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Solute–solvent interactions and the sweet taste of small carbohydrates. Part 1: Effect of solvent polarity on solution properties

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Solution properties (apparent specific volume, intrinsic and dynamic viscosities and surface tension) of D-glucose, D-fructose and sucrose were determined in ethanol–water binary solvent. Likewise, laser Raman spectra of water, 10% ethanol aqueous mixture and 2% (w/w) of each of the three sugars in a 10% ethanol aqueous solvent were recorded and the decomposition of the observed Raman bands in four calculated components performed.

The physicochemical properties of sugars in the binary solvent show a different behaviour from that observed in water. Such behaviour seems to be related to a pronounced effect of ethanol on water structure. Ethanol acts as a water structure enhancer probably because of its hydrophobic effect. In these ethanol–water mixtures, the differentiation of D-fructose from the two other sugars is also evident. These results are helpful in the interpretation of the effect of solvent polarity on the sweet taste of small carbohydrates.

INTRODUCTION

Solute–solvent interactions take place in saliva prior to accession of sweet stimuli to receptor sites (Birch & Shamil, 1988; Bradley, 1988). The role of solution properties in water and that of water structure in aqueous solutions (Mathlouthi, 1984; Mathlouthi & Seuvre, 1988) and of sugars with regard to the sweetness mechanism have been previously described. Reported differences of taste between α- and β-anomers of D-glucose (Shallenberger, 1973) or the effect of temperature on the sweet taste of D-fructose in water (Shallenberger, 1978) seemed to be related to their mutarotational equilibrium. The equatorial configuration of the OH in the β-anomer of D-glucose was found (Kabayama & Patterson, 1958) compatible with a long-range stable hydration which could be at the origin of a relatively lower sweetness intensity for this anomer (Shallenberger, 1973; Mathlouthi, 1984). On the other hand, the localised clustering of water molecules around sugars has been proposed (Birch & Shamil, 1988) and the non-participation of the anomeric centre in sweetness has been demonstrated (Birch *et al.*, 1986).

However, the stereochemistry of α- and β-D-glucopyranose is found (Travoska & Kozar, 1986) to depend on the nature of the solvent. The solvent properties, especially the dipole moment, seem to play a major role in quantitatively determining the anomeric ratio (Travoska & Kozar, 1986; Travoska & Bleha, 1989). The magnitude of the anomeric effect gradually decreases with increase of solvent polarity (Travoska & Kozar, 1986). A polar medium acts in a direction opposite to the anomeric effect and thus weakens its influence on the anomeric equilibrium of sugars. The effect of water on the conformational equilibrium of saccharides was found (Travoska & Kozar, 1983) to depend on the bulk water influence, i.e. on the dielectric continuum. Hence, both ring and glycosidic linkage oxygens act as weak monobases in water which creates a solvation shell.

The opposite hydrophilic and hydrophobic charac-

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ters in sweet molecules lead to an increased mobility of water and to a more intense sweet taste (Mathlouthi & Portmann, 1990). Thus, the notion of increased water mobility and that of increased localised hydration (Birch *et al.*, 1986) both predict increased sweetness and such 'polarisations' of sugar molecules in water can be monitored by measuring the contributions to the apparent molar volumes from the different chiral centres (Birch *et al.*, 1986; Birch & Kemp, 1989). The solvation of sugars in mixed aqueous solvents is more complicated and difficult to describe, especially if the solvent mixed with water is apolar. The ratio of solvent components in the hydration shell may be different from that in the bulk solution (Reichardt, 1988). The solute surrounds itself preferably by the component of the mixture which leads to the more negative Gibbs energy of solvation. This leads to a preferential solvation which may be caused by dielectric enrichment in the solvation shell or by specific hydrogen bonding interactions such as the equatorial OH–water association in sugar solutions. When water and ethanol are mixed, there is a shrinking in volume, probably due to the hydrophobicity of ethanol. The complexity of ethanol–water mixtures is demonstrated by their thermodynamic and volumetric properties (Franks & Ives, 1966). The excess enthalpy of mixing of water–ethanol mixtures is negative and undergoes a minimum at about 20% of ethanol. The excess of entropy, ΔS, is largely negative and also depends on concentration. ΔG is positive which clearly shows the preponderance of the entropy of solution (Franks & Ives, 1966). The influence of ethanol on water structure in the mixture is also observed by other properties such as viscosity and apparent specific volume. The authors have already (Shamil *et al.*, 1987; Kemp *et al.*, 1990) shown the importance of such solution properties as apparent specific volume and intrinsic viscosity for the sweet taste mechanism of sugars in water.

If, as the authors hypothesise (Mathlouthi, 1984; Shamil *et al.*, 1987; Birch & Shamil, 1988; Kemp *et al.*, 1990), the solution properties and water structure help in interpreting the sweet taste mechanism in aqueous solutions of sugars, the study of these sapid molecules in binary ethanol–water mixtures should be of relevance in accounting for the role of polarity of solvent in sweet taste chemoreception. The authors now study the solution properties (apparent specific volume, intrinsic viscosity and surface tension) and the effect on water structure of some nutritive carbohydrates in mixed ethanol aqueous solvent.

MATERIALS AND METHODS

D-Glucose (AR grade) was obtained from BDH Chemicals Ltd, Poole, UK. β-D-Fructopyranose and sucrose were Sigma products. The water used for physicochemical measurements was doubly distilled. The absolute ethanol used was obtained from Hayman Ltd, Witham, Essex, UK. Water used for surface tension measurement was normal water filtered with a 0·2 μm pore size filter. The apparent specific volumes were calculated from densities determined with a Paar densitometer (DMA 60) and density measuring cell (DMA 602) (Stanton Redcroft, London). The authors have applied a triple extrapolation procedure for accurate determination of intrinsic viscosity (Shamil *et al.*, 1987; Kemp *et al.*, 1990). Viscometric constants $[\eta]$ and k' were derived from the time necessary for a given volume to flow through a capillary at a constant temperature at 25 ± 0·1°C. Intrinsic viscosity is obtained from the triple extrapolation of reduced specific viscosity ($\eta_{sp/c} = (\eta - \eta_0)/\eta_0 c$), the inherent viscosity ($1/c \ln \eta/\eta_0$) and the reduced differential viscosity ($(\eta - \eta_0)/\eta c$) towards $c = 0$, where η and η_0 are the viscosities of the solution and solvent, respectively, c the concentration is in g 100 ml^{-1}, and $[\eta]$ is in cm^3 g^{-1}. Huggins constant k' was derived from the relation of Huggins (1942): $\eta_{sp/c} = [\eta] + k' [\eta]^2 c + ...$

The laser-Raman spectra of water and of EtOH–water and EtOH–water–sugar mixtures were obtained by use of a Jobin Yvon T800 spectrometer. The laser line was emitted by a Spectra Physics model 165 at a wavelength of 488·0 nm. To illuminate the samples 200 mW of power was used. The slit width was 2 cm^{-1}. The decomposition of experimental Raman bands into four calculated components is based on a semi-empirical method developed by Luu *et al.* (1982).

Dynamic viscosities of the sugars in binary water–ethanol solvent were recorded with a Contraves Rheomat 115 rotating cylinder viscometer.

RESULTS AND DISCUSSION

Solution properties

Apparent specific volumes (ASV)

The ASV of ethanol–water mixtures are shown in Fig. 1. The curve exhibits a minimum for a concentration of about 25% (w/w).

This result is in agreement with previous work of Franks and Ives (1966). A volume decrease accompanies the addition of ethanol in water until a certain concentration at which EtOH–EtOH hydrophobic interactions take place and provoke an increase in volume. The apparent specific volumes of D-glucose, D-fructose and sucrose were measured at various concentrations of sugar in different ethanol–water mixtures. The results are reported in Table 1 and are represented for the concentration 10% (w/w) of sugar in Fig. 2.

A maximum of ASV is observed at about 40–50% EtOH in the mixture for the studied sugars.

The apparent specific volumes of multisapophoric

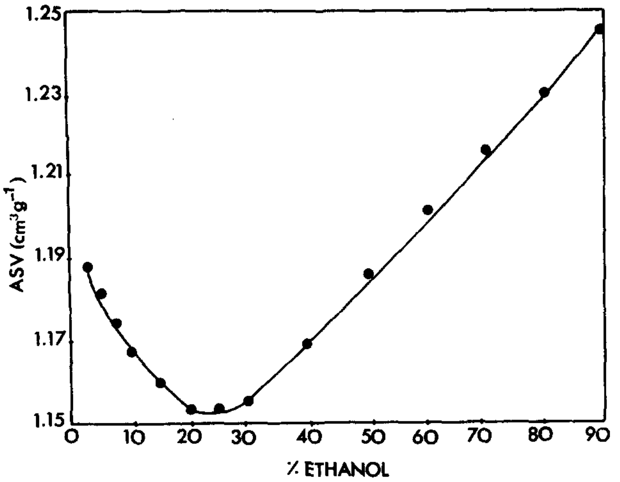

Fig. 1. ASV of ethanol–water mixtures versus the ethanol concentration (%, w/w).

molecules like sugars and amino acids were found to discriminate between their tastes (Shamil *et al.*, 1987). Indeed, sweet taste was found to correspond to the 0·52–0·71 $cm^3 g^{-1}$ range of ASV and bitter taste to the 0·71–0·93 $cm^3 g^{-1}$ range. All sugars were found to fit within a narrow range (0·60–0·62 $cm^3 g^{-1}$) whereas amino acids cover a much wider band (0·56–0·71 $cm^3 g^{-1}$).

The significance assigned to these results is that sugars have pure sweet taste while amino acids have a great range of taste qualities. An increase of ASV is generally related to an augmentation of hydrophobicity, which, when ASV reaches 0·71 $cm^3 g^{-1}$, becomes characteristic of bitterness. What tasters described as

Table 1. Apparent specific volumes of sugars at various concentrations (w/w) in ethanol–water mixtures

% Ethanol	Percentage of sugar				
	1	5	10	15	20
			Glucose		
10	0·624	0·616	0·618	0·620	0·622
20	0·616	0·620	0·621	0·623	0·624
30	0·643	0·626	0·629	0·630	0·631
40	0·648	0·635	0·638	0·634	0·634
50	0·606	0·627	0·632	0·633	0·632
60	0·645	0·627	0·626	0·628	0·625
70	0·633	0·628	0·624	0·625	ns
80	0·610	0·612	0·600	ns	ns
			Fructose		
10	0·608	0·610	0·612	0·614	0·616
20	0·617	0·617	0·618	0·619	0·620
30	0·640	0·630	0·628	0·628	0·630
40	0·521	0·627	0·631	0·633	0·633
50	0·672	0·638	0·633	0·634	0·634
60	0·610	0·629	0·632	0·633	0·634
70	0·617	0·630	0·629	0·632	0·619
80	0·409	0·608	0·627	0·625	0·624
90	0·447	0·605	ns	ns	ns
			Sucrose		
10	0·617	0·614	0·609	0·614	0·618
20	0·639	0·619	0·619	0·620	0·621
30	0·644	0·626	0·625	0·625	0·625
40	0·664	0·630	0·630	0·628	0·627
50	0·509	0·632	0·627	0·627	0·625
60	0·638	0·628	ns	ns	ns

ns, Non-soluble

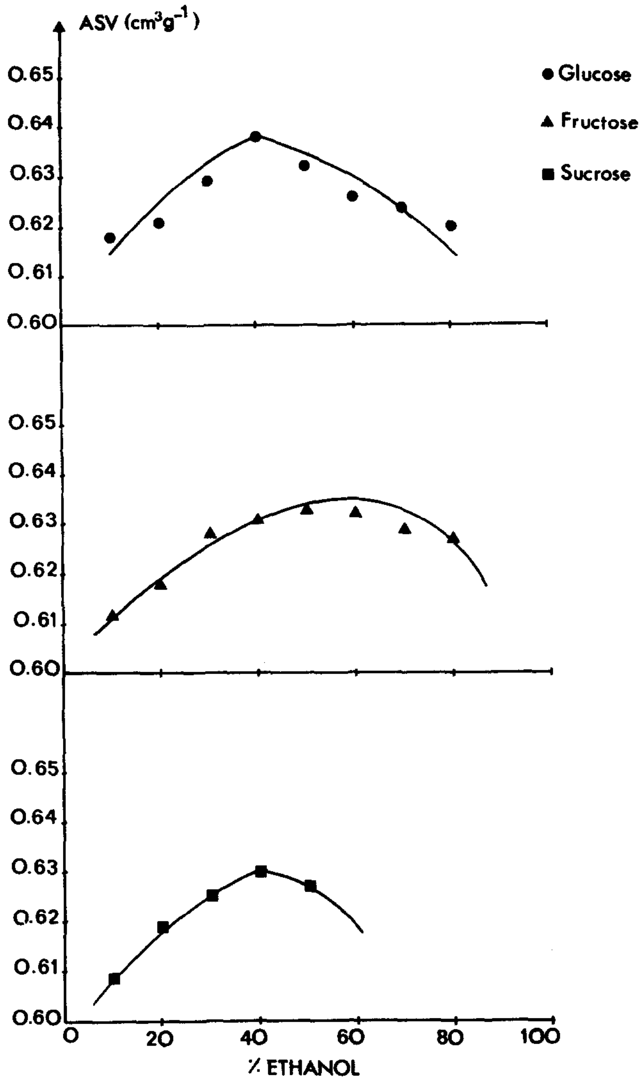

Fig. 2. ASV of 10% sugar versus per cent of EtOH in EtOH–water binary solvent.

Table 2. Intrinsic viscosities ([η] in $cm^3 g^{-1}$) and Huggins coefficients (k'_H)of sugars in water–ethanol mixtures

Sugar		% Ethanol (v/v)			
		0	10	25	50
Glucose	[η]	2·42	2·31	2·22	2·55
	k'_H	0·89	1·35	1·22	1·07
Fructose	[η]	2·33	2·20	2·02	2·33
	k'_H	0·84	1·17	1·33	0·94
Sucrose	[η]	2·48	2·42	2·40	2·75
	k'_H	0·95	1·16	1·29	1·48

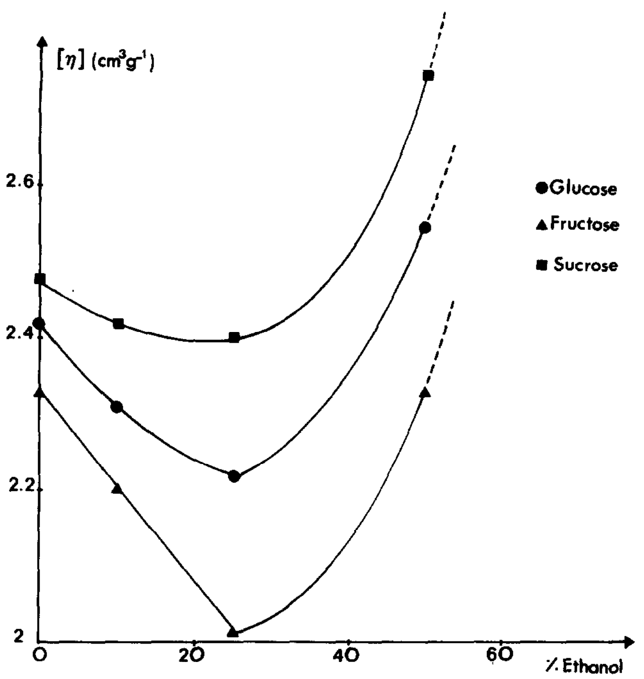

Fig. 3. Intrinsic viscosities of sugars in aqueous ethanol binary solvent.

an impression of dehydrating or bitter or astringent on tasting sugars in EtOH–water mixtures (Hoopman *et al.*, 1992) probably originates in the hydrophobic effect of ethanol. In these ternary solutions (water–EtOH–sugar) there is a preferential solvation of sugars by water. EtOH–EtOH interaction takes place at low concentration, as water hydrates the sugar. The hydrophobic contact between C_2H_5 groups in ethanol is preponderant and contributes to an increase in volume until a concentration of about 50% EtOH at which sugar–sugar interactions may occur together with water–alcohol contacts which contributes to a decrease in volume (see Fig. 2).

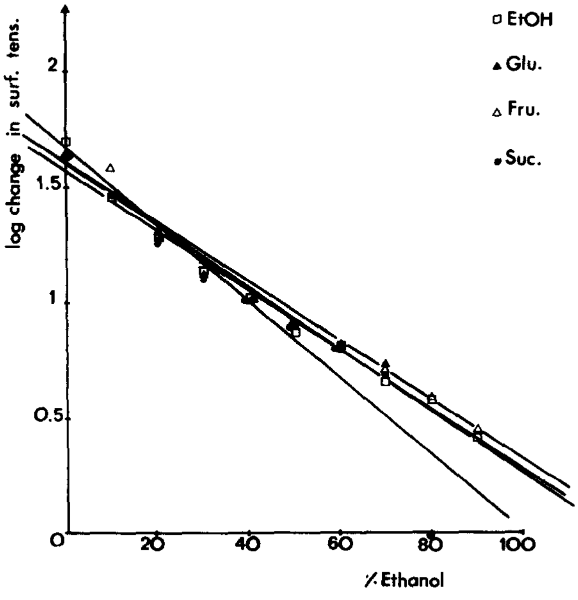

Fig. 4. The log of ($\gamma\%$ − γ 100%) of EtOH–water and a 5% sugar–EtOH–water mixture versus per cent of EtOH in the mixture.

Table 3. Surface tension (γ) and apparent parachor [*P*] of ethanol solutions at 25°C

% Ethanol	γ (mN/m)	[*P*]
0	72·50	143
10	50·30	131
20	42·38	125
30	35·50	120
40	32·03	117
50	29·27	114
60	28·25	113
70	26·25	112
80	25·55	110
90	24·35	109
100	21·78	106

Viscometric constants

Viscometric constants [η] and k' are reported in Table 2. The intrinsic viscosities [η] are drawn as a function

Table 4. Surface tension (γ) and apparent parachor [*P*] of water–ethanol–sugar mixtures at different ethanol percentages for a concentration of 5% sugar (w/w) at 25°C

% Ethanol	γ (mN/m)	[*P*]
D-Glucose		
0	64·40	142
10	50·77	134
20	41·17	127
30	35·27	122
40	31·89	119
50	29·80	117
60	28·50	116
70	27·17	114
D-Fructose		
0	64·20	143
10	59·90	135
20	41·70	128
30	37·40	125
40	32·50	120
50	29·70	118
60	28·30	116
70	26·90	115
80	25·70	114
90	24·60	112
Sucrose		
0	63·70	139
10	50·60	131
20	40·80	124
30	36·00	121
40	32·60	118
50	30·50	116
60	28·30	113
70	26·80	112
80	22·70	107

of EtOH concentration in the binary solvent (see Fig. 3).

The hydrodynamic volume of sugars seems to show a minimum at about 25% EtOH. However, only three concentrations (10–25–50%) were investigated which is insufficient to ascertain the existence of the minimum. The Huggins coefficient, k', generally called the interaction factor, is higher in EtOH mixtures than in water and no significant difference exists in the behaviour of the three sugars.

Surface tension

This is another solution property particularly adapted to study solute–solvent interactions and solvent cohesiveness in dilute solutions. Table 3 lists the surface tensions (γ) and apparent specific parachors ($V_2^0 \cdot \gamma^{1/4}$) for water–EtOH mixtures, and Table 4 gives the values of these parameters for sugar solutions (5%, w/w) in the binary solvent.

An important decrease in surface tension is observed when EtOH is added to water. In ternary solution (EtOH–sugar–water) the decrease in surface tension is more pronounced. Results are presented as log of change in surface tension ($\log(\gamma\% - \gamma\ 100\%)$) versus % EtOH in the binary solvent. They show a continuous linear decrease of surface tension with a rate of 1·26% of the EtOH percentage for the EtOH–water mixture, 1·32% of the EtOH solution containing fructose, 1·28% of the solution containing glucose and 1·68% for the sucrose solution.

Dynamic viscosity

This was measured for each of the studied sugars at 25°C in water and 25% of EtOH in the binary solvent. The results are reported in Fig. 5.

The viscosity is almost doubled for all concentrations (0 to saturation) investigated. This concentration of 25% was chosen because it corresponds to a maximum packing of water molecules under the effect of ethanol, which is manifested by a minimum in ASV (see Fig. 1) and a maximum in excess entropy of the mixture (Franks & Ives, 1966). The enhanced packing of water molecules contributes to an increase in shear stress, and hence in dynamic viscosity. The effect of the percentage of ethanol in EtOH–water mixture on the viscosity of a solution of about 4·5% sugar was checked. Results are reported in Table 5 and Fig. 6.

Table 5. Dynamic viscosities in mPa s of water–ethanol–sugar mixtures at different ethanol percentages and a concentration of 4·31% D-glucose, 4·77% D-fructose or 4·77% sucrose

% Ethanol	D-Glucose	D-Fructose	D-Sucrose
0	0·95	1·00	0·97
10	1·30	1·30	1·30
20	1·70	1·70	1·70
30	2·10	2·00	2·10
40	2·30	2·30	2·40
50	2·40	2·40	2·60
60	2·40	2·40	2·50
70	2·30	2·20	2·30
80		2·00	2·10
90		1·70	

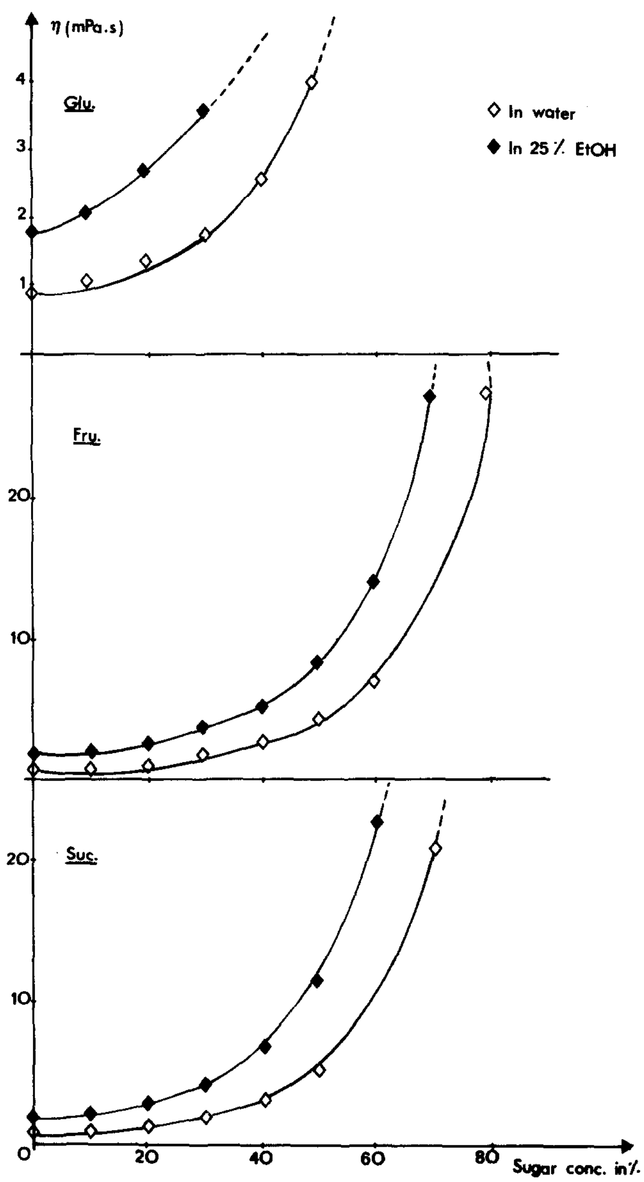

Fig. 5. Dynamic viscosities of D-glucose, D-fructose and sucrose in EtOH/water binary solvent in 25% ethanol aqueous solution (v/v).

As already observed for ASV (see Fig. 2), a maximum of dynamic viscosity is observed at about 50% of EtOH in the mixtures for all three sugars. Although interpretation of molecular interactions in ternary solutions is difficult, especially for liquids which undergo self-association, the same arguments as invoked for the maximum of ASV may be given. It is very likely that the rearrangement of the two solvents around the

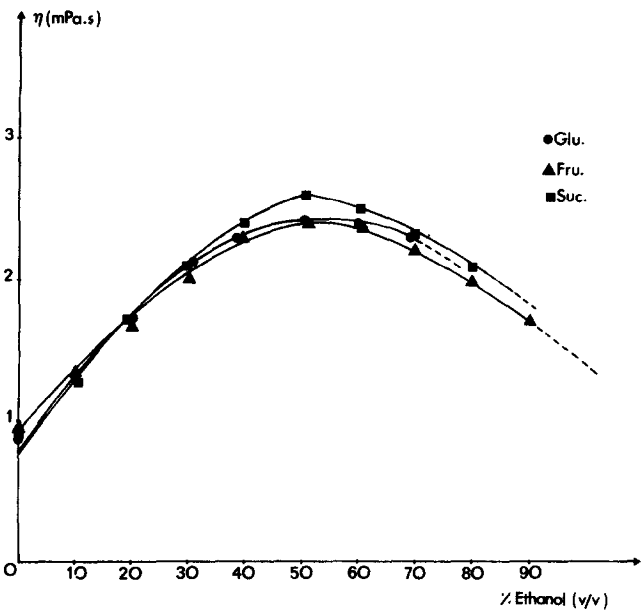

Fig. 6. Dynamic viscosities of sugars in aqueous-ethanol solvent as a function of ethanol percentage.

solute and a possible solute–solute interaction are concentration-dependent.

Lasar-Raman spectra

Because of the time constant of Raman scattering ($\approx 10^{-12}$ s), Raman spectroscopy is known as one of the most appropriate techniques to account for the establishing and rupturing ($\approx 10^{-11}$ s) of hydrogen bonds in such complex media as water and aqueous solutions. Rather than proposing a new model of water structure, the authors utilise the model of Luu *et al.* (1982) as a reference in a comparative study of the behaviour of the aqueous medium when such substances as ethanol or sugars are added. The model of Luu *et al.* (1982) is a semi-empirical model of decomposition of the experimental Raman band into four calculated components which are the product of Gaussian and Lorentzian contributions. Although the assignment of components (a), (b), (c) and (d) in the spectrum of water respectively to quasi-crystalline, solid-like amorphous, liquid-like amorphous and non-associated water molecules may be questionable, it is used in this study just as a reference mark to differentiate the effect of different solutes on the more (component (a) with O····O distance = 2·70 Å) or less (component (d) with O····O distance >3 Å) packed species in liquid water.

Table 6. Decomposition of the experimental Raman band of water

Component	Frequency (cm^{-1})	% Total area	Assignments
a	3 239	64·1	Quasi-crystalline
b	3 414	20·8	Amorphous pentameric tetrahedral clusters
c	3 537	13·5	Liquid-like amorphous
d	3 633	1·7	Non-associated water

The laser-Raman spectra of water and a 10% (v/v) of ethanol in EtOH–water mixture are reported in Fig. 7.

Results of decomposition of the experimental bands in the region (2800–3800 cm^{-1}) of OH stretching and assignments of the different calculated components are listed in Table 6 for water and Table 7 for the EtOH–water mixture.

The shifts of frequencies and modifications of integrated intensities (areas of bands) of the calculated components of the Raman band of water under the effect of 10% ethanol are given in Table 7. As a general rule, the more the OH oscillator is free (not engaged in H-bonds) the more its energy of vibration (frequency)

Table 7. Decomposition of the experimental Raman band of water–ethanol mixture

Component	ν cm^{-1}	% Total area	$\Delta\nu$	ΔArea%
a	3 217	50·4	−22	−13·7
b	3 414	42·7	+0	+21·9
c	3 561	5·5	+24	−8·0
d	3 636	1·4	+3	−0·3

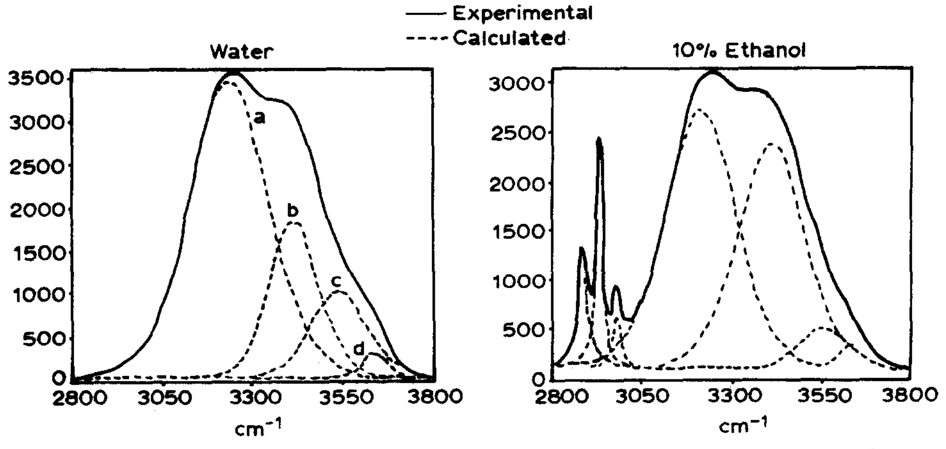

Fig. 7. Laser-Raman spectra of water and a 10% (v/v) ethanol aqueous binary solvent.

Table 8. Decomposition of the experimental Raman bands of water–ethanol–sugar mixtures (2% sugar in 10% EtOH–water solvent)

Component	ν cm^{-1}	% Area	$\Delta\nu$ in water cm^{-1}	$\Delta\nu$ in EtOH cm^{-1}	ΔArea % in water	ΔArea % in EtOH
D-Glucose						
a	3 220	54·3	−19	+3	+9·8	+3·9
b	3 408	35·8	−6	−6	−15·0	−6·8
c	3 545	8·0	+8	−16	+5·5	+2·5
d	3 633	1·9	+0	−3	−0·2	+0·5
D-Fructose						
a	3 221	53·0	−18	+5	−11·1	+2·5
b	3 422	40·4	+6	+8	−19·6	−2·0
c	3 585	5·9	+48	+24	−7·6	+0·4
d	3 647	0·8	+14	+11	−0·9	−0·6
Sucrose						
a	3 220	56·1	−18	+3	−8·1	−5·6
b	3 410	34·1	−4	−4	+13·3	−8·6
c	3 552	8·5	+15	−9	+5·0	+2·9
d	3 635	1·4	+2	−1	+0·3	+0·1

is elevated, and vice versa. If the interpretation of data given in Table 7 is based on this tenet, then it appears that the effect of ethanol mainly concerns components (a) and (c) with opposed actions on these clusters of water associates. The more organised species (a) undergoes a shift towards lower frequencies ($\Delta\nu = -22$ cm^{-1}) which is an indicator of the tightening of H-bonds in water under the effect of the hydrophobic interaction with ethanol. In the meantime, the proportion (% area) of this species is decreased (−13·7%). The less organised (liquid-like amorphous) clusters (component (c)) undergo a shift in frequency of 24 cm^{-1} towards higher frequencies. This means that hydrogen bonds in this species are loosened and the OH oscillators are more free to vibrate. The number of vibrating OH in this cluster (energy) is lowered (−8%) whereas the solid-like amorphous species undergoes a noticeable increase in intensity (Δarea = +21·9%). The non-associated water molecules (component (d) do not show any noticeable change in frequency or intensity. Only the area of OH stretching band (2900–3800 cm^{-1}) is taken into account. The C—H vibrations shown in Fig. 7 are not considered. The overall effect of ethanol (10%) on water structure derived from Fig. 7 and Table 7 seems ambivalent. Both structure enhancement (increase in ν_{OH} for component (a)) and structure breakage (decrease in ν_{OH} for component (c)) are observed. This is probably due to the fact that, at 10% concentration, both the hydrophobic (C_2H_5) and hydrophilic (OH) ends of the molecule exert their influence. A Raman study of the effect of ethanol concentration on water structure will be performed.

The behaviours of D-glucose, D-fructose and sucrose (2%, w/w) were studied in the 10% EtOH–water mixture. The Raman spectra of these ternary solutions are reported in Fig. 8 and the results of decomposition of these spectra into four components are listed in Table 8.

The shifts in frequencies and modifications in area are calculated by reference to water on the one hand

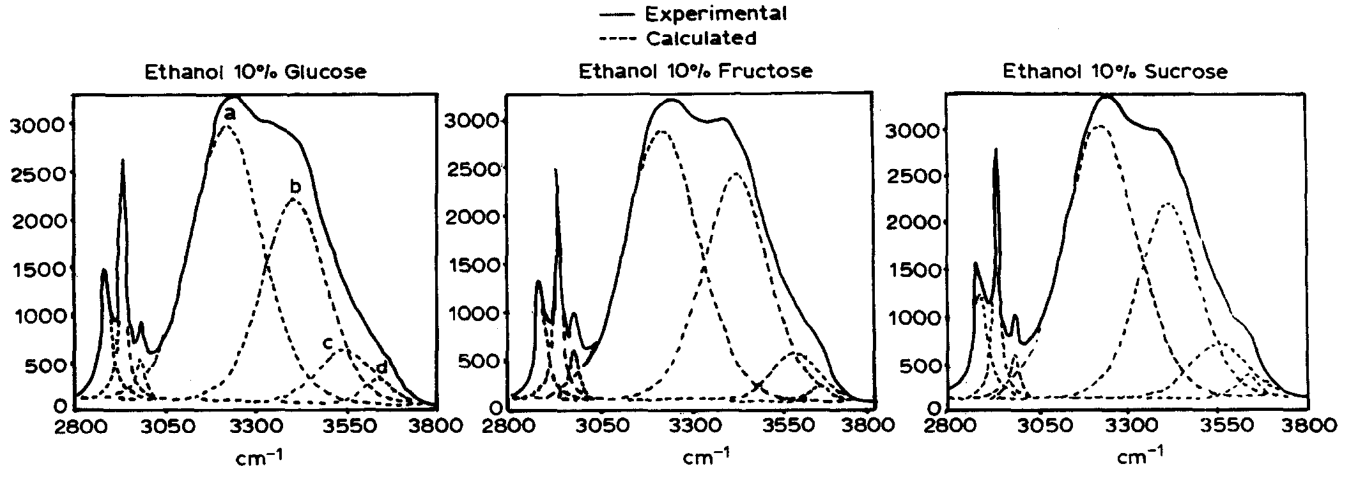

Fig. 8. Lasar-Raman spectra of sugars in 10% (v/v) ethanol mixture.

and to 10% ethanol mixture on the other. The frequencies and areas of references are given in Table 7. From the comparison of the effect of the addition of sugars on water alone ($\Delta\nu$ and Δarea% in water) and on water in the 10% EtOH mixture ($\Delta\nu$ and Δarea% in EtOH), it appears that the shifts observed in these solutions are lower than for the ethanol alone in water, except for D-fructose which shows a marked structure breaker effect ($\Delta\nu$ = +48 cm^{-1} for component (c) and +14 cm^{-1} for component (d)). That fructose has a differentiated behaviour from the other sugars as concerns its effect on the increasing of water mobility was previously observed (Mathlouthi, 1984; Mathlouthi & Seuvre, 1988). It seems that, in the binary solvent, fructose and ethanol act in a synergistic way to loosen the bonds of the less rigidly associated species. If the comparison is made between comparable EtOH–water solvent and sugar–EtOH–water mixture, it may be observed that the most affected component is again component (c) and the influences of D-glucose and sucrose on the one hand, and that of D-fructose, on the other, are opposed ($\Delta\nu$ = −16 and −9 cm^{-1}, respectively, for D-glucose and sucrose and +24 cm^{-1} for D-fructose).

The weight effect (Δ area %) of sugars on EtOH/water mixture is relatively weak. Although all is not understood about the structure of liquid water and aqueous solutions, the use of Raman spectra in a comparative way may help in differentiating the solutes and in generating a clearer picture of water mobility which, the authors believe, should be taken into account in sweet taste investigations.

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