

Solution Properties and Sweetness Response of Selected Bulk and Intense Sweeteners

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Two bulk sweeteners (sucrose and maltitol) and four intense sweeteners (acesulfame K, aspartame, sodium cyclamate, and sodium saccharin) are used in this study. Densities and sound velocity values of the sweeteners in solution are measured at 20 °C, and their apparent molar and specific volumes, their isentropic apparent molar and specific compressibilities, as well as their compressibility hydration numbers are calculated and reported. The introduction of solute molecules in water results in a volume change of the solvent as a result of attractive forces exerted by the solute molecules; such forces are in the form of electrostrictive or hydrogen-bonding forces, or charge–dipole attraction. Changes of molar volumes with increasing concentration give an indication of the extent of solute–solute interaction, whereas isentropic compressibilities give a direct measurement of the state of hydration of the solute molecules. The compressibility hydration numbers reported give an indication of the number of water molecules disturbed by the presence of each solute molecule in solution. Isentropic compressibilities seem to be a more sensitive parameter for distinguishing the bulk sweeteners from the artificial sweeteners. The sweetness response of the sweeteners is then explained in terms of their solution behaviors.

Keywords: *Solution properties; sweetness response; bulk sweeteners; intense sweeteners; apparent specific volume; isentropic compressibility; acesulfame K; aspartame; sodium cyclamate; sodium saccharin*

INTRODUCTION

Solution measurements give an overall picture of the packing characteristics of solutes within the three-dimensional hydrogen-bonded structure of water molecules and the order and state of hydration of their protons. This is important in considerations of the accession of taste stimuli to receptor sites through saliva followed by the correct orientation of the molecule on the receptor site. For any molecule to accede and fit on the receptor site, it must be of an optimum molecular volume and be of the right shape (Birch, 1991; Birch et al., 1994) to pack within the structure of water, which acts as the main carrier in the salivary fluid (Kemp et al., 1992). The stereochemistry of the solute will dictate the fit and hence the orientation of the molecule on the receptor.

Another aspect of the packing efficiency of solute molecules among water molecules is the mobility of water around the solute. Water mobility takes account of the changes in the hydration layer and the center of hydration of the solute after interaction with bulk water surrounding the solute. The extent of restructuring or collapse of water structure dictates how deeply the solute molecule can be transported in the taste epithelium, and it is thought that the different receptor sites for bitter, sweet, sour, and salty lie at different depths (Birch, 1991; Birch and Catsoulis, 1985). It is thought that the hydrophobic–hydrophilic balance of the solute affects the rate of exchange of water around the solute (Mathlouthi et al., 1993). The forces holding the solute

to the solvent, that is, electrostrictive forces and hydrogen-bonding forces, are also of interest. Hydrogen bonding apparently promotes water structure by fixing one or more water molecules. This concept of water mobility in the vicinity of the solute also leads to the classification of solute molecules into structure-formers and structure-breakers.

The solution parameters of importance to taste perception are apparent specific volumes, isentropic apparent specific compressibilities, and hydration numbers and are dictated by the structures of the solutes. Apparent specific volumes distinguish solutes of different molecular weights on the basis of their solute–solvent affinity, whereas isentropic compressibilities reflect the compactness of the hydration layers around the core of the solutes. Hydration numbers show the number of water molecules that are disturbed by the solutes in solution. All of these parameters take into account any solute and solvent interactions and, therefore, provide a direct measurement of the state of the hydration layer of the solute molecules.

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 neighborhood 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 tetraordinated hydrogen-bonded structure and is not affected by any of the above forces.

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Compressibility measurements measure the changes in the first two layers of solvent around the molecule. Evidently these two hydration layers are of particular importance for hydrogen-bonding of sugars and water and have been identified as such by molecular dynamics simulations (Astley et al., 1998) and cooperative hydrogen bonds in sugar-protein crystal complexes (Quiocho et al., 1989).

MATERIALS AND METHODS

Chemicals used in this experiment were of reagent grade and were obtained from BDH, (Lutterworth, Leicestershire, U.K.), Sigma Chemical Co. (Poole, Dorset, U.K.), Hoechst (Switzerland), and ICN Biochemicals Ltd. (Thame, Oxfordshire, U.K.). Water used for solution studies was of HPLC grade. All measurements were carried out at 20 °C and in duplicate to minimize errors.

Density and sound velocity measurements were determined using an Anton Paar density sound analyzer (DSA 48) from Paar Scientific Ltd. (Raynes Park, London, U.K.). 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/cm³ and ± 1 m/s, respectively.

Apparent molar volumes, ϕ_v (cm³/mol), and apparent specific volumes, ASV (cm³/g), were calculated from density values using the eqs 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/cm³), d = density of solution at the same temperature (g/cm³), m = molality of the solution (mol/kg of water), M_2 = molecular weight of solute

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

Isentropic apparent molar compressibilities ($K_{\phi(s)}$, cm³/mol·bar) were calculated from both density and sound velocity values using

$$K_{\phi(s)} = 1000(\beta_s - \beta_{s0})/md + \beta_s\phi_v \quad (3)$$

where β_s = isentropic compressibility coefficient of solution (bar⁻¹) and β_{s0} = isentropic compressibility coefficient of water (bar⁻¹). Isentropic compressibility coefficients are calculated from

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

where u = sound velocity of solution (m/s).

Isentropic apparent specific compressibilities ($K_{2(s)}$, cm³/g·bar) were obtained from

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

Compressibility hydration numbers (n_h) were calculated using the equation

$$n_h = (n_w/n_s)(1 - \beta_s/\beta_{s0}) \quad (6)$$

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

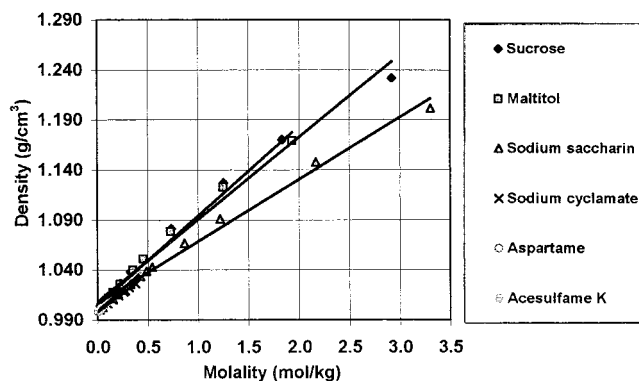


Figure 1. Plot of density against molality.

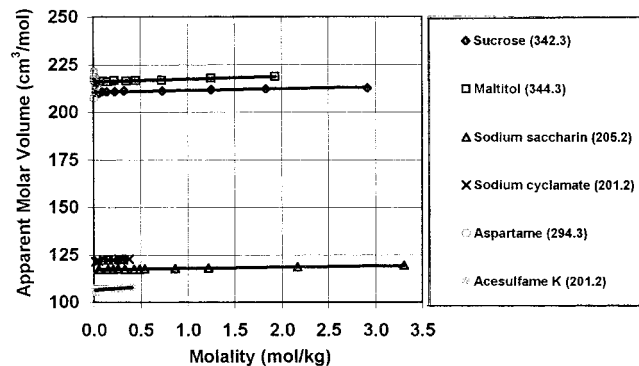


Figure 2. Plot of apparent molar volume against molality (molecular weight of solutes are provided in parentheses).

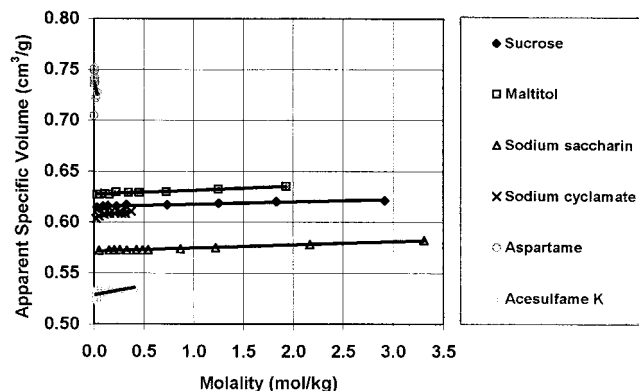


Figure 3. Plot of apparent specific volume against molality.

The partial values for molecular volumes and isentropic compressibilities were obtained at infinite dilution by extrapolating the best fit to the curves to zero concentration.

RESULTS

Plots of the solution measurements against increasing molality of solute are given in the figures. The parameters reported are density (Figure 1), apparent molar and specific volumes (Figures 2 and 3), isentropic apparent specific compressibility (Figure 4), and compressibility hydration number (Figure 5). The partial values, obtained by extrapolation of the lines for each solute, are reported in Table 1.

DISCUSSION

The chemical structures for the substances studied are given in Figure 6. Molecular weights are shown in parentheses. The concentrations of the sweeteners used, in particular the intense sweeteners, are far in excess

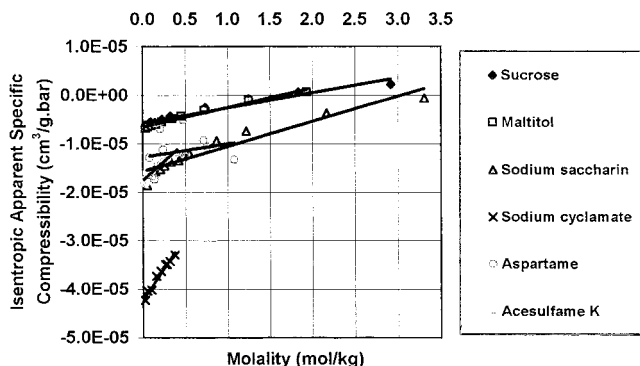


Figure 4. Plot of isentropic apparent specific compressibility against molality.

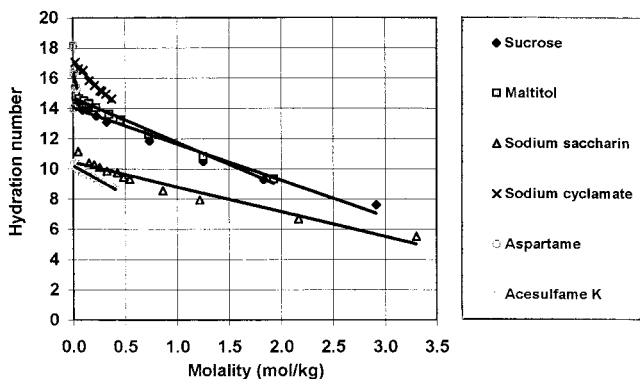


Figure 5. Plot of compressibility hydration number against molality.

of any of the usual tasting concentrations but provide vital information about the packing order of the solutes among water structure as solute–solvent interactions are replaced by solute–solute interactions.

Partial values (reported in Table 1), calculated at zero concentration, assume no solute–solute interaction but give an indication of solute–solvent interaction. All of the substances measured can be compared using their partial measured values, each substance exhibiting its individual characteristics within the structure of water.

Density reflects the packing characteristics of solute molecules among solvent molecules, in this case water molecules. It depends on the molecular structure of both the solute and the solvent. Because water is structured, interaction between the solute and solvent is complex. Electrostrictive forces exhibited by sugars counterbalance the displacement of water molecules so that sugars have higher densities than the intense sweeteners, as shown by the plot of density against increasing molality of solute molecules (Figure 1). Intense sweeteners pack less densely among water molecules as a result of their high hydrophobicity. Both sucrose and maltitol have a large number of equatorial hydroxyl groups that are available to hydrogen-bond to water molecules and, hence, pack neatly within the structure of water (Reiser et al., 1995). In addition, it is well-known that equatorial hydroxyl groups are more hydrated than axial hydroxyl groups. Vicinal hydroxyl groups in the equatorial configuration possess an O–O spacing similar to that of water and therefore fit easily into the existing water structure (Franks et al., 1972).

Molecular volumes can be computed from surface areas and van der Waals radii of the constituent atoms (Birch et al., 1994). The van der Waals volume (Figure 7) is the volume resulting from a set of spheres centered

on the atoms or groups of atoms forming the molecule; its dimensions are defined by the van der Waals radius. Molecular volumes are larger than van der Waals volumes because they represent the displacement of water molecules by the solute, and water molecules cannot fit into the fine crevices on the surface of the solute molecules.

Apparent molar volumes are even larger than the molecular volumes and are a real measurement of the molecular size of the hydrated molecules in solution. They are larger because the solute molecules actually create a void between themselves and the neighboring solvent molecules. The water molecules do not touch the surface of the solute; instead they are held to it by H-bonds. Apparent molar volumes represent the sum of three volume measurements: the intrinsic volume of the solute, the volume due to solute–solute interaction, and that contributed by solute–solvent interactions as shown in eq 7 (Galema and Hoiland, 1991).

$$\phi_v = \phi_{\text{solute}} + \phi_{\text{solute-solute}} + \phi_{\text{solute-solvent}} \quad (7)$$

The largest part of the partial volume is caused by the intrinsic volume of the carbohydrate. Solute–solvent interactions can result either in a pulling-in effect of water molecules toward the solute, as is most often the case, or in repulsion. In general, carbohydrates have small partial molar volumes due to extensive solute–solvent interactions (Galema and Hoiland, 1991). Partial molar volumes can be negative, as with sodium hydroxide and water.

Figure 2 shows that apparent molar volume increases with increasing concentration of the solute as solute–solute interaction replaces solute–solvent interaction, and the solutes become less hydrated. Apparent molar volumes generally increase with increasing molecular weight of the solute. The bulk sweeteners, sucrose and maltitol, are much larger molecules than the intense sweeteners, in accordance with this effect. However, it is possible for a molecule of large mass to have a smaller apparent molar volume than one of smaller mass (Shamil et al., 1989).

Apparent molar volume is therefore a measure of the packing efficiency of solute molecules among solvent molecules and is therefore governed by the interaction of solute structure with water structure. It can be thought of as a resultant of displacement and electrostrictive forces, the latter being constituted of H-bonds. The packing arrangement is such that molecules which are heavily hydrated (e.g., sugars) have smaller apparent molar volumes than those which are not (e.g., aromatic compounds). Heavily hydrated molecules have small apparent molar volumes because of their greater interaction with water, which causes greater electrostrictive forces and the collapse of water structure around them. A low apparent molar volume indicates better packing characteristics, hence better interaction with water structure. Molecules of similar constitution have apparent molar volumes that relate approximately to their molecular weight as shown in Figure 2. The apparent molar volumes of salts, in this case, the salts of the intense sweeteners, are smaller than those of comparable uncharged molecules because salts are completely dissociated in solution and there is a greater electrostrictive effect around the ions (Cohn et al., 1934).

Apparent specific volume, the apparent volume per unit mass (eq 2), appears to be a more appropriate parameter for comparing the packing characteristics of

Table 1. Solution Measurements on Selected Sweeteners at Infinite Dilution^a

sweetener	MW	ϕ_v^0 (cm ³ /mol)	V_2^0 (cm ³ /g)	$K_{\phi(s)}^0 \times 10^{-3}$ (cm ³ /mol·bar)	$K_{2(s)}^0 \times 10^{-6}$ (cm ³ /g·bar)	n_h^0
acesulfame K	201.2	106.3	0.529	-3.474	-17.27	10.28
aspartame	294.3	217.1	0.738	-3.622	-12.31	16.70
maltitol	344.3	215.9	0.627	-2.267	-6.874	14.86
sodium cyclamate	201.2	121.7	0.605	-8.700	-43.24	17.31
sodium saccharin	205.2	117.2	0.572	-3.759	-18.32	11.06
sucrose	342.3	210.6	0.615	-2.180	-6.370	14.33

^a Symbols: ϕ_v^0 , partial molar volume; V_2^0 , partial specific volume; $K_{\phi(s)}^0$, isentropic partial molar compressibility; $K_{2(s)}^0$, isentropic partial specific compressibility; n_h^0 , compressibility hydration number at infinite dilution.

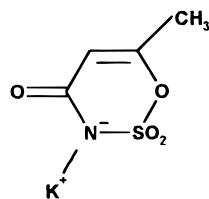
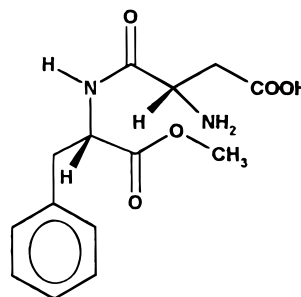
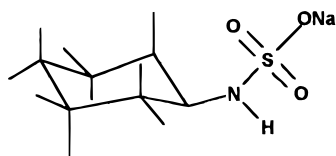
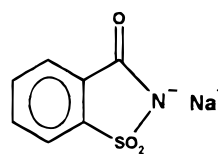
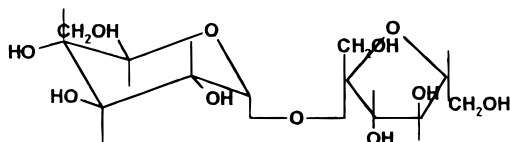
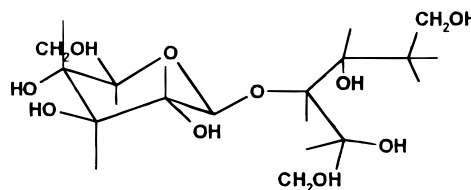
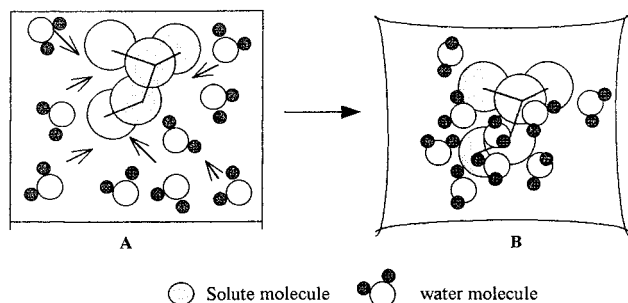
Acesulfame K (MW 201.2 g/mol)**Aspartame (MW 294.3 g/mol)****Sodium cyclamate (MW 201.2 g/mol)****Sodium saccharin (MW 205.2 g/mol)****Sucrose (MW 342.3 g/mol)****Maltitol (MW 344.3 g/mol)****Figure 6.** Molecular structures of selected bulk and intense sweeteners.

Figure 7. (A) Water box containing sapid and water molecules showing van der Waals volume; (B) water box showing the hydrated molecular volume of the molecule with electrostrictive forces pulling in toward the solute. Water molecules cluster toward the more hydrophilic region of the molecule.

sugars of different molecular weights. Experiments by Shamil et al. (1987) have shown that molecules exhibiting the basic four tastes can be grouped into different

Taste Quality	ASV (cm ³ /g)	
Salt	< 0.33	↑ More hydrophilic molecules More interactive with water structure Receptor sites lie deeper in the lingual epithelium
Sour	0.33 - 0.52	
Sweet	0.52 - 0.71	
Bitter	0.71 - 0.93	

Figure 8. Apparent specific volumes and taste quality (source: Shamil et al., 1987).

ASV ranges (Figure 8). Above an ASV of 0.93 cm³/g, molecules are thought to be volatile and possess olfactory properties instead of gustatory properties. The ASV of sweet molecules has been reported to lie within the range 0.52–0.71 cm³/g, whereas the range for bitterness is 0.71–0.93 cm³/g. Figure 3 shows that all of the molecules studied, except for aspartame, lie within the range specified for sweetness. The ASVs of sucrose and maltitol (refer to Table 1 and Figure 3) lie within the range 0.60–0.64 cm³/g reported for substances exhibit-

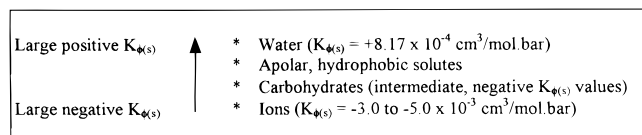


Figure 9. Isentropic apparent molar compressibility ranges of solutes and water (source: Galema and Hoiland, 1991).

ing a clean sweet taste (Birch, 1991; Birch et al., 1996). The other molecules do not lie within the pure sweet range, as can be expected from multisapophoric molecules, that is, molecules exhibiting more than one taste modality. Most of the intense sweeteners studied also have a bitter taste. Aspartame is unusual in that its ASV lies just within the bitter region of the ASV range, yet it also has a sweet taste and only becomes slightly bitter at increasing concentrations. However, aspartame does not taste like sucrose, and this may be ascribable to a small degree of accompanying bitterness.

Isentropic partial compressibility values reflect the compressibility of the hydration layer around the solute compared to that for pure water. Figure 9 shows a general breakdown of compressibility values with respect to solute structure. Inspection of the isentropic partial compressibility values in Table 1 shows that the hydration values of maltitol and sucrose are very different from the intense sweeteners; the two bulk sweeteners have intermediate negative compressibility values and therefore are more compressible than the intense ones. The intense sweeteners show the compressibility behavior of ionic structures (refer to Figure 4). These structures are presumably well dissociated in solution (Cohn et al., 1934), therefore making the hydration layer around the solutes less compressible than that around the bulk sweeteners. This happens as a result of electrostrictive forces from the ions, which causes water structure to collapse around them. It is important to note, however, that sodium cyclamate shows an anomalously low isentropic compressibility compared to the other intense sweeteners studied. This implies that the presence of sodium cyclamate in solution breaks water structure to a very large extent and causes a rearrangement of the water molecules in the hydration layer so that they are held even more tightly to the core of the solute.

Compressibility values are additive of the individual ions (Mathieson and Conway, 1974). Cations and anions hydrate differently. The compressibility of cations can be accounted for in terms of electrostrictive effects; in other words, the volume change in the hydration layer associated with charge–dipole attraction. Anions are more susceptible to pressure change, and the dipole orientation of the hydration layer in the immediate vicinity of the anion is different from that of the cations. Anions are less hydrated than cations; that is, their hydration shells are less firmly held. Ions that hydrogen-bond with water are also reported to have unusual compressibilities; for example, H^+ has an anomalously high compressibility of $8.6 \times 10^{-4} \text{ cm}^3/\text{mol}\cdot\text{bar}$, whereas OH^- has an extremely large negative compressibility of $-51.8 \times 10^{-4} \text{ cm}^3/\text{mol}\cdot\text{bar}$ (Mathieson and Conway, 1974).

Compressibility hydration numbers represent the number of water molecules that are disturbed by the presence of the solute molecule in solution (Galema and Hoiland, 1991). The equation used for calculating hydration numbers is based on compressibility measurements

and therefore derives from the disturbance of the first two hydration layers around the solute. It also assumes that the hydration layer around the solute is incompressible, which is not the case in this study; therefore, the numbers obtained can only be used to give an approximation of what is happening in solution. If the compressibilities of the hydration layers were to be included in the hydration numbers, the values would change only 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. In general, the bigger the compressibility hydration number, the higher the number of water molecules disturbed, but the better the packing of the solute within the hydrogen-bonded structure of water. As the concentration of solute is increased, solute–solute interaction replaces solute–solvent interaction, leading to a fall in the number of water molecules disturbed and, hence, a corresponding decrease in the compressibility hydration number (Figure 5). The larger molecules of the bulk sweeteners have high compressibility hydration numbers and hence show a good fit within water molecules. Among the intense sweeteners, sodium cyclamate and aspartame show unusually high compressibility hydration numbers. In the case of aspartame, it is thought that hydrophobic hydration around the molecule enhances water restructuring, causing the solute to fit tightly within the water structure. The compressibility hydration number of sodium cyclamate tallies with its very low isentropic compressibility, showing extensive interaction of the solute with the solvent.

A comparison of acesulfame K and sodium cyclamate, both having molecular weights 201.2 (refer to Table 1), shows that acesulfame K has a much lower apparent molar volume and apparent specific volume. Its compressibility is higher than that of sodium cyclamate, implying that its hydration layer is more compressible. The chemical structure of acesulfame K is much simpler than that of sodium cyclamate, so that the stereochemical disposition of its atoms in space would be expected to disturb water structure less, and this is indeed shown by its lower compressibility hydration number.

In addition to the above, it is very likely that the cation affects the structuring of water. The isentropic partial specific compressibility value of potassium cyclamate as compared to that of sodium cyclamate (refer to Table 2) shows that the sodium salt is less compressible than the potassium salt; that is, it is more interactive with water structure. It seems therefore very likely that the sodium ion causes more collapse of water structure around the molecule. This also explains the lower compressibility and higher compressibility hydration number of the sodium salt of cyclamate compared to those of acesulfame K. Mathieson and Conway (1974), who also investigated the changes undergone by the structure of water in the presence of an ion as a result of electrostriction and changes in hydrogen-bonding, suggested that cations smaller, or more highly charged, than the potassium ion are net structure-formers. Mathieson and Conway (1974) also report the compressibilities of Na^+ and K^+ as -33.5×10^{-4} and $-26.5 \times 10^{-4} \text{ cm}^3/\text{mol}\cdot\text{bar}$. Frank and Wen (1957) described the potassium ion as being slightly structure-breaking, which agrees with the results reported here. Samoilov (1957) explains hydration in terms of the rate of exchange, or mobility, of water molecules in the vicinity

Table 2. Solution Measurements on Sodium and Potassium Cyclamate at Infinite Dilution

sweetener	MW	ϕ_v^0 (cm ³ /mol)	V_s^0 (cm ³ /g)	$K^0_{\phi(s)} \times 10^{-3}$ (cm ³ /mol·bar)	$K^0_{2(s)} \times 10^{-6}$ (cm ³ /g·bar)
sodium cyclamate	201.2	121.7	0.605	-8.400	-43.24
potassium cyclamate	217.3	129.2	0.595	-8.728	-40.17

Table 3. Relative Sweetness Potency of Sweeteners Studied (Source: Bakal, 1983)

sweetener	relative sweetness (sweetness of sucrose = 1)	aftertaste
acesulfame K	200	slightly bitter
aspartame	200	very slightly bitter
maltitol	0.8	
sodium cyclamate	30	slightly bitter
sodium saccharin	300	metallic, bitter

of the ion. He suggests that Na⁺ decreases, whereas K⁺ increases, water mobility (compared to that of pure water) in its vicinity. Proton magnetic resonance studies by Arulmozhi and Rao Srinivasa (1993) also show that structure-formers (e.g., the sodium ion) restrict the overall motional freedom of water, whereas structure-breakers (e.g., the potassium ion) increase the freedom of movement of water in the vicinity of the solute.

Experiments by Mathlouthi et al. (1993) have also shown, through measurements of hydrodynamic volumes (i.e., viscosities) that sodium cyclamate has a larger influence on the structure of water than aspartame or sodium saccharin. They reported sodium cyclamate to have a large $B_{\text{structure}}:B$ ratio, where $B = B_{\text{size}} + B_{\text{structure}}$. B is the overall hydrodynamic molar volume of the solute (L/mol), B_{size} is the volume contribution due to the size and shape of the solute, and $B_{\text{structure}}$ is due to the effect of the solute on solvent structure.

Aspartame, being nonionic, seems to exhibit properties very different from those of the salts of intense sweeteners (Figures 2–4). Its very hydrophobic nature seems to dictate its hydration properties. It is thought to participate in hydrophobic hydration, in which its hydrophobic side repels water to such an extent that the water molecules restructure themselves in an organized fashion. This manifests itself as a large apparent specific volume (Figure 3) and increased isentropic compressibility (Figure 4). Mobility of water is also reduced in the process. Mathlouthi et al. (1993) report similar findings on aspartame through high intrinsic viscosity (denoted by $[\eta]$) and low Huggins constant (K') values. $[\eta]$ is a shape factor accounting for the hydrodynamic radius of the solvated molecule, and K' is the interaction factor accounting for the reactivity of the solute with the solvent, in this case the ease of rupturing and establishing intermolecular hydrogen bonds between the solute and water. Differences in these properties are due to differences in hydration of the solute molecules. Shamil et al. (1987) have also shown that intense sweeteners have lower intrinsic viscosities than sugars because of their hydrophobic character. Hydrophobic hydration has been extensively studied with respect to clathrate-like structures and seems to provide added stability to crystal structures (Rodger, 1992).

An attempt to correlate the taste intensities of sapid substances with their solution properties is complex but can be done in some cases by following the behavior of solutes in solution (Parke et al., 1996). In this study, maltitol, the sweetness of which is only slightly lower than that of sucrose (Table 3), has solution measure-

ments very similar to those of sucrose, although fine differences cannot be discriminated from volume or compressibility calculations. The intense sweeteners have solution properties quite different from those of sucrose, but solution properties alone are not sufficient to explain the range of sweetness intensities reported. The most plausible explanation for the high sweetness intensity of certain molecules is the result of an increase in the number of receptors recruited as well as decodification at the neural level. An increase in the concentration of sweetener molecules will result in increased sweetness until a maximum is achieved as postulated by Beidler (1954). The more free solute molecules that are present in solution, the more receptors they will occupy, until all of the receptors are taken up and a saturation plateau is reached. The nature of the solutes and their interaction with water is crucial in determining the number of sapid molecules that will be free to bind to the receptors and the maximum depth of the lingual epithelium they will be able to access, hence, the number of receptors available. This theory can also be used to explain the variation in the maximum sweetness intensity exhibited by different sweeteners. Once bound to the receptors, the type of interaction of the molecule and the complementarity of the solute with the receptor site will dictate the information sent to the brain. These will depend on the structure of the sapid molecule, the most favorable AH, B, γ sweetness triangle, and possibly more interaction sites as stated by the multipoint attachment theory (Nofre and Tinti, 1993). The decodification of the intensity of taste at the neural level depends on the message transmitted. The signal transmitted for intense sweeteners will, presumably, be stronger than that for sugars due to their hydrophobicity. Mathlouthi et al. (1993) explain the intensity of intense sweeteners in a homologous series by changes in the hydrophilic–hydrophobic balance of the molecule leading to increased water mobility and a corresponding rise in the intensity of sweetness.

Most intense sweeteners exhibit increased bitterness as their concentrations are raised, but at the low concentrations used in foods and beverages, bitterness is barely detectable. Hydrophobicity has been shown to correlate well with bitterness (Birch, 1987), but Sheridan et al. (1983) have shown that the intensity of bitterness depends on the region of the molecule which is more hydrophobic. The anions may also contribute to the bitterness of the salts of the intense sweeteners. Sodium saccharin, for instance, is 99.9% dissociated in solution. The saccharinic ion is hydrophobic (Rader et al., 1967), and the ASV of the anion has also been calculated to be 0.67 cm³/g, a value that is close to the bitter end of the ASV taste quality range, so we would expect the molecule to taste bitter. Concise reviews of intense sweeteners are given by Bakal (1983), Birch (1997), O'Brien Nabors and Gelardi (1991), and Van der Heijden (1993).

Another property of all intense sweeteners is their persistence of sweet taste. Intense sweeteners are very hydrophobic. Kier's tripartite theory, which suggests that lipophilicity increases sweetness, could also explain

persistence (Kier, 1976). The hydrophobic part of a compound permits ready access of the molecule to the taste bud receptor site, the membrane of which is lipoid in nature. As the molecule is strongly bound to the receptor site, it could give rise to persistence of sweetness. Persistence can also be explained by localized increases in stimulus concentration in the receptor environment resulting from the ionic surface of proteins in the taste cell membrane.

CONCLUSION

From the results obtained, a clear difference between the bulk sweeteners and the intense sweeteners can be identified. As all of the properties studied (densities, molar volumes, isentropic compressibilities, and compressibility hydration numbers) give an indication of the hydration of the molecule in water, it is possible to conclude that there is a distinct difference between the hydration of bulk and intense sweeteners. The shape, size, and stereochemistry of the solutes do affect their fit into water structure and hence can be expected to influence their transport to and orientation on the receptor site. The results also suggest that differences in hydration could be due to the hydrophobicity of the molecules, the intense sweeteners being much more hydrophobic than the bulk sweeteners, and this dictates the type and extent of hydration of the molecules. In addition to interaction at the neural level, solute-solute, solute-solvent, solute-receptor, solvent-solvent, and solvent-receptor interaction affinities are prime determinants of the mechanism of taste. The above study underscores how solution properties can be used to predict the qualitative effects of intense sweeteners, and this concept can be extended to explain the mechanism of action of noncaloric sugar substitutes.

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