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Apparent specific volumes and tastes of cyclamates, other sulfamates, saccharins and acesulfame sweeteners

Gordon G. Birch[a], Kieran A. Haywood[a], Gary G. Hanniffy[b], Catherine M. Coyle[b], Wm. J. Spillane[b,*]

[a]*School of Food Biosciences, The University of Reading, UK*
[b]*Department of Chemistry, National University of Ireland, Galway, Ireland*

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Abstract

Measurements of apparent specific volume (ASV) for a series of alternative sweeteners (cyclamates, sulfamates, saccharins, acesulfames and anilinomethanesulfonates) have been made. Taste data have been obtained for many of the new compounds unless the toxicity of the associated metals precluded this. Apparent molar volume (AMV), isentropic specific (IASC) and isentropic molar (IAMC) compressibilities were also measured. Sixteen metallic cyclamates cyc-$C_6H_{11}NHSO_3M$ and two phenylsulfamates $ArNHSO_3Na$, namely 3,5-dimethyl- and 3,4-dimethoxyphenylsulfamates have been examined. When the ASVs for these are combined with those for 15 aliphatic, aromatic and alicyclic sulfamates from a previous study, many of the values are seen to fall into the region that was previously identified as being the "sweet area", i.e. the ASVs lay between ~0.5 and ~0.7 (a few sweet compounds fall below this range and it is suggested that it could be extended slightly to accommodate these). Interestingly, the anilinomethanesulfonates, $ArNHCH_2SO_3Na$ (Ar = C_6H_5-, 3-MeC_6H_4- and 3-ClC_6H_4-) lie clearly in the sweet region but only one of them shows slight sweetness showing that the molecular structural change made (compared with the 'parent' sulfamate–$NHSO_3^-$) cannot be accommodated at the receptor site.

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1. Introduction

Cyclamate (cyc-$C_6H_{11}NHSO_3M$) sweeteners continue to attract interest for many reasons, not least being that the sodium (M = Na) and the calcium (M = Ca) salts and N-cyclohexylsulfamic acid (cyclamic acid) (M = H) are permitted in the EU (European Parliament and Council, 1994) and very many countries. They display good synergy (Nahon, Roozen, & de Graaf, 1998), are relatively inexpensive to produce (Sugden & Jolliffe, 1994) and have a number of other important qualities (Bopp & Price, 2001, chap. 9).

Over some years, the importance of the experimentally determined property apparent specific volume (ASV) as an index of taste modality, i.e. salty, sweet, bitter and sour and even of taste acceptability, has been developed (Parke, Birch & Dijk, 1999; Shamil & Birch, 1990). Sweetness is likely to occur for compounds that have ASVs in the range of ~0.5 to ~0.7 $cm^3\ g^{-1}$ and sugars, having the purest form of sweetness, fall in the middle of this range. Interestingly the only permitted alternative sweetener with an ASV value very close to the sugars is sodium cyclamate, with a value of 0.612 (Spillane, Morini, & Birch, 1992). Partly because of this, ASV values were measured for fifteen other sweet organic sulfamates and some of these are quite close to 0.61 (Spillane et al., 1992).

In this current work, we have extended our studies of ASV values for alternative sweeteners by measuring this property for fifteen other metallic cyclamates (various Ms), two sodium phenylsulfamates, namely, 3,5-dimethylphenylsulfamate, 3,5-diMe$C_6H_3NHSO_3Na$ and 3,4-dimethoxyphenylsulfamate, 3,4-diMeO$C_6H_3NHSO_3Na$, three anilinomethanesulfonates, $ArNHCH_2SO_3Na$, a

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* Corresponding Author. Tel.: +353-91-750428; fax: +353-91-525700.

E-mail addresses: kieranhaywood@onetel.net.uk (K.A. Haywood), gary.hanniffy@nuigalway.ie (G.G. Hanniffy), coyle_kate@hotmail.com (C.M. Coyle), william.spillane@nuigalway.ie (W..J. Spillane).

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few saccharins and sodium acesulfame. Taste data have been obtained where possible but the toxicity of some metals has precluded a taste assessment of some of the metallic cyclamates. Taste data have also been obtained for the phenylsulfamates, the anilinomethanesulfonates and for the saccharins.

2. Materials and methods

2.1. Materials

Sodium saccharin, acesulfame-K, sucrose, sodium cyclamate, aniline, 3-toluidine, 3-chloroaniline, N-cyclohexylsulfamic acid, formaldehyde bisulfite and the following hydroxides: magnesium, ammonium, calcium, potassium, sodium, caesium, barium, strontium, rubidium and aluminium, were obtained commercially.

2.2. Synthesis

2.2.1. Metallic hydroxides

Metallic hydroxides that were not available were made by reaction of the appropriate salt with sodium hydroxide, e.g.

$$\mathrm{ZnCl_2 + 2NaOH \rightarrow Zn(OH)_2{+}2NaCl}$$

Other chlorides used to synthesise hydroxides were $CuCl_2$ and $CoCl_2$.

2.2.2. Metallic cyclamates and saccharins

The metallic cyclamates (Table 1) and saccharins (Table 2) were made by titration of cyclamic acid or saccharin using the appropriate hydroxide; e.g. magnesium cyclamate was prepared as follows:

$$\mathrm{2cyc\text{-}C_6H_{11}NHSO_3H + Mg(OH)_2}$$
$$\mathrm{\rightarrow (cyc\text{-}C_6H_{11}NHSO_3)_2Mg + 2H_2O}$$

Thallium cyclamate was made from thallium ethoxide and cyclamic acid:

$$\mathrm{TlOEt + cyc\text{-}C_6H_{11}NHSO_3H}$$
$$\mathrm{\rightarrow cyc\text{-}C_6H_{11}NHSO_3Tl + EtOH}$$

The salts were recrystallised from aqueous ethanol and thoroughly dried *in vacuo* over phosphorus pentoxide. The IR, ^1H and ^{13}C NMR spectra were all consistent with the expected structures. Microanalytical (C,H & N) results for the compounds were all within ±0.5 except for $(cyc\text{-}C_6H_{11}NHSO_3)_2Zn.2H_2O$ which had C theory, 31.48 and found, 30.94. The yields of the pure metallic cyclamate salts varied from 11 to 82%, with an average of 52%. The yields of the saccharins varied from 32 to 54%.

2.2.3. Sodium anilinomethanesulfonates

Amines and reagents were distilled/recrystallised before use and dried. The anilinomethanesulfonates were synthesised by mixing formaldehyde bisulfite and the respective amine as outlined previously (Neelakantan & Hartung, 1959). ^1H and ^{13}C NMR spectra of the three compounds were consistent with the expected structures. Microanalytical (C,H & N) results were within ±0.5 of calculated percentages. The yields of pure sodium salts varied from 16 to 46%.

2.3. Apparent specific volume measurements

These were carried out using an Anton Parr precision density meter, as previously described (Birch & Catsoulis, 1985; Spillane et al., 1992). All measurements were carried out at 20±0.1 °C and the concentrations used, that depended on the solubility of the salts, are given in Tables 1 and 2. Isentropic apparent compressibilites, $K_{\phi(S)}$, cm^3 mol^{-1} bar^{-1} were obtained using the same instrument. Initially apparent specific volume measurements were made on sodium saccharin, acesulfame-K,

Table 1
Apparent molar and specific volumes and apparent molar and specific isentropic compressibilities for metallic cyclamates

Compound No.	M +[a]	%Conc (w/w)	AMV[b]	ASV[c]	IAMC[d]	IASC[e]
1	Mg^{2+}	0.69[g]	226	0.593	−0.0149	−4.06
2	NH_4^+	6.38	142	0.725	−0.0038	−1.93
3	H^+	13.64	107	0.595	−0.0002	−1.24[f]
4	Li^+	12.43[h]	123	0.666	−0.0050	−2.70
5	Ca^{2+}	12.5[g]	220	0.555	−0.0127	−3.19
6	K^+	3.09	134	0.615	−0.0064	−2.96
7	Na^+	13.64	123	0.612	−0.0055	−2.74
8	Cs^+	13.64	160	0.515	−0.003	−9.66
9	Ba^{2+}	2.88[g]	196	0.398	−0.0211	−4.28
10	Sr^{2+}	12.61[g]	210	0.473	−0.0034	−7.73
11	Rb^+	6.38	138	0.525	−0.0057	−2.17
12	Tl^+	1.01	132	0.344	−0.0074	−1.94
13	Al^{3+}	11.11	399	0.711	−0.0033	−6.33[f]
14	Zn^{2+}	0.4[g]	222	0.526	−0.0161	−3.82
15	Cu^{2+}	11.16[h]	247	0.588	−0.0091	−2.09
16	Co^{2+}	6.42[g]	226	0.545	−0.1358	−3.27

[a] M in $cyc\text{-}C_6H_{11}NHSO_3M$.

[b] Apparent molar volume (ϕ_v, cm^3 mol^{-1}).

[c] Apparent specific volume (ASV, cm^3 g^{-1}).

[d] Apparent molar isentropic compressibility ($K_{\phi(s)}$, cm^3 mol^{-1} bar^{-1}).

[e] Apparent specific isentropic compressibility ($K_{2(s)}$, cm^3 g^{-1} bar^{-1}), the values given are IASC×10^5.

[f] Values are for IASC×10^6.

[g] Compound has two molecules of water of hydration.

[h] Compound has one molecule of water of hydration.

Table 2
Apparent molar and specific volumes and apparent molar and specific isentropic compressibilities for test compounds, sulfamates, anilinomethanesulfonates, saccharins and sodium acesulfame

Compound No.	Name	%Conc (w/w)	AMV[a]	ASV[b]	IAMC[c]	IASC[d]
–	Sodium saccharin[f]	1.52	123	0.599	−0.0026	−1.24
–	Acesulfame-K	11.11	108	0.538	−0.002	−9.93[e]
–	Sucrose	11.11	111	0.615	−0.0009	−4.78[e]
17	3,5-Dimethylphenylsulfamate[g]	5.29	141	0.630	−0.0056	−2.56
18	3,4-Dimethoxyphenylsulfamate[h]	11.29	151	0.591	−0.0045	−1.81
19	Anilinomethanesulfonate[g]	11.21	124	0.591	−0.0047	−2.20
20	3-Tolylmethanesulfonate[g]	5.29	135	0.603	−0.0061	−2.76
21	3-Chloroanilinomethanesulfonate[g]	1.2	134	0.552	−0.0051	−2.00
–	Potassium saccharin[i]	0.6	129	0.584	0.1933	87.38
–	Magnesium saccharin[g]	0.6	266	0.685	0.0018	4.36[e]
–	Sodium acesulfame[g]	11.23	86	0.465	−0.0047	−2.56

[a] Apparent molar volume (ϕ_v, cm^3 mol^{-1}).
[b] Apparent specific volume (ASV, cm^3 g^{-1}).
[c] Apparent molar isentropic compressibility ($K_{\phi(s)}$, cm^3 mol^{-1} bar^{-1}).
[d] Apparent specific isentropic compressibility ($K_{2(s)}$, cm^3 g^{-1} bar^{-1}), the values given are IASC×10^5.
[e] Values are for IASC×10^6.
[f] Compound has 0.5 of a molecule of water of hydration.
[g] Compound has one molecule of water of hydration.
[h] Compound has two molecules of water of hydration.
[i] Compound has 0.25 of a molecule of water of hydration.

sucrose and sodium cyclamate to check and validify our method and in particular to compare our present measurements with those previously recorded in the literature [Mathlouthi, Bressan, Portmann & Serghat, (1993, chap. 9), Parke et al., (1999)]. The measurements recorded in Table 3 were carried out some years ago (Spillane et al., 1992).

2.4. Taste panel procedures

The procedures and methodology of the tasting were identical to that previously described (Spillane, Feeney, & Coyle, 2002). The same standards as before were used and in addition, for the tasting of all cyclamates and sulfamates, a 0.01 M (0.2% w/w) solution of sodium cyclamate (pH 5.62) was used. The number of panellists used for each tasting is indicated in Table 4. pH Measurements were made using an Orion 210A pH meter, buffered at 4.0, 7.0 and 9.2.

3. Results and discussion

Before commencing the ASV and related measurements, a series of test measurements were first carried out. For these we used the well-known sweeteners, sodium saccharin, acesulfame-K, sucrose and sodium cyclamate and the agreement between the ASV values measured in this work and those determined previously was very good. The results were as follows: compound, present ASV (Table 2), previous ASV (reference): sodium saccharin, 0.599 (Table 2), 0.57 (Parke et al., 1999) ; acesulfame-K, 0.538 (Table 2), 0.533, (Parke et al., 1999) ; sucrose, 0.615 (Table 2), 0.616 (Parke et al., 1999) ; sodium cyclamate, 0.612 (compound 7, Table 1), 0.610 (compound 7, Table 3), (Spillane et al., 1992).

Table 1 contains results for a series of sixteen metallic cyclamates, cyc-$C_6H_{11}NHSO_3M$. Many of these are new compounds. Taste data are available for compounds **2**, **5**, **6** and **7** and, in fact, some years ago relative sweetness (RS) was determined in water using 3% sucrose as standard for these four compounds. The RS was ∼39.5 for each of these and thus the cation M^+ did

Table 3
Apparent molar and specific volumes of organic sulfamates

Compound No.	R[a]	AMV[b]	ASV[c]
22	C_6H_5-	104	0.531
23	3-MeC_6H_4-	124	0.593
24	3-FC_6H_4-	99.0	0.466
25	3-ClC_6H_4-	121	0.525
26	3-BrC_6H_4-	120	0.439
27	4-BrC_6H_4-	124	0.451
28	exo-norbornyl-	127	0.596
29	endo-norbornyl-	123	0.578
30	cyc-octyl-	143	0.625
31	cyc-heptyl-	134	0.624
7[d]	cyc-hexyl-	123	0.610
32	cyc-pentyl-	108	0.578
33	*n*-propyl-	88.0	0.544
34	*n*-butyl-	107	0.610
35	iso-butyl-	108	0.616
36	iso-pentyl-	119	0.630

[a] R in $RNHSO_3Na$. Measurements were made using 5% (w/w) solutions of sodium salt in H_2O.
[b] Apparent molar volume (ϕ_v, cm^3 mol^{-1}).
[c] Apparent specific volume (ASV, cm^3 g^{-1}).
[d] See Table 1 for the value determined in this work.

Table 4
Percentage of assessors giving the taste quality[a] of compounds

Compound[b]	pH	No. of assessors	Sweet	Sour	Salt	Bitter	Tasteless	Predominant taste (⩾50% assessors)
1	5.2	8	100	0	0	0	0	Sweet
4	4.9	7	86	0	0	0	14	Sweet
13	2.0	7	100	29	0	14	0	Sweet
14	5.9	8	100	0	0	0	0	Sweet
19	6.2	8	0	0	0	75	0	Bitter
20	6.4	8	25	12.5	0	62.5	25	Bitter
21	5.1	8	12.5	12.5	12.5	62.5	12.5	Bitter
K Saccharin	3.1	8	87.5	0	0	12.5	0	Sweet
Mg Saccharin	2.8	8	100	12.5	0	0	0	Sweet

[a] All compounds with one exception were tasted as 0.01 M solutions made in distilled water of pH varying from 5.7 to 5.9. Magnesium saccharin was tasted at 0.005 M due to solubility difficulties.

[b] Barium cyclamate i.e. compound **9** was tasted by two assessors both found it to be intensely sweet.

not affect the degree of sweetness (Spillane, Ryder, Walsh, Curran, Concagh, & Wall, 1996). In the seminal work of Audrieth and Sveda (1944), they report that compounds **2** and **7** and the silver and cyclohexylammonium salts of cyclamate have a marked sweetness. Compound **3** (cyclamic acid) was said to possess "a lemon sour sweetness". Reported toxicity of some metals precluded taste studies of most of the other compounds in Table 1 but some taste data have been obtained. We have found that compounds **1**, **13** and **14** are intensely sweet with a very strong fruity flavour being observed in **1** and **13**. Compound **4** was found to be quite sweet too and was very comparable in taste and degree of sweetness to the standard sodium cyclamate used.

The phenylsulfamates, **17** and **18**, have been tasted in earlier work and were found to be "bitter but with a definite sweet aftertaste" (Spillane, Sheahan, & Ryder, 1993). The three anilinomethanesulfonates, **19**–**21**, have been tasted in this work and were found to be generally bitter; however, compound **20** was found to have some sweetness. Both magnesium and potassium saccharins were found to be intensely sweet and similar to sodium saccharin. Sodium acesulfame (and incidentally calcium acesulfame) are reported to have the same RS as acesulfame-K, i.e. 130, using 4% sucrose as standard (Clauss & Jensen, 1973).

For all but two of the compounds in Table 3, we have determined RS data some years ago. The RS data for compounds **23**–**26** are in Spillane, Sheahan, Simmie, Cunningham, McArdle, and Higgins (1989), for **28** and **29** in Drew, Wilden, Spillane, Walsh, Ryder, and Simmie (1998) while for substances **30**–**35** (Benson & Spillane, 1976) and for **36** in Benson (1976). The remaining two compounds, labeled **22** and **27** in Table 3, have also been tasted but RS data were not obtained. Compound **22** has been described (Audrieth & Sveda, 1944) as having a "sweet aftertaste" but a recent reassessment indicates that its sweetness is very intense and rather immediate (Spillane et al., 2002). Compound **27** is the odd one in the table being bitter with a sweet aftertaste (Spillane, Ryder & Sheahan, 1994).

In Fig. 1 there is a schematic representation of all 16 ASV values for the cyclamate salts in Table 1. All the salts more or less lie in the region previously delineated for sweetness i.e. ~0.5 to ~0.7 $\text{cm}^3\ \text{g}^{-1}$ ASV values (Parke et al., 1999; Shamil & Birch, 1990). Product **9**, which is intensely sweet, surprisingly falls outside this region, as do **10** and **12**. Of course, in the case of the latter two compounds we cannot say whether or not they are sweet since tasting has not been possible. It should be noted that **9** and **12** were measured at very low concentrations, as were those labeled **1** and **14** (see Table 1). These results are therefore of questionable accuracy. For the same reason, the measurements on the three saccharins (Table 2) may be slightly in error. This problem does not arise with the data in Table 3 since it was possible to carry out all measurements at 5% (w/w) of the sodium sulfamate. The concentration at which the ASV measurements were made varied considerably due to the differing solubilities of the salts under study in water and this is particularly noticeable with compounds **1** and **4** (Table 1) compared with the other metallic cyclamates. Though a recent study of the effect of varying concentration on ASV values has shown that, for sodium cyclamate, sodium saccharin and acesulfame-K over the range ~1 to ~10% (w/w), the ASV values for each of these compounds remains virtually unchanged (Giraud, 2001). However, measurements of ASV at very low concentrations are not seen as being as reliable as those carried out at higher concentrations.

We calculated charge densities for the 16 cations in Table 1 using the equation (Marcus, 1997)

$$\text{Charge density} = \text{ionic charge}/4\pi r^2$$

and found that plots of charge density vs. Apparent Molar Volume (AMV), ASV, Isentropic Apparent Molar Compressibility (IAMC) and Isentropic

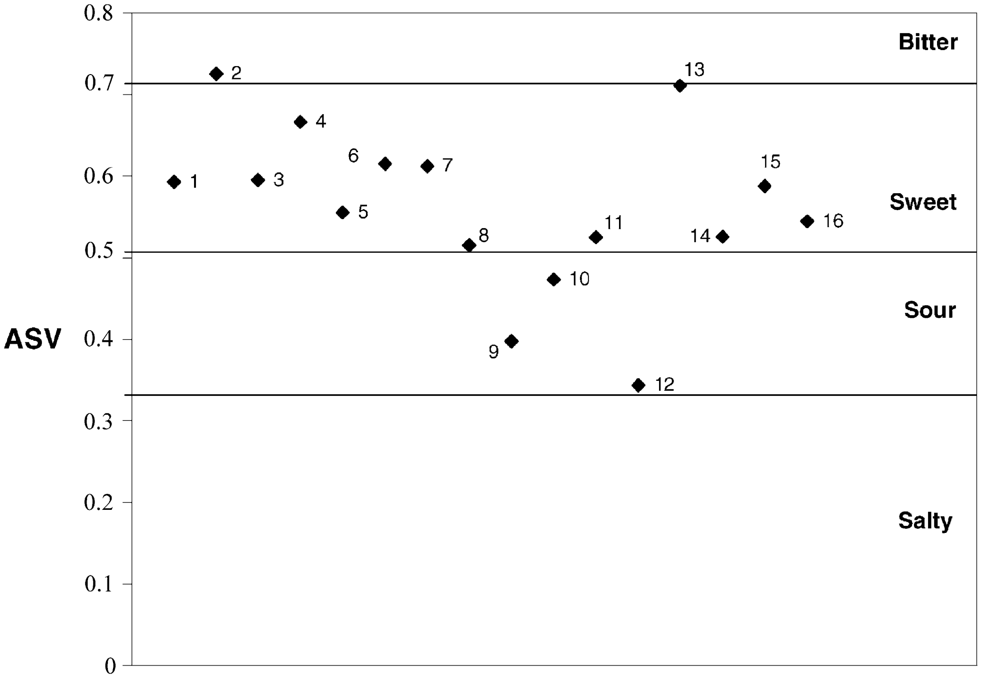

Fig. 1. Apparent specific volumes (ASVs) for 16 metallic cyclamates, cyc-$C_6H_{11}NHSO_3M$ schematically represented (Table 1 data).

Apparent Specific Compressibilty (IASC) showed no correlations.

It seems that the relationship between these parameters is not altogether clear and their interplay with other important solution effects, such as water mobility needs to be invoked for a full interpretation of taste quality (Aroulmoji, Mathlouthi, & Birch, 2000).

The results in Tables 1–3 neatly accord with previous reports (Parke et al., 1999; Shamil, Birch, Mathlouthi, & Clifford, 1987) of apparent specific volume as a predictor of taste quality in so far as sensory data are obtainable. It is noteworthy that among the metallic cyclamates and sodium sulfamates tasted not one compound has a low enough ASV to fall within the "salty range" and indeed, not one displays a salty taste. Most show sweetness in accordance with the ASV value and those that fall below the sweetness range (~0.51 to ~0.71 $cm^3\ g^{-1}$) do not possess an acidophore and therefore do not display a sour taste (range ~0.31 to ~0.51 $cm^3\ g^{-1}$). Compounds **2** and **13** (Table 1, Fig. 1) reach the bitter range and, in fact, **3** is close in ASV value to the borderline and displays both sweet and bitter tastes (Table 4). Its anomalously low pH and sour taste are hard to explain. Compounds **19**–**21** have ASV values within the sweet range (central region). Two of these (**20** and **21**) do show some sweetness but all three are predominantly bitter. These exceptions to the general rule must be attributable to the molecular structure, of these derivatives that embody a powerful "picrophore". If, as was originally hypothesized by Shamil et al. (1987), stimuli molecules must pass through shallow epithelial layers where bitter receptors are located to reach deeper sweet receptors then some powerful picophores might easily activate bitter receptors enroute. Cations generally make marked negative contributions to apparent specific volume, which can have a beneficial taste modulation effect which is useful in the food industry (Birch, 1999). The metallic cyclamates are particularly useful in this respect for accurate comparisons of volume contributions in relation to taste quality. Among the cations depicted in Table 1, only K^+, Rb^+ and Cs^+ make positive contributions to apparent specific volume (Marcus, 1997). Despite this difference, all the salts fall within the sweet range.

The compressibilities (IAMC, IASC) shown in the tables represent the compactness of the hydration layers around the ions. Compressibilities are related to ASV values, which show how well molecules pack into water structure. For any one solute, an increase in concentration will generally cause an increase of compressibility. However, for the 16 compounds in Table 1 a plot of IAMC, $K_{\phi\ (s)}$ vs. apparent molar volume (AMV) did not show any correlation.

Table 3 contains data that were determined some years ago for 16 mainly intensely sweet sulfamates (Spillane et al., 1992). When these data, together with all the data from Table 1 for the metallic cyclamates and the data for the sodium phenylsulfamates (**17** and **18**, Table 2) and the sodium anilinomethanesulfonates (**19**–**21**, Table 2) are presented schematically in Fig. 2 it is clear that the majority of the compounds fall in the sweet region. The deviation of compound **9**, and prob-

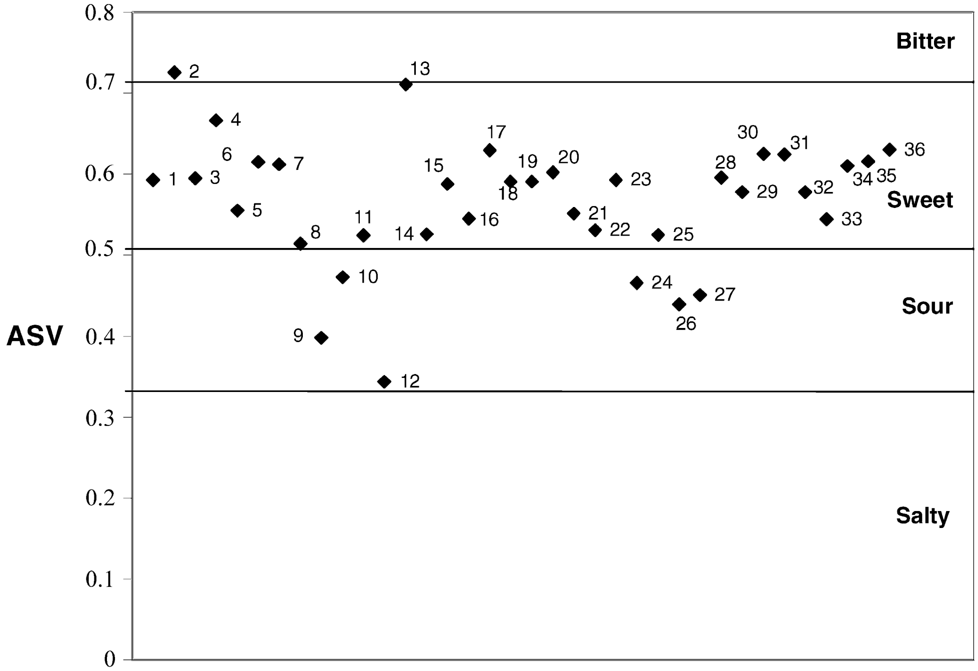

Fig. 2. Apparent specific volumes (ASVs) for 16 metallic cyclamates cyc-$C_6H_{11}NHSO_3M$ (compounds **1**–**16**, Table 1), sodium sulfamates (**17** and **18**, Table 2), sodium anilinomethanesulfonates (**19**, **20** and **21**, Table 2) and fifteen sulfamates (**23**–**36**, Table 3) schematically represented.

ably compounds **10** and **12** has been mentioned above. Compound **27** has been reported to be 75% bitter, 25% sweet and 50% sweet aftertaste so that the predominant taste ($\geqslant$50% assessors) was “bitter with a sweet aftertaste”. Some deviation of this compound might therefore be expected though one would have thought that it might have moved slightly into the bitter region rather than the sour one. The deviation of compounds **24** and **26** is surprising, especially since the closely related aromatic compounds, **23** and **25**, are clearly in the sweet region. These deviations, coupled with the deviation of sodium acesulfame (ASV = 0.465), may suggest that the sweet region should be extended somewhat to embrace alternative sweeteners.

Alternatively, some of the newer approaches to sweet taste chemoreception (e.g. involving the symmetry of the tastant molecule in relation to the chirality of the sweet receptor, or the surface properties of the tastants) may need to be invoked (Mathlouthi & Hutteau, 1999; Shallenberger, 1992, chap. 5; 1993). Indeed the disturbance of water structure by the cations involved in this study may be expected to exert a profound effect on mobility at the level of the receptor.

The sodium anilinomethanesulfonates have ASVs in the sweet region but, interestingly, taste data indicate that they are not sweet, except for some sweetness in compound **20**, thus showing that, although the ASV values of the three compounds are ideal for sweetness, the molecular structural change (compared to the parent-$NHSO_3^-$ moiety) cannot be accommodated at the sweet receptor site.

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