Food Chemistry 84 (2004) 351–357

Food Chemistry

www.elsevier.com/locate/foodchem

Rapid communication

Volumetric properties of aqueous solutions of some cyclohexylsulfamates at 25.0 °C

Darja Rudan-Tasic*, Cveto Klofutar

Department of Food Technology, Biotechnical Faculty, University of Ljubljana, SI-1000 Ljubljana, Slovenia

Received 21 January 2003; received in revised form 12 March 2003; accepted 12 March 2003

Abstract

The densities of aqueous solutions of some salts of cyclohexylsulfamic acid (lithium, potassium, ammonium and tetramethylammonium, synthesized in our laboratory) and of the commercially available sodium and calcium cyclohexylsulfamate, were measured in the concentration range from 0.003 to 1.000 mol kg^{-1} at a temperature of 25.0 °C. The apparent and partial molar volumes of the solutes studied were determined as a useful tool in elucidating the structural interactions (e.g. ion–ion and ion–solvent) occurring in solution. The apparent molar volumes mainly show small negative deviations from the Debye–Hückel's limiting law, though in some cases no deviations were observed. The concentration dependence of the apparent molar volumes was expressed in the form of a polynomial of second degree; the empirical constant B_v which can be used as a direct measure of the ion–ion interactions, equals zero or it is negative for the solutes investigated. Additionally, the partial molar ionic volume of the cyclohexylsulfamate anion was calculated and also the apparent specific volume of the solutes; in general the latter is closely associated with the taste quality. It was found that the values of the apparent specific volumes of the solutes investigated lie on the borderline between the values reported for sweet and bitter substances.

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Keywords: Solution properties; Apparent molar volume; Apparent specific volume; Cyclohexylsulfamates

1. Introduction

Cyclohexylsulfamic acid (cyclamic acid) and its sodium and calcium salts are used as intense sweeteners but are effectively non-caloric. According to the most widely accepted and relevant theory in the field of sweet-taste chemoreception (Shallenberger & Acree, 1967), all sweet substances should possess a hydrogen bond donor (AH) and a hydrogen bond acceptor (B), 2.5–4.0 Å apart, so this should be true of cyclohexylsulfamates (Benson & Spillane, 1976; Grenby, 1991, Fig. 1). Some authors (Spillane, Ryder, Walsh, Curran, Concagh, & Wall, 1996) pointed out that the sulfamate structure–taste relationship could be interpreted by the role of the cationic, sulfamate functions and the role of the radical. But the same authors showed that the cation has very little effect on the sweet taste of cyclamates. Just the opposite was recognized for the sulfamate function, which is essential for sulfamate sweetness. In the past, various structures of the radical group were tested; for example, the carbon ring was replaced by open-chain carbo-systems without destroying the sweet taste (Spillane, Ryder, & Sheahan, 1994; Spillane, Sheakan, Simmie, Cunningham, McArdle, & Higgins, 1989). Recently Spillane, Feeney, and Coyle (2002) reported the synthesis of sweet-tasting benzene sulfamates and found that some of the *meta*- substituted derivatives possess a strong sweetness but, in contrast, there was reduced sweetness in the *ortho*- and *para*- compounds. Their findings were unexpected since some authors (Audrieth & Sveda, 1944) suggested that a saturated carbon ring, such as cyclohexyl, is essential for sweetness.

A new approach to studying the mechanism of sweet taste chemoreception is now focused on the role of water (Birch, Karim, Lopez, & Morini, 1993). Namely, the interactions of sapid solutes with water may influence their accession to, and binding with, receptor sites, thus influencing their taste properties. Hence it is important to study the water interactions of analogous and homologous solutes in order to assess the contributions of molecular fragments to hydration processes. Solution

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* Corresponding author. Fax: +386-1-25-66-296.
E-mail address: darja.rudan.tasic@bf.uni-lj.si (D. Rudan-Tasic).

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doi:10.1016/S0308-8146(03)00229-2

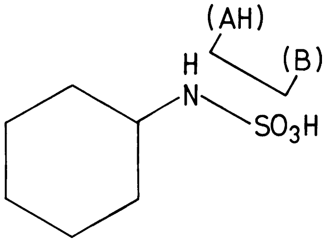

Fig. 1. Chemical structure of cyclamate illustrating the AH–B pair (Grenby, 1991).

properties offer a convenient means of investigating the behaviour of solutes in water. If all taste effects are mediated by water, the solution properties of several, systematically chosen salts of cyclohexylsulfamic acid may provide an understanding of their potential sapid effects in connection with the role of the cation (its size, charge and polarizability) and also of the cyclohexylsulfamate anion itself (Benson & Spillane, 1976; Spillane et al., 1996).

This study concentrates on the partial molar and specific volumes of some cyclohexylsulfamates (in terms of their ionic contributions) because no adequate data are available in the literature except for the sodium salt (Mathlouthi, Bressan, Portmann, & Serghat, 1993; Spillane, Morini, & Birch, 1992). Hydration of electrolytes is well-documented (Robinson & Stokes, 1959), and depends on the polarizing effect of the cation, which is in turn a function of the ionic radius and the electrical charge; Li^+, Na^+ and Ca^{2+} all tend to orient water molecules in their vicinity and are relatively highly hydrated, whereas K^+ and NH_4^+ are surrounded with water molecules, which are more mobile than bulk water. The previously mentioned cations were identified as water structure enhancers, whereas K^+ or NH_4^+ have the opposite effect and can be classified as structure breakers. In the case of ions with a large hydrophobic surface (e.g. R_4N^+ ions) water molecules at the surface of these ions are not strongly influenced by the ionic charge or the hydrocarbon portion of the molecule; water–water interactions next to a hydrophobic ion appear to have a higher degree of hydrogen bonding or structure and this type of ion can be classified as a hydrophobic structure-making ion (Millero, 1972). In general, anions are known to be less hydrated than cations, so this also applies to the cyclohexylsulfamate anion. If water interactions are responsible for affecting the shape, as well as the effective size, of the solute molecules, a study of solution properties might allow the prediction of taste quality in multisapophoric molecules. Therefore the volumetric data in this work were acquired with the objective of investigating whether there exists a relationship between these properties and sweet taste.

2. Materials and methods

Commercially available cyclohexylsulfamic acid (HCy) was purchased from Sigma. The compound was used without further purification and stored in a desiccator over P_2O_5. It was analysed by conductometric titration with sodium tetraborate and found to be at least 99.9% pure. Lithium (LiCy), potassium (KCy) and tetramethylammonium cyclohexylsulfamate [$(CH_3)_4NCy$] were obtained by careful neutralization of cyclohexylsulfamic acid with the corresponding base (Merck and Fluka) while sodium(NaCy) and calcium cyclohexylsulfamate [Ca(1/2)Cy] were purchased from Sigma. The purity of the prepared salts was checked after repeated recrystallizations from water (only the tetramethylammonium salt was recrystallized from 2-propanol) by analysis of the elements C, H, and N (Perkin-Elmer elemental analyser, 2400 CHN) and also by ion-exchange of the cations of salts with the hydrogen ion (Dowex, Type 50 WX8); a purity of 99.4% at least (lithium salt) or better (e.g. 99.8% for the potassium salt) was determined. Like the acid its salts were kept in a vacuum desiccator over P_2O_5.

The investigated solutions were prepared on a molal concentration scale by precise weighing, $\pm 1\times10^{-5}$ g (AT201 Mettler Toledo).

The solution densities d were measured at (25.00±0.01)°C using a digital densimeter (model DMA 60, A. Paar, K.G., Graz) with a reproducibility of 1×10^{-5} g cm^{-3}. The equipment was calibrated with water and air following the instruction manual.

3. Results and discussion

The apparent molar volume $V_{2,\Phi}$ (cm^3 mol^{-1}) of a solute with molar mass M_2 (g mol^{-1}) at molality m is defined by

$$V_{2,\Phi} = \frac{10^3(v - v_0)}{m} + vM_2 \qquad (1)$$

where $v = 1/d$ and $v_0 = 1/d_0$ are the specific volume of the solution and solvent, respectively. The values of the apparent molar volume of the investigated solutes are given in Table 1. For the salts investigated, the concentration-dependence of $V_{2,\Phi}$ was fitted with an equation of the type (Spedding, Pikal, & Ayers, 1966)

$$V_{2,\Phi} = V_{2,\Phi_0} + A_v m^{1/2} + B_v m + D_v m^{3/2} + \ldots \qquad (2)$$

where V_{2,Φ_0} is the apparent molar volume of the solute at infinite dilution, equal to $\overline{V}_2^0$ (i.e. the limiting partial molar volume of solute), A_v is the Debye constant (1.865 cm^3 mol$^{-3/2}$ kg$^{1/2}$ for a 1:1 electrolyte and 9.692 cm^3 mol$^{-3/2}$ kg$^{1/2}$ for a 2:1 electrolyte at 25 °C, Dunn, 1968) and B_v and D_v are empirical constants which

Table 1
Density, apparent molar volume, and partial molar volume of solute for aqueous solutions of some cyclohexylsulfamates as a function of the molal concentration at 25 °C

m (mol kg^{-1})	d (g cm^{-3})	$V_{2,\Phi}$ (cm^3 mol^{-1})	$\overline{V}_2$ (cm^3 mol^{-1})
LiCy			
0.00334	0.99724	126.11±6.06	127.7
0.10370	1.00283	128.84±0.20	128.4
0.20782	1.00847	128.93±0.10	128.8
0.29981	1.01340	128.74±0.04	129.1
0.40317	1.01874	128.80±0.05	129.3
0.49655	1.02337	128.90±0.04	129.5
0.59282	1.02829	128.66±0.04	129.7
0.70298	1.03323	129.25±0.03	129.9
0.80996	1.03828	129.16±0.03	130.0
0.99809	1.04661	129.33±0.02	130.3
NaCy			
0.00402	0.99737	119.97±5.05	123.0
0.10211	1.00494	123.26±0.20	123.7
0.20152	1.01234	123.56±0.10	124.1
0.30227	1.01961	123.91±0.07	124.3
0.40241	1.02679	123.77±0.05	124.6
0.51112	1.03422	124.03±0.04	124.8
0.60261	1.04032	124.18±0.03	125.0
0.69055	1.04605	124.31±0.03	125.1
0.78842	1.05218	124.58±0.03	125.3
0.88989	1.05843	124.74±0.02	125.4
1.00001	1.06535	124.57±0.02	125.6
KCy			
0.00257	0.99726	133.32±7.88	132.8
0.00536	0.99750	133.52±3.78	132.8
0.02088	0.99880	133.37±0.97	132.9
0.03093	0.99964	133.15±0.66	132.9
0.04853	1.00110	133.40±0.42	132.8
0.06244	1.00225	133.38±0.33	132.8
0.10157	1.00547	133.45±0.20	132.6
0.13658	1.00829	133.62±0.15	132.4
0.16654	1.01069	133.75±0.12	132.3
0.19730	1.01318	133.54±0.10	132.1
0.22520	1.01548	133.16±0.09	131.9
NH_4Cy			
0.00405	0.99727	140.60±4.98	144.6
0.05527	1.00005	141.74±0.37	142.1
0.10981	1.00292	142.18±0.19	142.3
0.15308	1.00516	142.37±0.13	142.5
0.20055	1.00772	141.77±0.10	142.7
0.25210	1.01023	142.38±0.08	142.8
0.30214	1.01267	142.59±0.07	142.9
0.35168	1.01506	142.74±0.06	143.1
0.40281	1.01760	142.59±0.05	143.2
0.44610	1.01973	142.46±0.05	143.3
$(CH_3)_4NCy$			
0.00542	0.99726	213.46±3.72	212.0
0.00949	0.99742	213.98±2.13	212.1
0.05460	0.99918	213.41±0.37	212.1
0.10031	1.00088	213.82±0.20	212.0
0.19757	1.00456	213.27±0.11	212.7
0.29706	1.00812	213.26±0.07	213.2
0.39577	1.00116	213.11±0.05	213.8
0.49431	1.01497	213.82±0.04	213.3
Ca(1/2)Cy			
0.00698	0.99764	113.27±2.90	113.4
0.09446	1.00478	115.65±0.22	115.9
0.18485	1.01195	116.03±0.11	116.9
0.26995	1.01854	116.25±0.08	117.4
0.36523	1.02577	116.38±0.06	117.8
0.44528	1.03154	116.89±0.05	117.9
0.53916	1.03843	116.80±0.04	118.1
0.63463	1.04502	117.17±0.03	118.1
0.71263	1.05045	117.19±0.03	118.1
0.80431	1.05680	117.11±0.03	118.0
0.89448	1.06246	117.57±0.02	117.9

depend on solvent, solute, and temperature. By combining Eqs. (1) and (2), Eq. (3) is obtained

$$(10^3 + mM_2)v - 10^3 v_0 - A_v m^{3/2} = V_{2,\Phi_0} m + B_v m^2 + D_v m^{5/2} + \ldots \tag{3}$$

from which the values of $V_{2,\Phi_0}$and the parameters B_v, $D_v\ldots$ can be estimated by least squares fitting. For the systems investigated, only two coefficients ($V_{2,\Phi_0}$and B_v) were sufficient to represent the data adequately, or even just one, i.e. V_{2,Φ_0} (lithium, sodium and ammonium salt). The regression values of the parameters of Eq. (3) are given in Table 2. It was found (Millero, 1971) that the magnitude and sign of the deviation constant B_v can be used as a direct measure of the ion–ion interactions. According to the Frank–Robinson model (Kiyosawa, 1988), ion–ion interactions can be affected by the influence of ions on the structure of water. Actually, apparent molar volumes represent the sum of three contributions: the intrinsic volume of the solute, the volume due to solute–solute interactions, and that contributed by solute–solvent interactions (Galema & Høiland, 1991). $V_{2,\Phi}$ values of the all electrolytes studied were found to approach the limiting law in dilute solutions, some of them even at higher concentrations (Table 2). However, only negative deviations from the limiting law were observed, indicating that solute–solute interactions (ion-pairing) are not the main contribution to $V_{2,\Phi}$. On the contrary, the largest part of the partial volume is caused by solute–solvent interactions which result in a pulling-in effect of water molecules toward the solute and increasing electrostriction in more concentrated solutions. From the literature (Parke & Birch, 1999) it is known that sodium cyclamate shows an anomalously low isentropic compressibility compared with the other intense sweeteners, e.g. aspartame. This implies that NaCy in solution acts as a very effective structure breaker (more than the potassium salt) 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; for the lithium and ammonium salts there are no data of this kind.

The partial molar volume of the solutes, $\overline{V}_2$ (cm^3 mol^{-1}), was obtained from Eq. (2) (Millero, 1972) and are collected in Table 1 and shown in Fig. 2). $\overline{V}_2$ values

Table 2
Values of the parameters of Eq. (5) and correlation coefficient, r for the investigated cyclohexylsulfamates at 25 °C

Solute	$\overline{V}_2^0$ (cm^3 mol^{-1})	$-B_v$	r
LiCy	127.52±0.05	–	0.99999
NaCy	122.81±0.04	–	1
KCy	133.50±0.24	4.66±1.31	0.99999
NH_4Cy	141.40±0.06	–	1
$(CH_3)_4NCy$	213.31±0.11	3.61±0.26	1
Ca(1/2)Cy	112.29±0.22	4.55±0.31	1

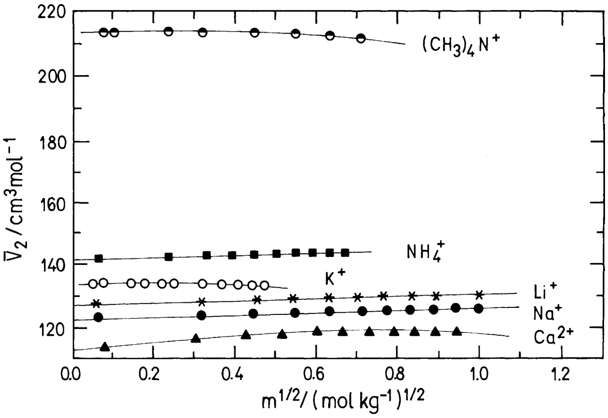

Fig. 2. The dependence of $\overline{V}_2$ on molality, *m*, for some cyclohexylsulfamates at 25 °C.

increase with increasing solute concentration for LiCy, NaCy and NH_4Cy, or reach a maximum value at a definite concentration, and then decrease in magnitude with increasing concentration.

Considering the separation of the limiting partial molar volume of an electrolyte into the individual volumes for the cation and anion (Millero, 1972), the limiting partial molar volume of the cyclohexylsulfamate ion, $\overline{V}^0_{Cy^-}$, was estimated according to

$$\overline{V}^0_{\mathrm{Cy}^-} = \overline{V}^0_2 - \overline{V}^0_{\mathrm{Cat}^+} \tag{4}$$

where for the limiting partial molar volume of the individual cation, $\overline{V}^0_{\mathrm{Cat}^+}$, the literature values were used (Table 3). The average value for $\overline{V}^0_{Cy^-}$ amounts to (128.62 ± 0.79) cm³ mol⁻¹ without taking into account the value of the calcium salt.

The limiting ionic partial molar volume can be attributed to the following components: the intrinsic partial molar volume, $\overline{V}^0_{\mathrm{int}}$, the electrostriction partial molar volume, $\overline{V}^0_{\mathrm{electr}}$, the disordered or void-space partial molar volume, $\overline{V}^0_{\mathrm{disord}}$, and to the caged or structured partial molar volume, $\overline{V}^0_{\mathrm{caged}}$ (Millero, 1972). For ions with a large hydrophobic surface, such as the cyclohexylsulfamate ion, the limiting ionic partial molar volume can be reduced to the sum of the intrinsic and electrostriction partial molar volumes. The true 'non-hydrated' partial molar volume of an ion in solution cannot be measured directly and is usually evaluated from the crystallographic volume, $\overline{V}^0_{\mathrm{cryst}}$, by assuming that the ions are perfect hard spheres

$$\overline{V}^0_{\mathrm{cryst}} = \frac{4\pi}{3} N 10^{-24} r^3 = 2,52 r^3 \tag{5}$$

where *r* is the crystal radius (Å) and *N* is the Avogadro constant. For the cyclohexylsulfamate ion the value of $\overline{V}^0_{\mathrm{cryst}}$ was found to be 127.65 cm³ mol⁻¹ and consequently, $r = 3.70$ Å (Leban, Rudan-Tasic, & Klofutar, to be published). The crystal volume for the Cy⁻ anion coincides very well with the value of the van der Waals volume ($V_{2,\mathrm{vdW}} = 128.27$ cm³ mol⁻¹) calculated from the corresponding volumes or atomic group contributions (Edward, 1970). From the structure of the cyclohexylsulfamate ion (Fig. 3), it may be assumed that the large sulfamic group, with its negative charge distributed not equally over the whole group but just over the three oxygen atoms, has little or no electrostriction.

Conway, Verrall, and Desnoyers (1966) assume that the limiting ionic partial molar volume can be related to the radius of the hydrated ion, r_h by the relation

$$\overline{V}^0_{\mathrm{ion}} = 2.15 r_{\mathrm{h}}^3 + 3.15 r_{\mathrm{h}}^2 \tag{6}$$

From this equation, r_{h} for the cyclohexylsulfamate ion was found to be 3.34 Å which, within experimental error, is equal to the crystal or van der Waals radius of the ion ($r_{\mathrm{vdW}} = 3.705$ Å); therefore no considerable

Table 3
Limiting partial molar volume, limiting ionic partial molar volume of some cations and of the cyclohexylsulfamate anion, and apparent specific volume of investigated cyclohexylsulfamates at 25 °C

Cation	$\overline{V}^0_2$ (cm³ mol⁻¹)	$\overline{V}^0_{\mathrm{Cat}^+}$ (cm³ mol⁻¹)	$\overline{V}^0_{\mathrm{Cy}^-}$ (cm³ mol⁻¹)	$\overline{v}^0_2$ (cm³ g⁻¹)
Li⁺	127.52	−1.29[a]	128.81	0.689
Na⁺	122.81	−6.15[a]	128.95	0.610
K⁺	133.50	6.08[a]	127.42	0.614
NH_4^+	141.40	12.40[c]	129.00	0.720
$(CH_3)_4N^+$	213.31	83.70[b]	129.61	0.845
H⁺	127.95	0.0[c]	127.95	0.714
Ca²⁺	112.29	−22.14[a]	123.36	0.566

[a] Hirakawa (1987).
[b] Krumgalz (1980).
[c] Millero (1971).

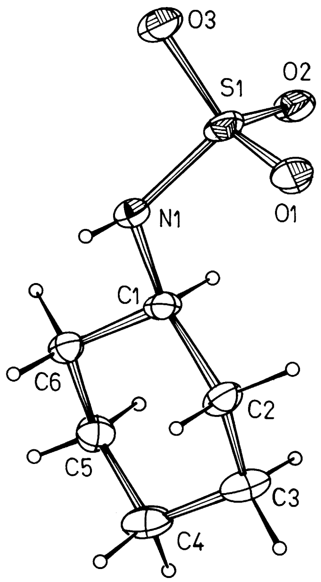

Fig. 3. Crystallographic structure of the cyclohexylsulfamate ion (Leban et al., to be published).

hydration of the cyclohexylsulfamate ion can be observed.

According to theoretical considerations advanced by many authors, the hydration number, n, for a 1:1 electrolyte may be given as (Noyes, 1964)

$$n = \frac{\left(\overline{V}^0_{\text{ion}} - \overline{V}^0_{\text{int}}\right)}{-2.1} = \frac{\overline{V}^0_{\text{electr}}}{-2.1} \qquad (7)$$

where -2.1 cm^3 mol^{-1} refers to the average theoretical electrostriction per mole of water. The hydration number for the cyclohexylsulfamate ion was found to be $n = 0.54$ where for $\overline{V}^0_{\text{electr}}$ the value of -1.13 cm^3 mol^{-1} was used.

The limiting apparent specific volume (cm^3 g^{-1}), $\overline{v}^0_2 (= \overline{V}^0_2 / M_2)$ appears to be an appropriate parameter for comparing the packing characteristics of solutes with the solvent structure. Since 1996, many $\overline{v}^0_2$ measurements of tastants have been made (Birch, 2002) and the idea of $\overline{v}^0_2$ as a broad determinant of taste quality has been confirmed; namely, the apparent specific volume was found to discriminate between the four basic tastes (salt $\sim$0.33 cm^3 g^{-1}, sour $\sim$0.33 to $\sim$0.52 cm^3 g^{-1}, sweet $\sim$0.52 to $\sim$0.71 cm^3 g^{-1} and bitter $\sim$0.71 to $\sim$0.93 cm^3 g^{-1}, Shamil, Birch, Mathlouthi, & Clifford, 1987). Above $\overline{v}^0_2$ of 0.93 cm^3 g^{-1}, molecules are thought to be volatile and possess olfactory properties instead of gustatory properties. The explanation of the results in Table 4 may be related to disturbance of the water structure. Evidently the different values of apparent specific volume are related to differences in taste receptor signals. For example, the receptor cells might be sensitive to fine disturbances of water structure, or alternatively, they might be located at different layers of the taste epithelium (Birch & Shamil, 1988). Thus it is possible that the apparent specific volume reflects the accession efficiency of solute stimulus on the receptor. Protons and ionisable salts are most compatible with water structure (i.e. small $\overline{v}^0_2$) and they may be conveyed quicker by water to deeper layers of the taste epithelium than are sugar molecules.

For a molecule to elicit a particular basic taste it must first accede to an appropriate region and, secondly, must possess an appropriate structural ‘sapophore’. Molecules possessing more than one basic taste are known as multisapophoric molecules. For example, many sugar derivatives are bitter–sweet and their $\overline{v}^0_2$ fall neatly in the border region between the basic tastes, at ca. 0.7 cm^3 g^{-1} (Birch & Shamil, 1988).

Table 4
Taste quality and apparent specific volume, $\overline{v}^0_2$ (Shamil et al., 1987)

Taste quality	$\overline{v}^0_2$ (cm^3 g^{-1})
Salty	0.33
Sour	0.33–0.52
Sweet	0.52–0.71
Bitter	0.71–0.93

For intense sweeteners (sweet–bitter molecules), a wide range of $\overline{v}^0_2$ was reported by Parke, Birch, and Dijk (1999), e.g. from 0.53 cm^3 g^{-1} (acesulfame K) to 0.72 cm^3 g^{-1} (aspartame) or 0.88 cm^3 g^{-1} (ethylene glycol). Similarly, the investigated cyclohexylsulfamates cover a wider range of $\overline{v}^0_2$, between values reported for sweet and for bitter molecules (Table 3). In general, which sapophores on the molecule will govern its taste properties mainly depend on the hydrophilic–hydrophobic balance of the molecules; the hydrophobic side of the sweet molecule repels water molecules, the hydrophilic (AH-B) side attracts them. This contributes to the change in distribution of hydrogen bonding in the bulk water whose mobility is increased. Increasing the mobility of water leads to rupture of the iso-osmotic equlibrium between saliva and intracellular serum on the two sides of the receptor membrane, which results in a more active Na^+/K^+ transfer and consequently a more intense sweet taste (Kobatake, Kurihara, & Kamo, 1978; Mathlouthi et al., 1993).

Most intense sweeteners, including cyclohexylsulfamates, 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, McHale, Birch, and Rathbone (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 intense sweeteners; e.g. for the hydrophobic saccharinic ion (sodium saccharin is 99.9% dissociated in water) $\overline{v}^0_2$ was calculated to be 0.67 cm^3 g^{-1}, a value that is close to the bitter end of the $\overline{v}^0_2$ taste quality range, so we would expect the molecule to taste bitter (Parke & Birch, 1999). Because we found the value of $\overline{v}^0_2$ for the cyclohexylsulfamic anion to be 0.722 cm^3 g^{-1} we would expect the molecule to taste even more bitter. However, the cation (e.g. Na^+ or strongly positively charged Ca^{2+}) that makes a negative contribution to $\overline{v}^0_2$, brings the value down. In contrast, $\overline{v}^0_2$ of $(CH_3)_4NCy$ is 0.845 g cm^{-3}. According to the theory of Birch, Lee, and Ray (1977) multisapophoric molecules, e.g. sweet–bitter ones, may be ‘polarised’ on taste receptors meaning that the hydrophilic/hydrophobic molecule attaches itself to the sweet and bitter receptor sites simultaneously. 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, which means that the cyclohexylsulfamic anion, as concerns its hydrophobic and polar structural features and dimensions, fits this location very well, and is able to span both types of receptor simultaneously.

Fig. 4 shows the relationship between the molecular weight of some taste solutes (sweet–bitter) and their

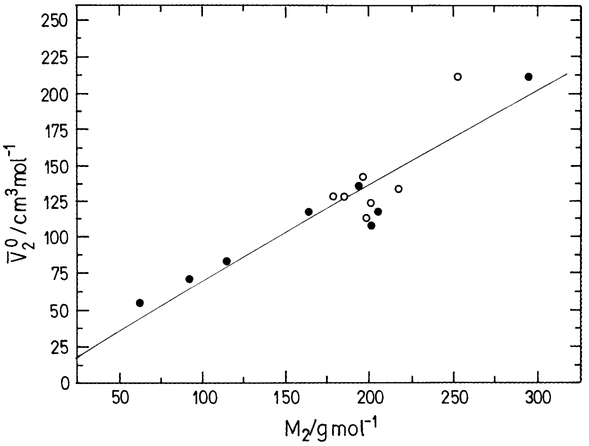

Fig. 4. Plot of apparent molar volume against molecular weight (●, Parke et al., 1999, Table 1, all sweet–bitter substances, ○, investigated cyclohexylsulfamates).

apparent molar volumes. As expected, apparent molar volumes increase with increasing molecular weight and a plot of all tested substances, i.e. of the investigated cyclohexylsulfamates and those taken from the literature (Parke et al., 1999, Table 1, all sweet–bitter substances), shows good correlation, with the correlation coefficient $r = 0.911$. The range of apparent specific volumes reported in the literature and in our experiment are from 0.53 to 0.88 cm^3 g^{-1} for sweet–bitter substances. Therefore one can conclude that investigated cyclohexylsulfamates broadly fit this category of substances.

From the results obtained it is suggested that cyclohexylsulfamates, as salts which are completely dissociated in solution, exhibit their volumetric properties (e.g. limiting apparent molar volume and apparent specific volume) as a sum of the contributions of two components, the anion and the cation, i.e. anion–solvent and cation–solvent interactions. The cyclohexylsulfamate anion is less hydrated than its cations and its hydrophobicity seems to predominate in its intrinsic hydrophilic/hydrophobic balance. It seems 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 of the anion. Thus, the result for the solute as a whole depends on the cation (its charge, charge density and character) which can cause a possible negative or even great positive effect on the apparent specific volume. The above study helps to illuminate how volumetric properties can be used to predict the qualitative effect of intense ionic sweeteners.

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