For each system Φ_V with m were used to calculate limiting partial molar volume (Φ_v^o) and experimental slope (S_v) according to the following equation.

$$\Phi_v = \Phi_v^o + S_v m \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(2)}$$

Here, Φ_v^o (cm^{3}mol^{-1}) denotes the solute-solvent interactions and is equal to the partial molar volume of solute at infinite dilution and S_v provides information of solute-solute interaction. **Fig. 5** shows that the Φ_V of *D*(-)-fructose increases at lower concentrations and decreases gradually at higher concentrations. Moreover, with increasing temperature the Φ_V of *D*(-)-fructose increases. Since this trend reverses at higher concentrations, it was assumed that the fructose-fructose interaction increases at higher concentrations. Therefore, *D*(-)-fructose has an optimum molality after which the trend of interactions in fructose-water and fructose-fructose reverses.

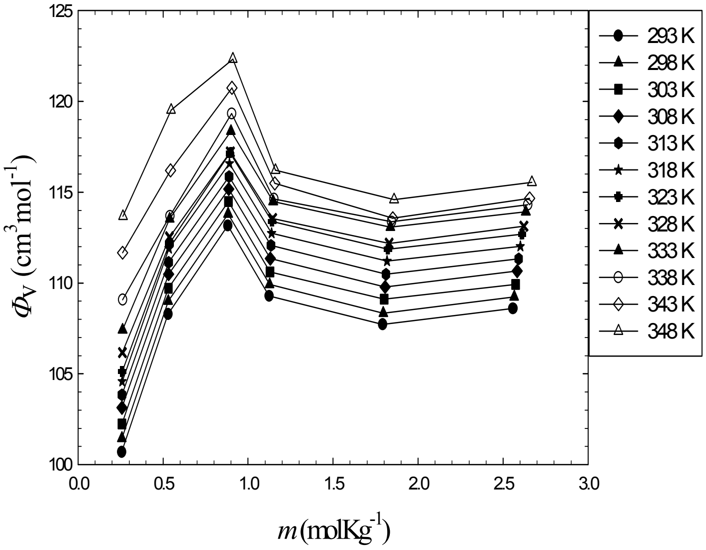


Fig. 5 Apparent molar volume of *D*(-)-fructose as a function of concentration and temperature.

From **Table 1** it is clear that the Φ_v^o increases and the S_v decrease with increasing temperature. The values indicate that fructose-water interaction increases with the rise of temperature whereas fructose-fructose interaction decreases.

Table 1. Density related parameters from apparent molar volume of *D*(-)-fructose

Temperature (*T*), K	$\boldsymbol{\varphi_v^o}$	$\boldsymbol{S_v}$

293	96.436	19.690
298	97.251	19.469
303	98.068	19.255
308	99.036	18.891
313	99.739	18.812
318	100.497	18.739
323	100.914	18.777
328	102.278	17.170
333	104.656	15.497
338	104.951	15.964
343	108.177	14.063
348	110.974	13.141

When *D*(-)-fructose is added to water, water-water hydrogen bonding in other words, clusters of water is disrupted and new water-fructose hydrogen bonding forms. The initial increase of the Φ_V confirms the increasing interaction in water-fructose at lower concentrations. Due to the formation of hydrogen bond in water-fructose the change of apparent molar volume with concentration of *D*(-)-fructose is higher than the corresponding change with temperature. As a result it can be suggested that *D*(-)-fructose acts as water structure-breaker at lower concentrations.

The opposite phenomena were observed for higher concentrations of *D*(-)-fructose in water. With increasing *D*(-)-fructose concentration, the intermolecular interaction in *D*(-)-fructose molecules is increased. Therefore, water molecule is tetrahedrally arranged i.e. organized ice like structure is formed around the fructose molecules. *D*(-)-fructose thus strengthens the water cluster. *D*(-)-fructose may thus act as water structure-maker at higher concentrations.

The data of viscosities of solutions of *D*(-)-fructose are used to study the solute-solute and solute-solvent interactions using Jones-Dole constants *A* and *B* in the Jones-Dole equation.^{33}

$$\frac{\eta_{sp}}{\sqrt{C}} = A + B\sqrt{C} \qquad \text{………………………………………………………… …………..} \quad \textbf{(3)}$$

where η_{sp} is the specific viscosity and A and B represent solute-solute interaction and structural modification induced by the solute-solvent interaction, respectively. **Table 2** represents the variation of Jones-Dole constants and B derivative with increasing temperature. From **Table 2** it could be observed that with the rise of temperature fructose-fructose interaction increases as A increases. Conversely, most of the B-coefficient values decrease with the rise of temperature. The negative values of temperature derivatives of B-coefficient provide important information regarding the water structure-breaking ability of *D*(-)-fructose. It is clear that *D*(-)-fructose has the water cluster structure-breaking capability at lower concentrations. At higher concentrations the fructose-fructose interaction becomes stronger as they aggregate surrounding water cluster which have weak influence on disrupting water-cluster. As a result, the water molecules become more ordered around the *D*(-)-fructose molecules by forming weaker hydrogen bonding.

The free energy change of activation for viscous flow has been calculated by using Eyring equation.

$$\Delta G= RT\ln\frac{\eta V}{hN} \quad \ldots\ldots \quad \textbf{(4)}$$

The Gibbs free energy change of activation, ΔG is related to the work needed to form a hole in the liquid for the viscous flow.

Table 2. Jones-Dole constants for viscosity of *D*(-)-fructose solutions with *B* derivative.

Temperature ***(T)***, K	***A***	***B***	***dB/dT***
293	0.0343	0.5223	-0.00598
298	0.0414	0.4924	-0.00744
303	0.0575	0.4479	-0.00514
308	0.0522	0.4410	-0.00357
313	0.0627	0.4122	-0.00559
318	0.0705	0.3851	-0.00493
323	0.0733	0.3629	-0.00464
328	0.0764	0.3387	0.00009
333	0.0414	0.3638	-0.00124
338	0.0715	0.3263	-0.00459
343	0.0684	0.3179	-0.00340
348	0.0799	0.2923	-0.00512

Fig. 6 shows that the ΔG values increases with increase in concentration of *D*(-)-fructose and temperature. The positive values of ΔG increase with the increase in concentration of *D*(-)-fructose and also with the rise of temperature. This indicates the association of the fructose molecules with water. The ΔG controls the rate of flow in fluid which is governed by the ability of molecules to move in to the hole and the readiness with which liquid produce the hole.[34] **Fig. 6** shows that the values of ΔG increase with increase in temperature due to increase in fructose-water interaction.

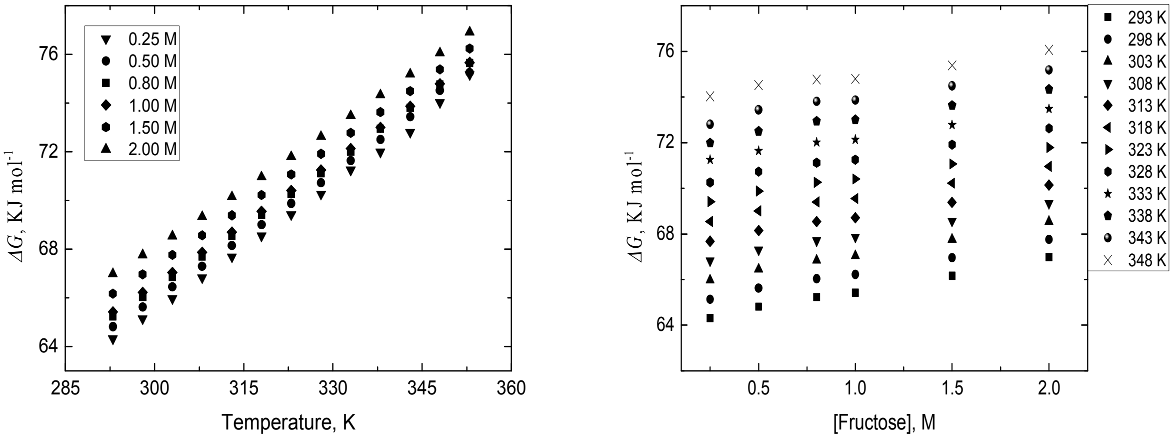


Fig. 6 Variation of activation free energy change for viscous flow as a function of temperature and concentration of *D*(-)-fructose.

The enthalpy of activation energy of viscous flow, Δ*H* is obtained from the following thermodynamic relation.

$$\Delta H = \Delta G + T\Delta S \quad \ldots\ldots\ldots\ldots \quad \mathbf{(6)}$$

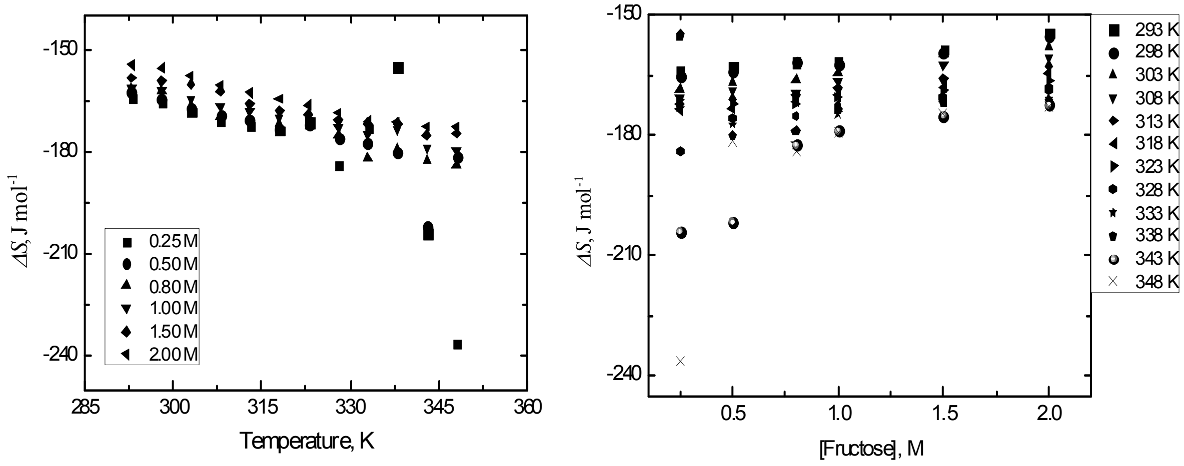


Fig. 7 Variation of change in entropy of activation for viscous flow as a function of temperature and concentration of *D*(-)-fructose.

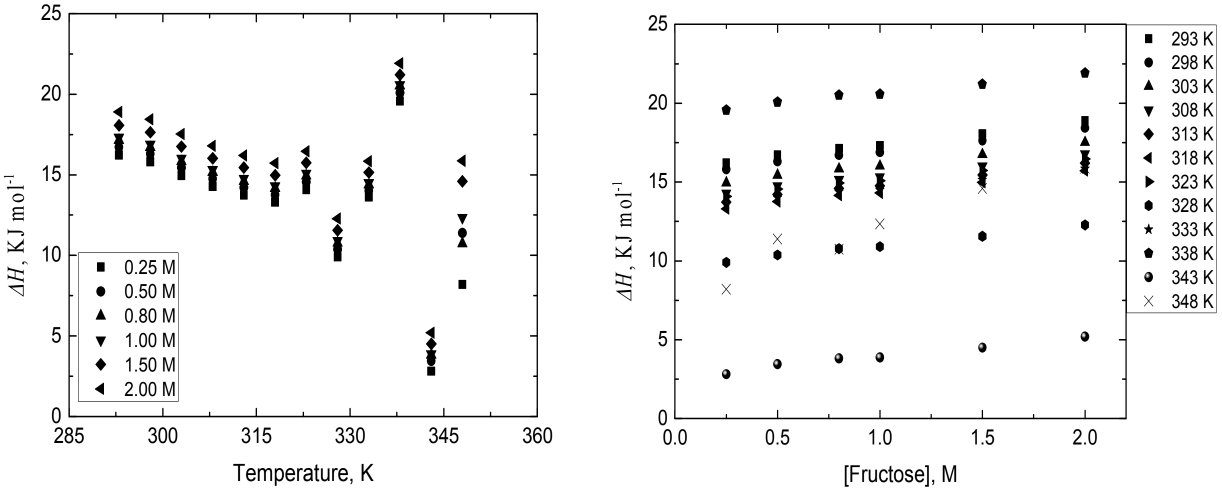


Fig. 8 Variation of activation enthalpy change for viscous flow as a function of temperature and concentration of *D*(-)-fructose.

The entropy of solution at all temperature has been found negative and despite some discontinuity (**Fig. 7**), increases with increasing concentration of *D*(-)-fructose and decreases with increase in temperature to indicate more ordered arrangement in the system. The negative values of ΔS show that the species are formed at activated state and are more ordered than the initial state.[35] The positive values of ΔH indicate that the solvation of *D*(-)-fructose in water is an endothermic process. The temperature change of the solution can also be observed during the mixing of solute in water. **Fig. 8** shows that the ΔH increases with an increase in concentration of *D*(-)-fructose to hinder the mobility of molecules and cause an ultimate increase in the energy of activation. This is based on the hole theory which states that holes are necessary for solvents to flow.[36-37]

Water-fructose interaction on water structure modification

The study of NIR spectra of water in presence of *D*(-)-fructose shows that the hydrogen bonding capability of the axial and equatorial OH groups of this additive with water molecules is mainly responsible for the characteristic behavior observed. Though *D*(-)-fructose contains axial OH group at position 5, due to lack of a free OH at position 6 water-sugar intermolecular hydrogen bonding predominates over intramolecular hydrogen bonding in *D*(-)-fructose which ultimately influences the breaking of water cluster.

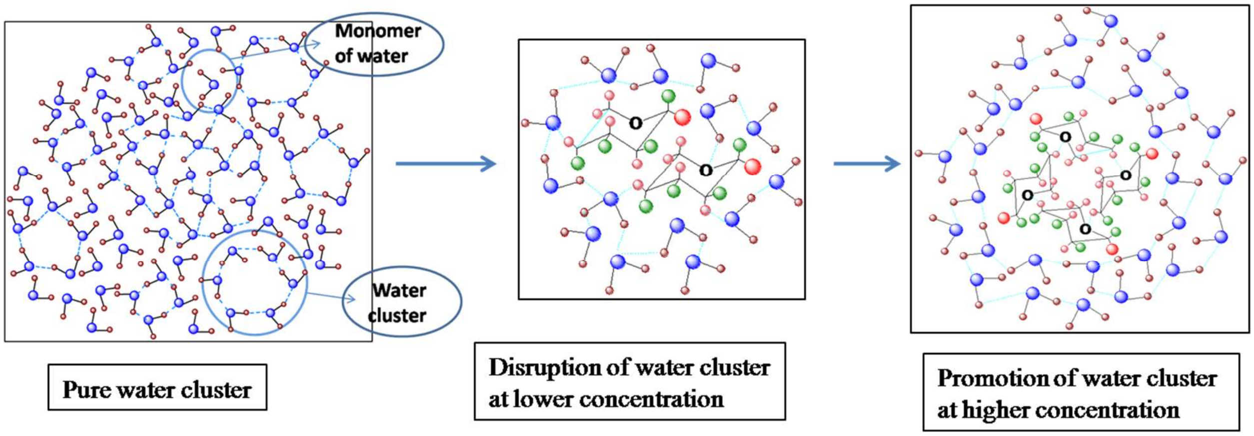
At higher concentrations, as the number of axial OH group increases, the extent of the cooperativity of strong cis-vicinal and syndiaxial intramolecular hydrogen bonding between adjacent OH groups become more prominent than intermolecular hydrogen bonding in solvent molecules. Another fact is that the methylene group at carbon 6 in *β-D*-fructopyranose acts as a hydrophobic site and due to repulsion with water, it strengthens the hydrogen bonds of the molecules in the bulk water which arrange themselves in a clathrate- like or more ordered structure. Consequently, water structure surrounding polar (OH-OH) pairs exhibits relatively more ordered structure.

The 2D correlation analysis also confirms the above facts. Moreover, the volumetric and viscometric analysis showed that at lower concentrations water-fructose interaction is higher compared to that at higher concentrations. Therefore, we can suggest *D*(-)-fructose as water structure-breaker at lower concentrations and water-structure maker at higher concentrations.[38]

The possibility of change of conformation and configuration with temperature and consequent changes in water structure modification may not be overruled. In case of the *β-D*-fructopyranose, the anomeric and the steric effects act together in favor of the C-2 OH axial chair conformer. The combined stabilizing effect makes this chair much more stable than *β-D*-fructofuranose. At lower temperature higher amounts of *β-D*-fructopyranoses exist in solution, while at higher temperatures different types of tautomers are likely to make the system more complex[25]. As the temperature increases the amount of open chain form is expected to increase, but to a small extent. Furthermore, open chain form is not stable and is readily converted to furanose form and consequently the sweetness of *D*(-)-fructose decreases. After dissolution in water due to thermal mutarotation and also for hydrophobic character the sweetness is considerably reduced. However, the percentage of *β-D*-fructopyranose becomes higher compared to other tautomers even at higher temperature (e.g. 60 ˚C). It may be noted that in the gas phase, the free hexoketose is conformationally locked in a single dominant *β*-pyranose structure[20]. Moreover, intermolecular association in aqueous solutions of *D*(-)-fructose supposes that the hydration spheres are stable and an increase in concentration causes the hydrated molecules to come progressively to closer approach due the presence of hydrophobic methylene group.

Within the temperature and concentration range studied, *β-D*-fructopyranose (Scheme 1) is the most stable and dominant form and we therefore mainly focused on the difference in hydrogen bonding capability of *D*(-)-fructose in aqueous solution on the basis of the position of the OH group. The possible change in conformation and configuration with change in temperature did not affect our conclusions, which is supported by literature[25]. Analysis of NIR results in a much broader temperature range might help to explain further water structure modification by such additives taking possible change in conformation, especially at very high temperatures into account. We shall focus our attention on this in our future work.

On the basis of 2D correlation analysis of NIR results, the structural modification can be schematically represented as shown in **Scheme 2**.



Scheme 2. Water structure modification by *D*(-)-fructose at different concentrations.

4. Conclusion

Water is composed of three structural components of different hydrogen bonding strengths. Concentrations of weaker and stronger hydrogen bonds are altered in a cooperative manner with an increase in temperature while the concentration of the third component is much more resistant on the temperature changes and remains relatively stable in the range 20–75 ^{o}C. NIR spectroscopic study of water reveals that the addition of *D*(-)-fructose significantly modifies the water structure through water-fructose interaction at different concentrations and temperatures. With the rise of temperature the number of free OH group increases and bond length decreases as higher energy is required to vibrate the molecules. *D*(-)-fructose behaves as water structure-breaker at low concentrations and at high concentrations act as structure-maker. The spectroscopic analyses are also supported by the volumetric and viscometric analyses of *D*(-)-fructose in aqueous solutions at different temperatures and concentrations. The thermodynamic parameters for instances, the activation free energy change,ΔG and the entropy change,ΔS for viscous flow depict the association of solute molecules with water with increasing the concentration and temperature. Moreover, the increase in the energy of activation, ΔH with an increase in concentration of *D*(-)-fructose may be due to hindrance in the mobility of molecules. The difference in the number and hydrogen bonding capability of axial and equatorial OH groups in *D*(-)-fructose is mainly responsible for this characteristic behavior.

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