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Some Taste Molecules and their Solution Properties

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Abstract

The solution properties of a variety of different sapid substances from all four basic taste modalities, namely, sweet ($n = 24$), salty ($n = 7$), sour ($n = 11$) and bitter ($n = 2$), have been investigated. Some multisapophoric molecules, i.e. molecules exhibiting more than one taste, have also been included in the study in an attempt to define their properties in relation to the tastes they exhibit; eight sweet–bitter and three salty–bitter molecules were used. The density and sound velocity of their solutions in water have been measured and their apparent volumes, apparent compressibilities and compressibility hydration numbers calculated and compared. Apparent molar volumes (ϕ_V) and apparent specific volumes (ASV) reflect the state of hydration of the molecules, and thus their extent of interaction with water structure. The range of ASVs reported are 0.13–0.49 cm^3/g for salty molecules, 0.55–0.68 cm^3/g for sweet molecules, 0.53–0.88 cm^3/g for sweet–bitter molecules and a much wider range (0.16–0.85 cm^3/g) for sour molecules. Isentropic apparent specific compressibilities range from -2.33×10^{-5} to -8.06×10^{-5} $cm^3/g.bar$ for salty molecules, -3.38×10^{-7} to -2.34×10^{-5} $cm^3/g.bar$ for sweet molecules, $+6.35 \times 10^{-6}$ to -2.22×10^{-5} $cm^3/g.bar$ for sweet–bitter molecules and $+6.131 \times 10^{-6}$ to -2.99×10^{-5} $cm^3/g.bar$ for sour molecules. Compressibility hydration numbers are also determinable from the measurements of isentropic compressibilities and these reflect the number of water molecules that are disturbed by the presence of the solutes in solution. This study also shows that it is possible to group isentropic apparent molar compressibility values by the taste quality exhibited by the molecules in the same order as for ASV.

Introduction

The mechanism of taste is thought to consist of the following major steps: firstly, accession of the stimulus to the receptor site through the saliva followed by the correct orientation of the molecule on the receptor site; then the transmission of the taste through nerve impulses, a process known as transduction (Kinnamon, 1988); and finally, recognition of the taste perceived in terms of its quality and intensity (Margolskee, 1995). The first two steps suggest that, for any molecule to accede and fit on the receptor site, it must be of an optimum molecular volume and of the right shape (Birch, 1991; Birch *et al.*, 1993, 1994) to pack within the structure of water. This has led to a lot of work on the molar volumes of substances (Birch *et al.*, 1993, 1994). Molecules must also have the respective sapophores to be able to evoke a taste sensation, e.g. an AH, B, γ glucophore for sweetness (Shallenberger and Acree, 1967; Shallenberger, 1993), protons for sourness (Ganzevles and Kroeze, 1987). Also important is the stereochemistry of the molecule, particularly the hydroxyl groups at positions 2 and 4 in carbohydrate molecules (Galema and Hoiland, 1991) which affect their fit within water structure. The hydrophilic and hydrophobic balance in the molecule is thought to affect the mobility of water in the vicinity of the solute (Mathlouthi *et al.*, 1993).

Recently the emphasis has been on the role of water in the mechanism of taste (Kemp *et al.*, 1992; Mathlouthi *et al.*, 1993), more specifically to the changes in the hydration layer and the centre of hydration of the solute in the solvent which affects the transport of the molecules to the appropriate receptors and/or their positioning on the receptors. The collapse of water structure, and hence enhanced hydration, effectively allows the molecule to be transported to different layers of the taste epithelium, where it is thought the different receptor sites for bitter, sweet, sour and salty lie. The changes in hydration layer can be studied using isentropic molar compressibilities and hydration numbers (Hoiland and Holvik, 1978; Hoiland, 1986a,b; Galema and Hoiland, 1991).

The hydration of a solute molecule in water is based on the Frank and Wen (1957) model of solute–solvent interaction, which pictures three different solvent-structure regions in the neighbourhood of the solute. Just outside the molecule is a layer of immobilized, compressed water as a result of electrostrictive and other attractive forces exerted by the solute. This layer is surrounded by a slightly

less compressed or 'structure-broken' region of water molecules, distantly affected by those forces. The outermost layer is bulk water, which possesses the typical tetracoordinated hydrogen-bonded structure and is not affected by any of the above forces. Compressibility measurements measure the changes in the first two layers of solvent around the molecule.

Materials and methods

Chemicals used in this experiment were reagent grade and were obtained from BDH (Lutterworth, Leicestershire, UK), Sigma Chemical Co. (Poole, Dorset, UK), Hoechst (Switzerland) and ICN Biochemicals Ltd (Thame, Oxfordshire, UK). Water used for solution studies was HPLC grade. All measurements were carried out at 20°C and in duplicate to minimize errors. Since all the parameters measured vary with the concentration tested, implying changes in the nature and extent of solute–solvent interaction and the hydration layer, all measurements were made at 3% w/w for comparison purposes.

Density and sound velocity measurements were determined using an Anton Paar Density Sound Analyser (DSA 48) from Paar Scientific Ltd (Raynes Park, London, UK). Temperature was maintained at 20 ± 0.1°C. The density of the sample was measured from the period of oscillation of an oscillating U-tube. The sound velocity was calculated from the propagation speed of ultrasonic pulses in a known distance within the sample in the measuring cell. The instrument was calibrated once using air and distilled water. Density and sound velocity measurements were accurate to $\pm 1 \times 10^{-4}$ g/cm^3 and ±1 m/s respectively.

Apparent molar volumes, ϕ_v (cm^3/mol), and apparent specific volumes, ASV (cm^3/g), were calculated from density values using equations (1) and (2) respectively.

$$\phi_v = 1000(d_0 - d)/mdd_0 + M_2/d \quad (1)$$

where d_0 = density of water at one temperature (g/cm^3), d = density of solution at the same temperature (g/cm^3), m = molality of the solution (mol/kg of water) and M_2 = molecular weight of solute (g/mol).

$$\text{ASV} = \phi_v/M_2 \quad (2)$$

The isentropic apparent molar compressibilities, $K_{\phi(s)}$ (cm^3/mol.bar), were calculated from both density and sound velocity values using equation (3):

$$K_{\phi(s)} = 1000(\beta_s - \beta_{so})/md + \beta_s\phi_v \quad (3)$$

where β_s = isentropic compressibility coefficient of solution (bar^{-1}) and β_{so} = isentropic compressibility coefficient of water (bar^{-1}). The isentropic compressibility coefficients are calculated from equation (4):

$$\beta_s = 100/u^2d \quad (4)$$

where u = sound velocity of solution (m/s). The isentropic apparent specific compressibilities, $K_{2(s)}$ (cm^3/g.bar), were obtained from equation (5) below:

$$K_{2(s)} = K_{\phi(s)}/M_2 \quad (5)$$

Compressibility hydration numbers, n_h, were calculated using the following equation:

$$n_h = (n_w/n_s)(1 - \beta_s/\beta_{so}) \quad (6)$$

where n_w = number of moles of water (mol/kg solution) and n_s = number of moles of solute (mol/kg solution).

Results

Table 1 presents the solution measurements of 65 taste

Table 1 Solution measurements of some taste substances in water (all measurements were made at 3% solute concentration unless specified otherwise)

Solute	Taste	Mol. wt (g/mol)	Density (g/cm^3)	Molality (mol/kg)	ϕ_v (cm^3/mol)	ASV (cm^3/g)	$K_{\phi(s)}$ (cm^3/mol.bar)	$K_{2(s)}$ (cm^3/g.bar)	n_h
Barium chloride	salt	208.27	1.021	0.148	52.55	0.252	–7.891E-03	–3.789E-05	12.70
Calcium chloride	salt	110.99	1.020	0.279	33.14	0.299	–6.898E-03	–6.215E-05	10.35
Ferric chloride	salt	162.21	1.019	0.191	50.31	0.310	–8.058E-03	–4.968E-05	12.73
Lead nitrate	salt	334.00	1.025	0.093	45.74	0.137	–7.790E-03	–2.332E-05	12.28
Lithium chloride	salt	42.40	1.014	0.730	20.57	0.485	–3.089E-03	–7.286E-05	4.90
Magnesium chloride	salt	95.23	1.021	0.304	28.96	0.304	–7.083E-03	–7.440E-05	10.35
Sodium chloride	salt	58.44	1.019	0.529	17.77	0.304	–4.713E-03	–8.064E-05	6.79
Potassium iodide	salt–bitter	166.00	1.020	0.186	45.74	0.275	–2.634E-03	–1.587E-05	5.82
Sodium tartrate	salt–bitter	194.06	1.016	0.159	80.06	0.413	–9.266E-03	–4.775E-05	15.79
Ammonium chloride	salt–bitter	53.49	1.008	0.577	36.70	0.686	–1.758E-03	–3.286E-05	4.12
Formic acid	sour	46.03	1.006	0.668	34.44	0.748	2.822E-04	6.131E-06	1.54
Gluconic acid	sour	196.16	1.014	0.159	97.12	0.495	–5.868E-03	–2.991E-05	12.52
Hydrochloric acid	sour	36.46	1.003	0.848	30.57	0.839	8.176E-04	2.242E-05	0.69

Lactic acid	sour	90.08	1.005	0.343	69.56	0.772	1.777E-04	1.973E-06	3.58
Nitric acid	sour	63.02	1.009	0.490	40.16	0.637	8.585E-04	1.362E-05	1.17
Phosphoric acid	sour	98.00	1.015	0.315	44.19	0.451	–9.480E-04	–9.674E-06	3.61
Propanoic acid	sour	74.08	1.001	0.416	67.52	0.911	3.568E-04	4.817E-06	3.23
Quinic acid (4.1%)	sour	192.20	1.014	0.223	118.96	0.619	–1.688E-03	–8.783E-06	8.56
Sulphuric acid	sour	98.08	1.018	0.314	34.99	0.357	–4.417E-04	–4.503E-06	2.50
Tartaric acid	sour	150.10	1.012	0.206	82.40	0.549	–1.926E-03	–1.283E-05	6.89
Trichloroacetic acid	sour	163.39	1.013	0.189	82.95	0.508	–2.198E-03	–1.345E-05	7.27
3-*O*-Methyl-D-glucopyranose	sweet	194.20	1.008	0.160	132.95	0.685	–1.145E-03	–5.894E-06	8.66
α,α-Trehalose (2.71%)	sweet	342.30	1.008	0.081	219.54	0.641	–2.058E-03	–6.011E-06	14.56
D-Arabinose	sweet	150.13	1.010	0.203	92.55	0.616	–2.264E-03	–1.508E-05	7.83
D-Fructose	sweet	180.10	1.010	0.171	109.79	0.610	–2.456E-03	–1.364E-05	9.01
D-Galactose	sweet	180.16	1.010	0.172	109.69	0.609	–2.374E-03	–1.318E-05	8.91
D-Glucose	sweet	180.16	1.010	0.172	111.34	0.618	–2.073E-03	–1.151E-05	8.63
D-Mannitol	sweet	182.20	1.009	0.171	118.94	0.653	–1.744E-03	–9.571E-06	8.63
D-Mannose	sweet	180.16	1.010	0.171	111.18	0.617	–1.852E-03	–1.028E-05	8.35
D-Xylose	sweet	150.10	1.009	0.206	94.80	0.632	–1.585E-03	–1.056E-05	7.13
Inositol	sweet	180.16	1.012	0.173	100.05	0.555	–4.207E-03	–2.335E-05	10.62
L-Arabinose	sweet	150.13	1.010	0.205	93.03	0.620	–2.156E-03	–1.436E-05	7.72
L-Fucose	sweet	164.16	1.008	0.187	108.05	0.658	–2.688E-03	–1.637E-05	9.17
L-Sorbose	sweet	180.20	1.010	0.172	110.81	0.615	–2.329E-03	–1.292E-05	8.91
Lactose	sweet	342.30	1.010	0.090	208.37	0.609	–3.641E-03	–1.064E-05	15.87
Lactulose	sweet	342.30	1.010	0.089	207.53	0.606	–5.390E-03	–1.575E-05	17.94
Maltose	sweet	342.30	1.009	0.090	217.39	0.635	–1.923E-03	–5.617E-06	14.27
Methyl-α-D-glucopyranoside	sweet	194.20	1.008	0.159	132.75	0.684	–1.845E-03	–9.503E-06	9.50
Methyl-β-D-galactopyranoside	sweet	194.20	1.008	0.158	130.91	0.674	–2.107E-03	–1.085E-05	9.72
Palatinose	sweet	342.30	1.009	0.090	219.36	0.641	–2.232E-03	–6.521E-06	14.75
Raffinose (2.55%)	sweet	504.52	1.007	0.052	336.09	0.666	–1.707E-04	–3.383E-07	18.68
Sorbitol	sweet	182.18	1.009	0.169	118.41	0.650	–1.809E-03	–9.927E-06	8.68
Sucrose	sweet	342.30	1.010	0.091	210.79	0.616	–2.389E-03	–6.979E-06	14.49
Trichlorogalactosucrose	sweet	397.65	1.010	0.078	241.59	0.607	–2.576E-03	–6.478E-06	16.42
Xylitol	sweet	152.00	1.008	0.203	101.43	0.667	–1.513E-03	–9.955E-06	7.39
Acesulfame K	sweet–bitter	201.17	1.012	0.154	107.29	0.533	–3.146E-03	–1.564E-05	9.75
Aspartame (0.5%)	sweet–bitter	294.31	1.000	0.017	212.46	0.722	–4.884E-03	–1.659E-05	17.68
Ethylene glycol	sweet–bitter	62.07	1.002	0.498	54.73	0.882	3.941E-04	6.350E-06	2.50
Glycerol	sweet–bitter	92.11	1.005	0.336	70.58	0.766	–2.252E-04	–2.445E-06	4.12
L-Proline	sweet–bitter	115.13	1.007	0.269	82.55	0.717	–2.557E-03	–2.221E-05	7.58
Methyl-β-D-glucopyranoside	sweet–bitter	194.20	1.007	0.158	136.10	0.701	–1.125E-03	–5.791E-06	8.81
Methyl-β-D-xylopyranoside	sweet–bitter	164.20	1.007	0.188	116.56	0.710	–1.089E-03	–6.630E-06	7.69
Sodium saccharin (2.55%)	sweet–bitter	205.17	1.009	0.128	116.87	0.570	–3.549E-03	–1.730E-05	10.76
Caffeine	bitter	194.20	1.008	0.159	133.96	0.690	–4.830E-04	–2.487E-06	7.92
Quinine hydrochloride	bitter	360.90	1.004	0.086	287.08	0.795	–7.193E-06	–1.993E-08	15.64
Citric acid	sour-sweet	192.12	1.010	0.161	115.20	0.599	–9.726E-04	–5.063E-06	7.52
D-Glucono–1,5-lactone	sweet-sour–bitter	178.14	1.011	0.173	103.63	0.582	–2.374E-03	–1.333E-05	8.59
Glucosamine hydrochloride	salt-sour–bitter	215.60	1.011	0.144	122.79	0.569	–4.996E-03	–2.317E-05	12.83
Monosodium glutamate (2.71%)	umami	169.10	1.011	0.165	87.78	0.519	–6.973E-03	–4.124E-05	13.33
Potassium hydroxide	soapy	56.11	1.017	0.547	21.87	0.390	–4.130E-03	–7.360E-05	6.27
1-Propanol		60.10	0.993	0.514	69.71	1.160	2.830E-04	4.710E-06	3.38
2-Propanol		60.10	0.993	0.513	70.95	1.180	1.706E-04	2.839E-06	3.58
Acetone		58.08	0.994	0.533	65.98	1.136	8.315E-04	1.432E-05	2.55
Ethanol		46.07	0.993	0.669	54.55	1.184	6.407E-04	1.391E-05	2.16
Tetrahydrofuran		72.11	0.997	0.431	76.09	1.055	2.754E-04	3.820E-06	3.76

Key to symbols: ϕ_v: apparent molar volume; ASV: apparent specific volume; $K_{\phi(s)}$: isentropic apparent molar compressibility; $K_{2(s)}$: isentropic apparent specific compressibility; n_h: compressibility hydration number.

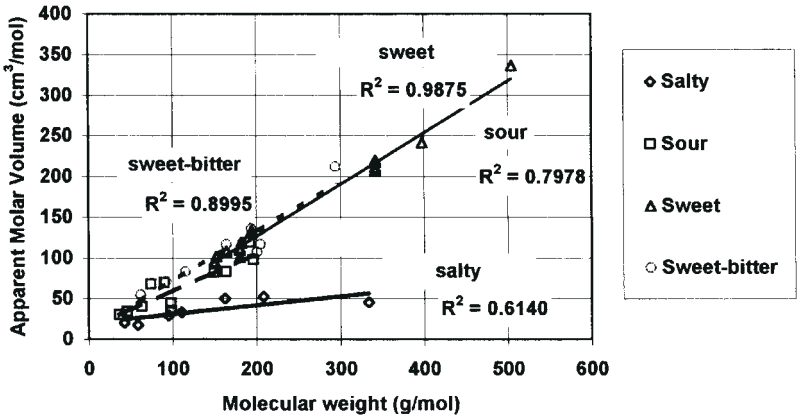

Figure 1 Plot of apparent molar volume against molecular weight.

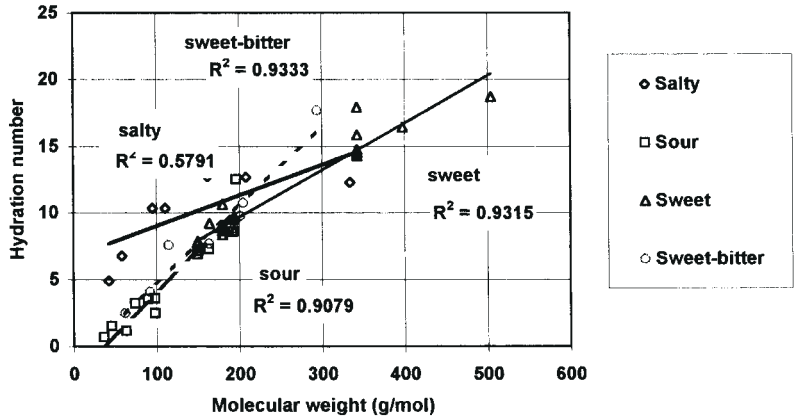

Figure 2 Plot of compressibility hydration number against molecular weight.

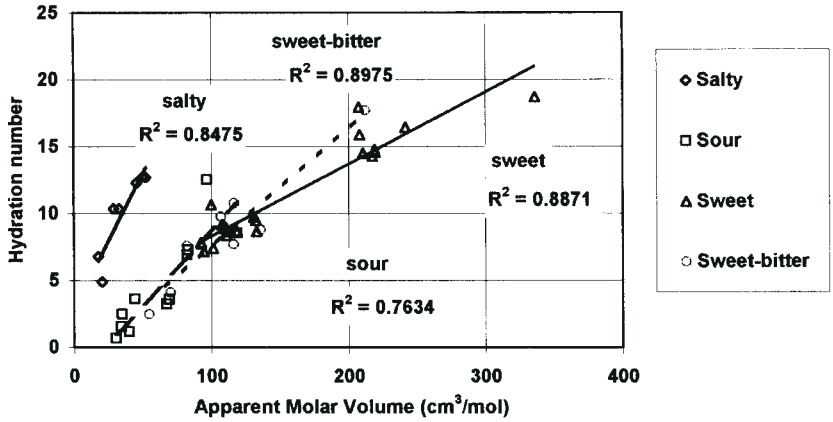

Figure 3 Plot of compressibility hydration number against apparent molar volume.

substances examined. The dominant taste(s) of each are reported alongside their respective measurements in water.

Figures 1–4 show the relationships between the molecular weight of the solutes, their apparent molar volumes, their isentropic apparent molar compressibilities and their compressibility hydration numbers respectively, divided into different taste categories.

Discussion

As would be expected, apparent molar volumes increase as

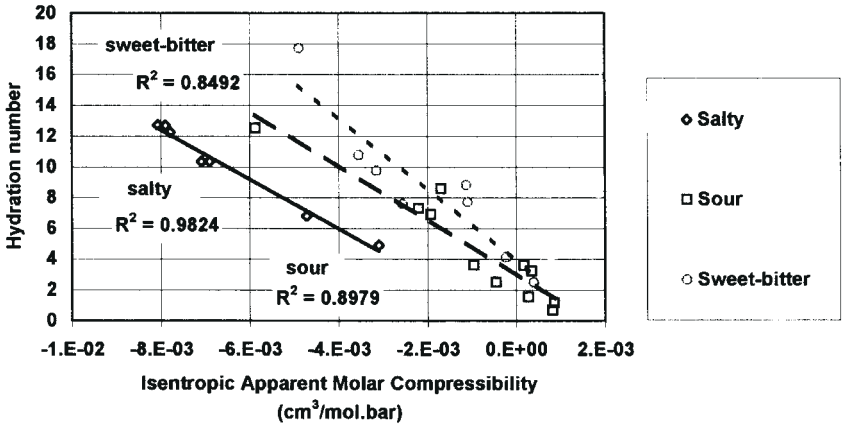

Figure 4 Plot of compressibility hydration number against isentropic apparent molar compressibility.

molecular weight increases (Figure 1). A plot of the molar volume of all 65 tested substances against molecular weight also shows good correlation, with R^2 = 0.8009. Apparent molar volumes reflect the size of the hydrated molecules in solution, and hence the extent of interaction of the solute molecules with water structure. This property has previously been investigated in relation to the taste quality of sugars and some polyols (Birch and Catsoulis, 1985; Birch and Shamil, 1986; Hoiland, 1986a,b; Kemp *et al.*, 1990; Birch and Kemp, 1989).

Division of the apparent molar volume value by the molecular weight of the substance yields the apparent specific volume, which accounts for ways in which the different forms of molecular architecture are interactive with water structure. Shamil *et al.* (1987) previously reported the parameter ASV as being a broad determinant of taste quality, with the four basic tastes occupying predominantly certain ranges of ASVs as listed in Figure 5. The range of ASVs reported in this experiment are 0.13–0.49 cm^3/g for salty molecules, 0.55–0.68 cm^3/g for sweet molecules, 0.53–0.88 cm^3/g for sweet–bitter molecules and a much wider range (0.16–0.85 cm^3/g) for sour molecules. The sweet-tasting molecules fit nicely in the ASV range of 0.52–0.71 cm^3/g defined by Shamil *et al.* (1987), with those substances exhibiting a clean sweet taste in the range 0.60–0.64 cm^3/g (Birch, 1991, 1996; Birch *et al.*, 1996). The calculated ASV values of the molecules investigated broadly fit these categories except for the sour-tasting substances, which can have unusually high values; the latter point will be discussed later.

Low apparent molar volumes and low apparent specific volumes show that the solute molecule is heavily hydrated, and therefore hydrophilic. Salts are assumed to be completely dissociated in solution into their respective ions, which by electrostriction pull in water molecules closer to themselves. This results in a small apparent molar volume (Table 1). This high solute–solvent affinity also seems to exist in sour-tasting molecules. The higher the interaction or affinity between the solute and the solvent (in this case water), the higher the probability of the ease and rapidity of transport

Taste quality	ASV (cm^3/g)	
Salt	<0.33	more hydrophilic molecules
Sour	0.33-0.52	more interactive with water structure
Sweet	0.52-0.71	receptor sites lie deeper in the lingual epithelium
Bitter	0.71-0.93	

Figure 5 Apparent specific volumes and taste quality (Shamil *et al.*, 1987).

of the solute molecule to the receptor. The solute may thus be transported to deep layers of the lingual epithelium, which leads to the conclusion that salty and sour receptors lie deeper in the lingual epithelium than sweet and bitter ones (Birch *et al.*, 1993). Green and Frankmann (1987) provide physiological evidence that salty and sour receptor sites lie deep in the epithelium, and Hiji and Ito (1977) have shown that sweet receptors lie close to the surface of the tongue. Further evidence that salty and sour molecules exert a higher interactive effect on water structure than sweet and bitter ones is provided by Frank and Korchmar (1985), who showed that salty and sour substances have shorter reaction times.

Is it logical to expect those molecules possessing more than one basic taste, also known as multisapophoric molecules, to have ASVs close to the ASV of the dominant taste of the compound? This conclusion does seem to apply to most of the multisapophoric molecules (e.g. potassium iodide, salty–bitter, 0.2755 cm^3/g; sodium tartrate, salty–bitter, 0.4126 cm^3/g; citric acid, sour–sweet, 0.5996 cm^3/g). In the case of the sweet–bitter tasting compounds studied above, the ASVs lie on the borderline between the ASVs reported for the sweet and the bitter substances. It is not always possible to predict the solution behaviour of multisapophoric molecules from their tastes and vice versa. Which

sapophores on the molecule will govern its taste properties will depend on the medium used, the hydrophilic–hydrophobic balance of the molecule and the dissociation constant of the molecule, all of which will influence the solution behaviour of the solute. It should also be noted that when more than one taste sensation is experienced, it can either be tasted simultaneously or in isolation, an example of the latter being the effect of aftertaste exhibited by some of the common artificial sweeteners (Birch, 1996). Sometimes the taste quality is too complex for any taste modality to be experienced individually. Other substances are also known to change their taste in solution, a well-investigated one being D-glucono-1,5-lactone (Parke *et al.*, 1997). The change in taste of the solution from sweet to increasingly sour can also be followed using solution properties and can be explained in terms of changes in solute volume and its hydration layer.

Some sweet molecules, such as artificial sweeteners, have opposed hydrophilic and hydrophobic sides, and this has been associated with increased sweetness (Mathlouthi *et al.*, 1993). Bitter molecules, on the other hand, are very hydrophobic in character (Birch, 1987), and Sheridan *et al.* (1983) have shown that the intensity of bitterness is related to the region of the molecules in which hydrophobicity resides. Bitter receptors have also been shown to be hydrophobic in nature (Venanzi, 1984). In substances with large apolar surfaces, it is thought that hydrophobic hydration is the main form of solute–solvent interaction. This is structurally enhanced water, also called 'stiffened' water, formed from the rearrangement of the molecules in an organized fashion with strong hydrogen bonds between them, and is less compressible than bulk water.

Isentropic partial molar compressibilities [$K_{\phi(s)}$] can be expressed as the extent to which the water of hydration around the solute molecule can be compressed. Galema and Hoiland (1991) have reported the compressibility values of some carbohydrate molecules. Figure 6 gives an overview of the concept of isentropic compressibility. Solutions become less compressible as $K_{\phi(s)}$ values become more negative. The method used to calculate $K_{\phi(s)}$ assumes that the solutes themselves are incompressible. The three-dimensional hydrogen-bonded structure of water is such that it has a large positive $K_{\phi(s)}$ value, meaning that the structure around each water molecule can be collapsed to a fairly large extent. The hydration layer of a hydrophobic solute is less compressible than that of water. The hydrophobic end of the solute molecule causes the water molecules to form strong hydrogen bonds amongst themselves. This restructuring of the water of hydration is often referred to as hydrophobic hydration (Arnett *et al.*, 1965). In the case of carbohydrate molecules, the water structure is slightly disturbed by the hydrogen-bonded network around the solute; this holds the water around the solute firmly, making the hydration layer even less compressible. Ions, with their electrostrictive forces, cause the water structure to collapse around the solute. This water of hydration is tightly held to the ions, reducing compressibility even further.

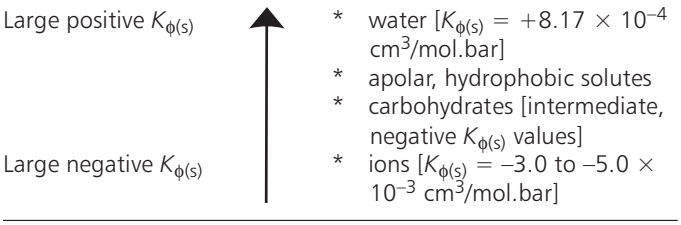

Figure 6 Isentropic apparent molar compressibility ranges of solutes (Galema and Hoiland, 1991).

In general, isentropic apparent molar compressibilities do not correlate well with molecular weight, but tend to become increasingly negative as molecular weight increases, implying that the bigger the molecule the more tightly water molecules are held around it. Salty molecules, consisting of ionic structures, which almost completely dissociate in solution, have the smallest $K_{\phi(s)}$ values (ranging from -3.089×10^{-3} to -8.058×10^{-3} cm^3/mol.bar) caused by electrostriction. Sweet molecules also give negative compressibilities (the largest value reported is -1.707×10^{-4} cm^3/mol.bar) but the isentropic apparent molar compressibility never reaches a more negative value than -5.390×10^{-3} cm^3/mol.bar. Sweet–bitter molecules cover a wider range of compressibilities ($+3.941 \times 10^{-4}$–4.844×10^{-3} cm^3/mol.bar), between values reported for sweet and for bitter molecules. This study shows that isentropic compressibility values can also be grouped by the taste quality exhibited by the molecules, in the same order as for ASV, with salty showing the largest negative values and bitter at the top of the range (see Table 2 and Figure 7).

The equation used to calculate compressibility hydration numbers in this paper shows the number of water molecules which are disturbed by the presence of the solute in solution. The equation, however, assumes that the hydration layer around the solute is incompressible, which is clearly not the case in this study; therefore the numbers obtained can only be used as an approximation of the overall picture in solution. If the compressibilities of the hydration layers were to be included in the hydration numbers, the values would only change slightly, but the same trend would be obtained. Hydration numbers vary with the method used to calculate them, so that numbers obtained through other methods cannot be directly compared. Figure 2 shows that, the bigger the molecule, the higher the number of water molecules disturbed, therefore the better the fit of the solute into the hydrogen-bonded structure of water. A plot of compressibility hydration number against molecular weight for the different taste categories shows good correlation ($R^2 = 0.7860$). Compressibility hydration numbers also seem to

Table 2 Range of isentropic apparent specific compressibility [$K_{2(s)}$] observed for the taste substances studied

	$K_{2(s)}$ (cm^3/g.bar)
salty	-2.332×10^{-5} to -8.064×10^{-5} (lead nitrate to sodium chloride)
sour	$+6.131 \times 10^{-6}$ to -2.991×10^{-5} (formic acid to gluconic acid)
Sweet	-3.383×10^{-7} to -2.335×10^{-5} (raffinose to inositol)
Bitter	-1.993×10^{-8} to -2.487×10^{-6} (quinine hydrochloride to caffeine)

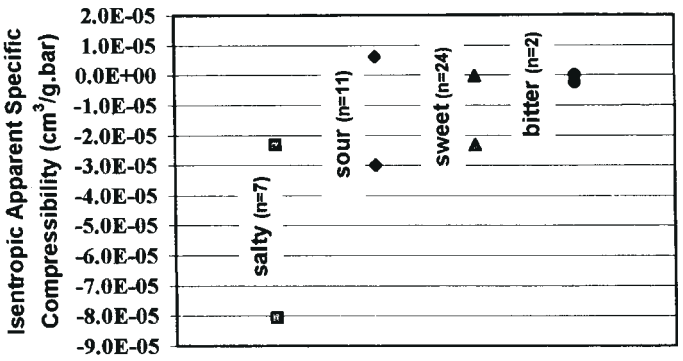

Figure 7 Isentropic apparent specific compressibility ranges for some sapid substances.

relate fairly well to apparent molar volumes as shown in Figure 3. The salty, sour and sweet–bitter molecules studied also correlate well with isentropic apparent molar compressibilities (Figure 4). However, sweet molecules do not (R^2 = 0.0735). Among compounds with the same apparent molar volumes (Figure 3), salty molecules displace a bigger number of water molecules than sour and sweet molecules. Therefore the salty structures, which break water structure with their ions, have higher compressibility hydration numbers than the other molecules. In addition, for the same number of water molecules disturbed, salty molecules display lower apparent molar volumes and more negative isentropic apparent molar compressibilities (Figure 4) than sour molecules, which in turn have lower values than sweet molecules. These findings agree with the hydrophilicity of the molecules and their degree of interaction with the water structure, both of which decrease from salty to sour to sweet.

Limiting the ASV range of sour-tasting molecules to 0.33–0.52 cm^3/g, as quoted by Shamil *et al.* (1987), may not be truly appropriate. Analyses of acids are very sensitive to structural behaviour. Acids are made up of three components, the anion, the cation and the undissociated molecule. The proportions of each of these components in solution depend upon the dissociation constant of the molecule and the temperature at which measurements are taken, so that the apparent volumes and the apparent compressibilities of their hydration layers are averages of the properties of all three components in solution. This explains the wide range of values obtained for sour molecules (ASVs lie between 0.16 and 0.85 cm^3/g, and isentropic specific compressibilities range from $+6.131 \times 10^{-6}$ to -2.99×10^{-5} cm^3/g.bar). For some of the low molecular weight acids (<75 g/mol), namely formic acid, hydrochloric acid, lactic acid, nitric acid and propanoic acid, the calculated isentropic compressibility values are positive (with molar compressibilities of 2.822×10^{-4}, 8.176×10^{-4}, 1.777×10^{-4}, 8.585×10^{-4} and 3.568×10^{-4} cm^3/mol.bar respectively). Hydrochloric acid and nitric acid solutions have molar compressibilities that are higher than that reported for water (the isentropic molar compressibility of pure water is $+8.17 \times 10^{-4}$ cm^3/mol.bar). These acids have relatively simple, open structures compared with the other acids analysed, and therefore probably fit easily within the structure of water. The low hydration numbers (1–4) associated with these particular acids also support this fact.

Molecules with two tastes, such as artificial sweeteners, which taste both sweet and bitter, could be polarized on taste receptors (Birch *et al.*, 1977) and span both receptor sites at the same time (Birch and Mylvaganam, 1976). Chemical modification of sugars (Birch, 1976) has shown that one end of the molecule (the 3,4-α glycol group of glucopyranoside types of structures) elicits sweetness and the other end (first and second hydroxyl groups, ring oxygen atom and primary alcohol group of glucopyranoside types of structures) elicits bitterness. This also suggests that at least some of the sweet and bitter receptor sites might be extremely close to one another, probably within 3–4 Å. It is, however, essential to note that sweet and bitter receptors are separate. Support for this is provided by the action of gymnemic acid, which has the ability to block sweetness without affecting the bitter response (Bartoshuk, 1977). The same is true of the sodium salt of 2(-4-methoxyphenoxy)-propanoic acid, another sweetness inhibitor (Johnson *et al.*, 1994).

Conclusion

Isentropic apparent compressibilities, as opposed to apparent volumes, seem a more sensitive parameter for measuring structural changes in solution as they allow precise monitoring of changes in the hydration layer of the solute. The whole concept of compressibility accords well with that of apparent molar and apparent specific volumes. Isentropic molar compressibility values can also be grouped by the taste quality exhibited by the molecules in the same order as for ASV (with salty showing the largest negative values and bitter at the top of the range), although no clear boundaries can be given based on this experiment. A low

$K_{\phi(s)}$ also reflects a heavily hydrated solute molecule, and therefore high solute–solvent affinity. Low isentropic apparent molar and specific compressibilities as well as low apparent molar and specific volumes (as in the case of ionic structures, which impart saltiness and/or sourness) show that the solute is heavily hydrated and therefore hydrophilic. This in turn implies that there is high solute–solvent interaction, and therefore the molecule can be more easily and rapidly transported to the deeper layers of the lingual epithelium wherein the appropriate receptors lie (Birch *et al.*, 1993). Ions (produced from salty and sour structures) also cause a big spread in isentropic compressibility values, with large negative values exhibited by salts.

It is still very difficult to relate hydration to the stereochemistry of any molecule. There are several considerations to be taken into account: intramolecular hydrogen bonding, which makes certain functional groups unavailable for bonding with water molecules; the fact that equatorial hydroxyl groups of carbohydrate structures are better hydrated than axial hydroxyl groups; rotating C–C bonds, which make measurements very difficult; the anomeric forms of different sugars, which cause their hydration layers to be different; and the steric dispositions of substituents of ring systems, which affect bonding distances. Nevertheless, the solution measurements reported help to illuminate hydration mechanisms which mediate taste quality.

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