

# Apparent Molar Volume and Apparent Molar Expansibility of Sodium Saccharin, Potassium Acesulfame and Aspartame<sup>†</sup>

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## Abstract

The apparent molar volume of sodium saccharin, potassium acesulfame and aspartame was determined from the density data of their aqueous solutions at 293.15, 298.15, 303.15, 313.15, 323.15 and 333.15 K. Solutions of sodium saccharin and potassium acesulfame were treated as 1:1 strong electrolyte, while aspartame was considered as a non-electrolyte. From the apparent molar volume, determined at various temperatures, the limiting apparent molar expansibility was calculated. The limiting apparent molar volume and expansibility of ionic solutes were divided into their ionic components and discussed in terms of the various effects of the ion in solution on the structure of water. The limiting apparent molar volume of aspartame was discussed in terms of the scaled particle theory. The density of the investigated aqueous solutions can be adequately represented by an equation derived by Redlich. The coefficients of thermal expansion of the investigated solutions at 298.15 K were calculated and are presented graphically. The thermal expansion coefficient,  $\alpha^*$  defined as  $\alpha^* = 1/V_{2,\phi}^0 (\partial V_{2,\phi}^0 / \partial T)_p$  and their temperature dependence was estimated. It was shown that  $\alpha^*$  of electrolyte solutes is greater than that of aspartame and that  $\alpha^*$  of ionic solutes decreases linearly with increasing temperature, while  $\alpha^*$  of aspartame shows a slight increase with temperature. The limiting apparent molar volume and expansibility were correlated with the relative sweetness of the sweeteners investigated and some other alternatives.

**Key words:** density data, expansibility, sweeteners, aqueous solutions

## 1. Introduction

The volumetric behaviour of electrolyte and non-electrolyte solutions can provide useful information regarding solute-solvent and solute-solute interactions. Of particular relevance is the nature of the interactions of water with solute species, especially with ions possessing non-polar groups which effect the structural properties of water. Therefore the apparent and partial molar volumes and expansibilities of solute have proven to be very useful tools in elucidating the structural interactions occurring in solution, e. g.<sup>1,2</sup>

Among many sweeteners currently approved as food additives, sodium saccharin, saccharin-Na (2,3-dihydroxo-3-oxobenzisulfonazole-Na salt), potassium acesulfame, acesulfame-K (6-methyl-1,2,3-oxathiazine-4-(3H)-one-2,2-dioxide-K salt) and aspartame (*N*-L- $\alpha$ -aspartyl-L-phenylalaline-1-methyl ester) have received wide commercial use in the food industry.<sup>3</sup> The alkali salts of saccharin are of special interest because of their pronounced solubility in water in comparison with saccharin. From the structural point of view,

the saccharin nitranion has attracted appreciable scientific attention. Both nitranions of saccharin and acesulfame feature the sulfocarboximide moiety and thus three different groups, imino, sulfonyl and carbonyl, connected to each other.

Aspartame, as dipeptide, contains structural elements such as a peptide bond, a charged zwitterionic group, a phenyl and an acetyl group which interact with water in different fashions. Therefore, the interactions of nitranions of saccharin and acesulfame and the molecule of aspartame with water molecules proceed as a subtle balance between the hydrophobic and hydrophilic characteristics of the mentioned groups.

The partial molar and apparent specific volumes of various solutes have been used in assessing drug potency and in sweet taste chemoreception. In the past volumetric parameters were measured especially as a parameter to describe solute-water interactions in sweet-taste chemoreception. These results are limited to two temperatures, namely at 293.15 and 298.15 K and at a definite concentration.<sup>4-10</sup> In this paper we report results of the experimental determination of

the apparent molar volumes and expansibilities of saccharin-Na, acesulfame-K and aspartame over a broad range of concentration and in the temperature range from 293.15 to 333.15 K. Aqueous solutions of saccharin-Na and acesulfame-K were treated as 1:1 electrolyte solutions, while aqueous solution of aspartame as a non-electrolyte solution, despite the fact that aspartame exists as a dipolar ion.<sup>11–13</sup>

## 2. Results and Discussion

The values of density,  $d(\text{g}\cdot\text{cm}^{-3})$ , measured at various temperatures as a function of molality,  $m(\text{mol}\cdot\text{kg}^{-1})$ , are given in Table 1. The apparent molar volume,  $V_{2,\Phi}(\text{cm}^3\cdot\text{mol}^{-1})$ , of a solute with molar mass,  $M_2(\text{g}\cdot\text{mol}^{-1})$ , is given by<sup>14</sup>

$$V_{2,\Phi} = \frac{10^3(d_0 - d)}{cd_0} + \frac{M_2}{d_0} \quad (1)$$

where  $d_0$  is the density of pure water ( $\text{g}\cdot\text{cm}^{-3}$ ) and  $c$  is the molarity ( $\text{mol}\cdot\text{L}^{-1}$ ). In calculation of the probable error in the apparent molar volume,  $\delta V_{2,\Phi}$ , only the uncertainty due to density measurement,  $(\delta V_{2,\Phi})_d$  was taken into account, using the relation

$$(\delta V_{2,\Phi})_d^2 = \left( -\frac{10^3}{cd_0} \right)^2 (\delta d)^2 \quad (2)$$

since  $\delta V_{2,\Phi}$  is not seriously influenced by errors in molarity.<sup>14</sup> The probable error of  $\delta V_{2,\Phi}$  amounts at the lowest concentrations studied to 0.08, 0.20 and 2.0  $\text{cm}^3\cdot\text{mol}^{-1}$ , while at the highest concentrations these values are 0.04, 0.013 and 0.286  $\text{cm}^3\cdot\text{mol}^{-1}$  for saccharin-Na, acesulfame-K and aspartame, respectively. Due to the low solubility of aspartame its  $(\delta V_{2,\Phi})_d$  values are much higher than for other two solutes.

The dependence of  $\delta V_{2,\Phi}$  on molarity at a definite temperature was fitted for saccharin-Na and acesulfame-K with an equation of the type<sup>15</sup>

$$V_{2,\Phi} = V_{2,\Phi}^0 + A_v c^{1/2} + B_v c + D_v c^{3/2} \quad (3)$$

which is typical of an electrolyte.

The relation (3) represents the apparent molar volume at infinite dilution, equal to the limiting partial molar volume of solute,  $V_2^0(\text{cm}^3\cdot\text{mol}^{-1})$ ,  $A_v(\text{cm}^3\cdot\text{L}^{1/2}\cdot\text{mol}^{-3/2})$  is the Debye-Hückel limiting slope for the apparent molar volume, and  $B_v$  and  $D_v$  are empirical constants which depend on solute, solvent and temperature. The experimental values of  $V_{2,\Phi}$  of acesulfame-K can be adequately represented without parameter  $D_v$ . In calculation of the parameters of Eq. (3), the coefficient  $A_v$ , taken from ref.<sup>16</sup>, was divided by the square root of

the density of pure water at the desired temperature.<sup>17</sup> The experimental  $V_{2,\Phi}$  values of aspartame were treated as those of a non-electrolyte using the relation

$$V_{2,\Phi} = V_{2,\Phi}^0 + B_v c \quad (4)$$

The regression values of the parameters of Eqs. (3) and (4), together with the standard error of the estimation,  $s$ , are given in Table 2. The values of the parameters of Eqs. (3) and (4) obtained were tested by a Redlich equation of the type<sup>18</sup>

$$d = d_0 + \left[ \frac{(M_2 - V_{2,\Phi}^0 d_0)}{1000} \right] c - \left( \frac{A_v d_0}{1000} \right) c^{3/2} - \left( \frac{B_v d_0}{1000} \right) c^2 - \left( \frac{D_v d_0}{1000} \right) c^{5/2} \quad (5)$$

for saccharin-Na, and without the last term for acesulfame-K. A similar equation to Eq. (5) can be obtained for a non-electrolyte, taken into account relations (4) and (1)

$$d = d_0 + \left[ \frac{(M_2 - V_{2,\Phi}^0 d_0)}{1000} \right] c - \left( \frac{B_v d_0}{1000} \right) c^2 \quad (6)$$

The calculated density, using the relations (5) and (6), are within  $2.1 \times 10^{-5}$ ,  $1.2 \times 10^{-5}$  and  $0.5 \times 10^{-5}$   $\text{g}\cdot\text{cm}^{-3}$  equal to the experimental values given in Table 1 for saccharin-Na, acesulfame-K and aspartame, respectively.

The apparent molar volume or the apparent specific volume of the investigated compounds have also been measured previously, e. g.<sup>4–10</sup> However, these results are confined to only two temperatures, namely 293.15 and 298.15 K, and at infinite dilution or at a specific concentration. Comparison of the apparent molar volumes at 293.15 and 298.15 K obtained in this work with those reported in the literature is shown in Table 3. Our values were calculated using relation (3) or (4) and the appropriate parameters from Table 2. The difference between the literature values of  $V_{2,\Phi}$  for acesulfame-K and ours is reasonable; and the differences for aspartame are more or less satisfactory, occasionally exceeding 2–3  $\text{cm}^3\cdot\text{mol}^{-1}$ . There are also great differences within the literature data for aspartame, e. g. between 206.04<sup>4</sup> and 212.46  $\text{cm}^3\cdot\text{mol}^{-1}$ .<sup>6</sup> The published data for  $V_{2,\Phi}$  of saccharin-Na are higher than ours, except for the value of 106.7  $\text{cm}^3\cdot\text{mol}^{-1}$ .<sup>4</sup> Such differences may be ascribed to the substances used, especially those containing crystalline water.

**Table 1.** Density of aqueous solutions of saccharin-Na, acesulfame-K and aspartame from 293.15 to 333.15 K.

<i>m</i> (mol·kg <sup>-1</sup> )	<i>d</i> (g·cm <sup>-3</sup> ) at <i>T</i> (K)					
	293.15	298.15	303.15	313.15	323.15	333.15
Saccharin-Na						
0.05255	1.00305	1.00184	1.00039	0.99687	8.99262	0.98772
0.10505	1.00786	1.00658	1.00507	1.00146	0.99713	0.99216
0.10514	1.00787	1.00660	1.00510	1.00149	0.99716	0.99219
0.12605	1.00977	1.00847	1.00695	1.00331	0.99895	0.99396
0.17413	1.01408	1.01273	1.01116	1.00743	1.00301	0.99796
0.20229	1.01658	1.01520	1.01361	1.00984	1.00538	1.00030
0.21499	1.01771	1.01631	1.01469	1.01089	1.00640	1.00131
0.22767	1.01884	1.01743	1.01581	1.01199	1.00750	1.00239
0.25514	1.02124	1.01981	1.01816	1.01430	1.00976	1.00462
0.30220	1.02536	1.02387	1.02218	1.01824	1.01364	1.00845
0.35697	1.03007	1.02852	1.02677	1.02274	1.01807	1.01283
0.40485	1.03410	1.03250	1.03072	1.02661	1.02187	1.01657
0.41338	1.03487	1.03326	1.03147	1.02736	1.02261	1.01729
0.45701	1.03856	1.03691	1.03508	1.03089	1.02604	1.02072
0.50658	1.04264	1.04094	1.03906	1.03479	1.02992	1.02450
0.50878	1.04284	1.04115	1.03928	1.03501	1.03014	1.02472
0.61330	1.05129	1.04949	1.04752	1.04310	1.03810	1.03257
0.70799	1.05882	1.05694	1.05489	1.05033	1.04521	1.03959
0.79997	1.06588	1.06392	1.06180	1.05712	1.05190	1.04619
0.93037	1.07569	1.07363	1.07142	1.06657	1.06120	1.05537
0.99524	1.08040	1.07830	1.07604	1.07112	1.06569	1.05980
1.15241	1.09150	1.08928	1.08691	1.08180	1.07621	1.07018
1.29500	1.10108	1.09875	1.09630	1.09103	1.08531	1.07917
Acesulfame-K						
0.05017	1.00291	1.00170	1.00026	0.99674	0.99250	0.98761
0.10426	1.00790	1.00665	1.00514	1.00155	0.99723	0.99228
0.20672	1.01718	1.01582	1.01424	1.01049	1.00604	1.00098
0.30185	1.02556	1.02410	1.02244	1.01855	1.01399	1.00883
0.40251	1.03425	1.03271	1.03097	1.02693	1.02225	1.01699
0.50031	1.04246	1.04083	1.03901	1.03484	1.03005	1.02470
0.60021	1.05068	1.04897	1.04707	1.04278	1.03788	1.03243
0.69808	1.05852	1.05673	1.05477	1.05036	1.04535	1.03982
0.79783	1.06635	1.06450	1.06247	1.05793	1.05282	1.04720
0.89698	1.07395	1.07203	1.06993	1.06528	1.06008	1.05437
Aspartame						
0.01043	0.99903	0.99786	0.99646	0.99301	0.98882	0.98396
0.01474	0.99937	0.99820	0.99679	0.99334	0.98914	0.98428
0.01982	0.99977	0.99859	0.99718	0.99372	0.98952	0.98465
0.02532	1.00021	0.99903	0.99761	0.99414	0.98993	0.98505
0.03137	1.00068	0.99950	0.99808	0.99460	0.99038	0.98549
0.03546	1.00100	0.99981	0.99839	0.99490	0.99067	0.98579
0.04097	1.00144	1.00024	0.99880	0.99530	0.99107	0.98618
0.04597	1.00182	1.00062	0.99919	0.99569	0.99145	0.98654
0.05042	1.00214	1.00097	0.99953	0.99603	0.99178	0.98686
0.05505	1.00255	1.00133	0.99989	0.99636	0.99211	0.98720
0.06140	1.00306	1.00183	1.00038	0.99684	0.99258	0.98765
0.06764	1.00355	1.00231	1.00085	0.99730	0.99303	0.98809

**Table 2.** Limiting apparent molar volume,  $V_{2,\Phi}^0$ , Debye-Hückel limiting law slope,  $A_v$ , deviation constants  $B_v$  and  $D_v$ , and standard error of estimate,  $S$ , of saccharin-Na (Sac-Na), acesulfame-K (Acs-K) and aspartame (Asp) in aqueous solution at the indicated temperature.

Solute		<i>T</i> (K)					
		293.15	298.15	303.15	313.15	323.15	333.15
Sac -Na	$V_{2,\Phi}^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	112.06±0.03	113.19±0.04	114.18±0.04	116.04±0.05	117.50±0.05	118.88±0.05
	$A_v$ (cm <sup>3</sup> ·L <sup>1/2</sup> ·mol <sup>-3/2</sup> )	1.7488	1.8332	1.9256	2.1339	2.3743	2.6497
	$-B_v$ (cm <sup>3</sup> ·L·mol <sup>-2</sup> )	4.93±0.25	5.05±0.28	5.04±0.26	5.69±0.35	5.67±0.37	6.43±0.38
	$D_v$ (cm <sup>3</sup> ·L <sup>3/2</sup> ·mol <sup>-5/2</sup> )	4.76±0.23	4.67±0.26	4.50±0.25	4.77±0.33	4.51±0.35	4.91±0.36
	$S$	0.06	0.06	0.06	0.08	0.08	0.08
Acs -K	$V_{2,\Phi}^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	106.60±0.02	107.58±0.02	108.59±0.06	110.22±0.03	111.58±0.02	112.74±0.03
	$B_v$ (cm <sup>3</sup> ·L·mol <sup>-2</sup> )	0.56±0.03	0.39±0.05	0.00	-0.36±0.06	-0.68±0.05	-0.97±0.05
	$S$	0.03	0.03	0.05	0.04	0.04	0.04
Asp	$V_{2,\Phi}^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	215.44±0.11	216.37±0.11	217.10±0.11	219.02±0.11	220.77±0.10	223.17±0.10
	$B_v$ (cm <sup>3</sup> ·L·mol <sup>-2</sup> )	-14.0±2.6	-8.6±2.6	-2.4±2.7	2.2±2.7	6.4±2.5	3.3±1.2
	$S$	0.15	0.16	0.16	0.16	0.15	0.07

From Table 2 it can be seen that the deviation constant  $B_v$  is negative throughout the temperature range studied for saccharin-Na, with a small but negative value of  $\partial B_v / \partial T$  ( $-0.036$  cm<sup>3</sup>·L·mol<sup>-2</sup>·K<sup>-1</sup>), while for acesulfame-K this constant is positive at low temperature and changes its sign at higher temperature to a negative value of  $\partial B_v / \partial T$  ( $-0.039$  cm<sup>3</sup>·L·mol<sup>-2</sup>·K<sup>-1</sup>).

Similar behaviour was also found for aspartame with  $\partial B_v / \partial T = 1.08$  cm<sup>3</sup>·L·mol<sup>-2</sup>·K<sup>-1</sup> at 298.15 K. The deviation constant  $B_v$  for aspartame is relatively high compared to the corresponding value of  $B_v$  for dipeptide glycylglycine which amounts to 1.30 cm<sup>3</sup>·L·mol<sup>-2</sup> at 298.15 K.<sup>12</sup> As was shown by Millero,<sup>19</sup> the magnitude and sign of the deviation constant  $B_v$  of an electrolyte

**Table 3.** Comparison of the apparent molar volumes of saccharin-Na, acesulfam-K and aspartame at 293.15 and 298.15 K obtained in this work with literature values.

Compound	Concentration	T (K)	$V_{2,\Phi}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	
			This work	Literature
Saccharin	2.55 % (w/w)	293.15	112.27	106.7 <sup>11</sup>
			112.26	123.0 <sup>15</sup>
	0.128 mol·kg <sup>-1</sup>	298.15	112.27	116.87 <sup>13</sup>
			112.06	117.2 <sup>14</sup>
			112.06	117.12 <sup>10</sup>
Acesulfame	0.154 mol·kg <sup>-1</sup>	293.15	106.88	107.29 <sup>13</sup>
			108.26	108.0 <sup>15</sup>
	11.11 % (w/w)	298.15	107.30	106.0 <sup>16</sup>
			106.60	106.3 <sup>14</sup>
			107.58	107.13 <sup>12</sup>
Aspartame	0.5 % (w/w)	293.15	215.20	206.4 <sup>11</sup>
			215.20	212.46 <sup>13</sup>
	at infinity dilution	298.15	215.44	217.1 <sup>14</sup>
			216.37	218.67 <sup>12</sup>

solute is a function of size, charge, temperature and the solvent used, and is a direct measure of the ion-ion interactions that cause the deviation. The main contributions to deviations from the limiting law in moderately concentrated solutions are those associated with long-range Coulombic interactions, primary hydration of ions, and ion-pairing. According to this view, a positive deviation from the limiting law may indicate that ion-pairing occurs. The change in the sign of the deviation constant may be explained by a change in solution structure, or a change in the form of the ion radical distribution function as found by Kirkwood.<sup>20</sup> The deviation constant  $D_v$  found for saccharin-Na in the relatively high concentration range with a small and negative value of  $\partial B_v / \partial T = -0.014$  (cm<sup>3</sup>·L<sup>3/2</sup>·mol<sup>-5/2</sup>·K<sup>-1</sup>) at 298.15 K can be attributed to long-range Coulombic interactions and to formation of contact ion-pairs or solvent separated pairs of higher order.<sup>21</sup>

The utility of the limiting apparent molar volume of electrolytes lies in the additivity principle, i. e.  $V_{2,\Phi}^{\circ}$  is equal to the sum of its ionic components,  $\bar{V}_{M^+}^{\circ}$  and  $\bar{V}_{X^-}^{\circ}$ . The limiting partial molar ionic volume of saccharin and acesulfame ions,  $\bar{V}_{X^-}^{\circ}$  at a definite temperature can be obtained as

$$\bar{V}_{X^-}^{\circ} = V_{2,\Phi}^{\circ} - \bar{V}_{M^+}^{\circ} \quad (7)$$

where for the limiting partial molar ionic volumes of sodium and potassium ions literature values were used.<sup>1</sup> The so-called conventional partial molar ionic volumes, based on the assumption that  $\bar{V}_{H^+}^{\circ}$  is zero, were considered. The  $\bar{V}_{M^+}^{\circ}$  values for temperatures other than 298.15 K were obtained by analytical interpolation to Millero's data using the values between 273.15 and

323.15 K. The calculated values of  $\bar{V}_{ion}^{\circ}$  are given in Table 4 together with  $\bar{V}_{X^-}^{\circ}$  values obtained via relation (7).

The partial molar volume of an ion at infinite dilution,  $\bar{V}_{ion}^{\circ}$ , can be represented as the sum of four terms<sup>1</sup>

$$\bar{V}_{ion}^{\circ} = \bar{V}_{int}^{\circ} + \bar{V}_{elect}^{\circ} + \bar{V}_{disord}^{\circ} + \bar{V}_{caged}^{\circ} \quad (8)$$

where  $\bar{V}_{int}^{\circ}$  is the intrinsic volume, which is the geometric volume occupied by the ion itself, usually evaluated from the crystal volume,  $\bar{V}_{elect}^{\circ}$  is the electrostriction partial molar ionic volume,  $\bar{V}_{disord}^{\circ}$  is the disordered or void-space partial molar ionic volume, and  $\bar{V}_{caged}^{\circ}$  is the caged or structured partial molar ionic volume.

**Table 4.** Limiting partial molar ionic volume,  $\bar{V}_{ion}^{\circ}$  (cm<sup>3</sup>·mol<sup>-1</sup>), of sodium, potassium, saccharin and acesulfame ions at indicated temperatures.

Ion	T(K)					
	293.15	298.15	303.15	313.15	323.15	333.15
Na <sup>+(a)</sup>	-1.56	-1.21	-0.92	-0.50	-0.30	-0.33
Sac <sup>-</sup>	113.62	114.40	115.10	116.54	117.80	119.21
K <sup>+(a)</sup>	9.04	9.02	9.23	9.51	9.57	9.43
Acs <sup>-</sup>	97.56	98.56	99.36	100.71	102.01	103.31

<sup>a)</sup> Ref.<sup>1</sup>

The intrinsic partial molar ionic volume can be approximated by the van der Waals volume,  $V_w$ , which is the volume of the ion impenetrable to solvent molecules. By setting  $\bar{V}_{int}^{\circ} = V_w$  in equation (7), the difference between the partial molar ionic volume and its van der Waals volume,  $(\bar{V}_{ion}^{\circ} - V_w)$ , is positive for the saccharin and acesulfame nitranions. The van der Waals volume of the nitranion has been evaluated using the approach of Bondi.<sup>22</sup> For the saccharin nitranion we obtained a value of 88.07 cm<sup>3</sup>·mol<sup>-1</sup> and for the acesulfame nitranion 79.01 cm<sup>3</sup>·mol<sup>-1</sup>. The short-range solvating properties of an ion may be discussed by considering the sign of the difference  $(\bar{V}_{ion}^{\circ} - V_w)$  for the ion. When this quantity is negative, the ion is classified as an electrostatic "positive solvating ion", and when the quantity is positive, the ion can be classified as a "negative solvating ion".<sup>1</sup> According to this classification, saccharin and acesulfame nitranions are negative solvating ions.

It seems reasonable to regard the nitranions of the investigated sodium and potassium salts as ions which disorganize the bulk water structure while organizing a portion of the solvent water by the attraction of the nitranions for water molecules. This effect compresses a portion of the water and thus shrinks the system. The shrinking is much greater at high temperature than at low. Prediction of the electrostriction partial molar ionic volume,  $\bar{V}_{elect}^{\circ}$ , is difficult owing to uncertainty about the

form of the interaction of an ion and the water molecule. From IR measurements and from an ab initio force field treatment of the saccharin nitranion it is known that the nitranionic charge is delocalized over the phenyl group (0.29  $e$ ), sulfonyl group (0.26  $e$ ), nitranionic centre (0.25  $e$ ) and carbonyl group (0.20  $e$ ), where  $e$  is the elementary charge.<sup>23</sup> On the other hand, from the crystal structure of ammonium saccharin it follows that the 3-oxo-3H-benzisothiazolyl group is flat and that the carbonyl group is more basic than the sulfonyl group.<sup>24</sup> An analogous structure may be anticipated for the nitranion of the acesulfame ion since both ions have a sulfocarbamide group. The partial molar ionic electrostriction volume,  $\bar{V}_{\text{elect}}^{\circ}$ , was calculated from Millero's semiempirical relation<sup>1</sup>

$$\bar{V}_{\text{elect}}^{\circ} = -\frac{BZ^2}{r} \quad (9)$$

where  $B$  is a constant ( $13.0 \text{ cm}^3 \cdot \text{\AA} \cdot \text{mol}^{-1}$ ),  $Z$  is the valence of the ion, and  $r$  is the ionic radius ( $\text{\AA}$ ). The radius of nitranions was obtained from  $V_{\text{W}}$  assuming that the volume of a nitranion is a perfect hard sphere using De Ligny's relation<sup>25</sup>

$$2r = \left( \frac{6V_{\text{W}}}{\pi N_{\text{A}}} \right) \quad (10)$$

where  $N_{\text{A}}$  is the Avogadro's number. Applying relation (9) we obtained values of  $\bar{V}_{\text{elect}}^{\circ}$  for the saccharin nitranion of  $-4.0 \text{ cm}^3 \cdot \text{mol}^{-1}$  and  $-4.1 \text{ cm}^3 \cdot \text{mol}^{-1}$  for the acesulfame nitranion at 298.15 K. From the  $\bar{V}_{\text{elect}}^{\circ}$  part of the ionic volume, the theoretical solvation number can be estimated using the Padova relation<sup>26</sup>

$$n = \frac{\bar{V}_{\text{elect}}^{\circ}}{-2.1} \quad (11)$$

which takes into account the fact that the average electrostriction ionic volume per mole of water is about  $-2.1 \text{ cm}^3 \cdot \text{mol}^{-1}$ . Thus from relation (11) it follows that the average hydration number of the investigated nitranions is about 2.0, i. e. two molecules of water are bound for each 3-oxo-3H-benzisothiazolyl group.

The disordered partial molar ionic volume,  $\bar{V}_{\text{disord}}^{\circ}$  was calculated by the empirical equation<sup>1</sup>

$$\bar{V}_{\text{disord}}^{\circ} = (A - 2.52)r^3 \quad (12)$$

where  $A$  is a constant ( $4.48 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{\AA}^{-3}$ ).<sup>27</sup> The radius of the nitranion was calculated from rel. (10). At 298.15 K we obtained for  $\bar{V}_{\text{disord}}^{\circ}$  the values of  $68.5 \text{ cm}^3 \cdot \text{mol}^{-1}$  for the saccharin nitranion, and  $61.3 \text{ cm}^3 \cdot \text{mol}^{-1}$  for the acesulfame ion. These volume effects may be visualized as the void space caused by the solvated ions, including the electrostricted region. The large

$\bar{V}_{\text{disord}}^{\circ}$  effects of the investigated anions appear to be related to their structure breaking properties. However, the relative contribution of  $\bar{V}_{\text{disord}}^{\circ}$  to  $\bar{V}_{\text{ion}}^{\circ}$  depends upon the magnitude of the electrostricted region, i. e. on  $Z^2/r$ . For ions with a small electrostricted region (small  $Z^2/r$ ) the disordered region is very important. So, where  $(\bar{V}_{\text{ion}}^{\circ} - V_{\text{W}})$  is positive, the  $\bar{V}_{\text{disord}}^{\circ}$  region is greater than the  $\bar{V}_{\text{elect}}^{\circ}$  region and the nitranions can be classified as structure-breaking ions.

The investigated nitranions cause structural effects that are different from those of simple monovalent ions. Both ions show little electrostriction and a high disordering effect. The difference between  $\bar{V}_{\text{ion}}^{\circ}$  and other components, given in rel. (8), may be ascribed to the caged or structural partial molar ionic volume,  $\bar{V}_{\text{caged}}^{\circ}$ . Its value amounts to  $-38.2 \text{ cm}^3 \cdot \text{mol}^{-1}$  for the saccharin nitranion and  $-37.59 \text{ cm}^3 \cdot \text{mol}^{-1}$  for the acesulfame nitranion.

The apparent molar volume of aspartame at infinite dilution was treated as a sum of the intrinsic volume of unsolvated molecules, and terms which contain volume changes for the solvation of the solute molecules. According to the theory which treats solvent and solute molecules as scaled particles, the apparent molar volume of a solute at infinite dilution is defined by<sup>28, 29</sup>

$$V_{2,\phi}^{\circ} = \bar{V}_{\text{cav}}^{\circ} + \bar{V}_{\text{int}}^{\circ} + \beta_{T_0} RT \quad (13)$$

where  $\bar{V}_{\text{cav}}^{\circ}$  is the volume for cavity formation in the liquid phase,  $\bar{V}_{\text{int}}^{\circ}$  is the volume contribution due to solute-solvent intermolecular interaction,  $\beta_{T_0}$  is the isothermal compressibility of the solvent, and  $R$  is the gas constant. The last term  $\beta_{T_0} RT$ , is a correction for the standard state change from the gaseous to liquid state.

The formation of a cavity in a liquid is by definition a positive contribution to the limiting apparent molar volume of the solute, while the intermolecular solute-solvent interaction contribution to  $V_{2,\phi}$  is negative due to the shrinking of cavities caused by intramolecular attraction forces in the liquid. Thus the cavity volume was calculated by<sup>30</sup>

$$\bar{V}_{\text{cav}}^{\circ} = \beta_{T_0} RT \left[ \frac{y}{1-y} + \frac{3yz(1+z)}{(1-y)^2} + \frac{9y^2z^2}{(1-y)^3} \right] + \frac{\pi\sigma_2^3 N_{\text{A}}}{6} \quad (14)$$

where  $y$  represents the ratio of a mole of solvent molecules in the form of hard sphere solvent particles to the molar volume of solvent,  $V_1^{\circ}$

$$y = \frac{\pi\sigma_1^3 N_{\text{A}}}{6V_1^{\circ}} \quad (15)$$

and  $z$  the ratio of the diameter of a scaled sphere molecule of solute,  $\sigma_1$  (nm) and solvent,  $\sigma_2$  (nm);

$z = \sigma_2 / \sigma_1$ . Thus from Eq. (14) it follows that the cavity contribution to the limiting apparent molar volume depends on the intrinsic size of the solute and solvent molecule, as well as on the isothermal compressibility of the solvent.

The hard sphere diameter of the solute,  $\sigma_2 = 0.798$  nm, was calculated by the De Ligny relation (10) using the van der Waals molar volume estimated by the Bondi<sup>22</sup> approach;  $V_w = 160.0$  cm<sup>3</sup>·mol<sup>-1</sup>. The value of  $y$  was calculated from (15) by using the diameter of the water molecule,  $\sigma_1 = 0.275$  nm.<sup>29</sup> The values of  $\beta_{T_0} = 45.2472 \times 10^{-6}$  bar<sup>-1</sup> and  $V_1^0 = 18.069$  cm<sup>3</sup>·mol<sup>-1</sup> were taken from ref.<sup>17</sup>

The calculated value of  $\bar{V}_{\text{cav}}^0$  is positive and amounts to 238.3 cm<sup>3</sup>·mol<sup>-1</sup>. Thus, from relation (13), the value of  $\bar{V}_{\text{int}}^0$  is negative and amounts to -23.0 cm<sup>3</sup>·mol<sup>-1</sup>. The interaction volume of a solute can be treated as the sum of the volume contributions due to dispersion intermolecular forces,  $\bar{V}_{\text{disp}}^0$ , dipole-dipole forces,  $\bar{V}_{\text{dip}}^0$ , and dipole-induced dipole forces,  $\bar{V}_{\text{ind}}^0$ <sup>31</sup>:

$$\bar{V}_{\text{int}}^0 = \bar{V}_{\text{disp}}^0 + \bar{V}_{\text{dip}}^0 + \bar{V}_{\text{ind}}^0 \quad (16)$$

The main contribution to  $\bar{V}_{\text{int}}^0$  in Eq. (16) are dipole-dipole forces between polar or charged groups and polar water molecules which are manifested as hydrogen bonds and dipole-induced dipole forces. Beside these, hydrophobic hydration takes place between non-polar parts of the aspartame molecule and the water molecule.

The limiting apparent molar expansibility of solute,  $\Phi_{2,E}^0 = (\partial V_{2,\Phi}^0 / \partial T)_p$ , was calculated from the temperature dependence of  $V_{2,\Phi}^0$  given as

$$V_{2,\Phi}^0 = a_0 + a_1(T - T_0) + a_2(T - T_0)^2 \quad (17)$$

where  $a_0$ ,  $a_1$  and  $a_2$  are empirical constants depending on solute and solvent, and  $T_0 = 298.15$  K. Eq. (17) is quadratic and consistent with the volumes going through a maximum; the latter behaviour is characteristic of most salts that have been studied in aqueous solution, as shown by Helgeson and Kirkham.<sup>32</sup> The values of the constants of relation (17) are given in Table 5 together with the standard error of the estimate. From relation (17) it follows that within our rather limited temperature

range  $\Phi_{2,E}^0$  is a linear function of temperature and that  $\Phi_{2,E}^0 = a_1$  at 298.15 K. The limiting apparent molar expansibility at other temperatures studied are given in Table 6. From these results it is apparent that  $\Phi_{2,E}^0$  for both electrolytic solutes decreases with increasing temperature, while for aspartame the reverse was observed. The partial molar expansibility of aspartame at 298.15 K is greater than that of diglycine which amounts to  $(0.115 \pm 0.015)$  cm<sup>3</sup>·mol<sup>-1</sup>·K<sup>-1</sup>. The  $\Phi_{2,E}^0$  values of diglycine also decrease with increasing temperature.<sup>33</sup> The fact that  $\Phi_{2,E}^0$  is a linear function of temperature with a negative coefficient for the temperature term (-0.0027 and -0.0028 for saccharin-Na and acesulfame-K) means that the second derivative of  $V_{2,\Phi}^0$  with respect to temperature is also negative. As Hepler<sup>34</sup> has pointed out,

$$T \left( \frac{\partial^2 V_{2,\Phi}^0}{\partial T^2} \right)_p = - \left( \frac{\partial \Delta C_p^0}{\partial P} \right)_T \quad (18)$$

and a positive value of  $\partial \Delta C_p^0 / \partial T$  is evidence that the investigated ionic solutes behave as structure breaking solutes in water over the experimental temperature range studied. On the other hand, aspartame with a small but negative value of  $\partial \Delta C_p^0 / \partial T$  may be regarded as a structure making solute in water.

**Table 5.** Values of the constants  $a_i$  of relation (17) and standard error of estimate,  $s$ .

Solute	$a_0$	$a_1$	$a_2$	$s$
Saccharin-Na	113.16±0.03	0.2092±0.04	-0.00133±0.0001	0.026
Acesulfame-K	107.60±0.02	0.1948±0.003	-0.00139±0.0001	0.036
Aspartame	216.31±0.05	0.1742±0.009	0.00019±0.0001	0.084

As for the limiting apparent molar volume, the limiting apparent molar expansibility of ionic solutes permits us to calculate the limiting partial molar expansibility of the individual ions by dividing the  $\Phi_{2,E}^0$  value of the electrolyte into its ionic components as<sup>35</sup>

$$\Phi_{2,E}^0 = \bar{E}_{M^+}^0 + \bar{E}_{X^-}^0 \quad (19)$$

where  $\bar{E}_{M^+}^0$  and  $\bar{E}_{X^-}^0$  are the corresponding limiting partial molar ionic values.

**Table 6.** Limiting apparent molar expansibility  $\Phi_{2,E}^0$  (cm<sup>3</sup>·mol<sup>-1</sup>·K<sup>-1</sup>) of saccharin-Na, acesulfame-K and aspartame in aqueous solutions at the indicated temperatures.

Solute	$\Phi_{2,E}^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> ·K <sup>-1</sup> ) at T(K)					
	293.15	298.15	303.15	313.15	323.15	333.15
Saccharin-Na	0.223±0.004	0.209±0.004	0.196±0.004	0.169±0.005	0.143±0.007	0.116±0.010
Acesulfame-K	0.209±0.003	0.195±0.003	0.181±0.003	0.153±0.004	0.125±0.006	0.097±0.007
Aspartame	0.172±0.010	0.174±0.009	0.176±0.010	0.180±0.016	0.184±0.023	0.187±0.031

The limiting apparent molar ionic expansibility of saccharin and acesulfame nitranions were calculated from relation (19) using  $\bar{E}_{M^+}^{\circ}$  values of sodium ( $0.039 \pm 0.009 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ) and potassium ( $0.062 \pm 0.016 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ) ions determined at 298.15 K.<sup>36</sup> The values of  $(0.17 \pm 0.01) \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  for the saccharin ion and  $(0.13 \pm 0.02) \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  for the acesulfame ion at 298.15 K, were obtained. On the other hand, the limiting partial molar ionic expansibility of the saccharin and acesulfame nitran ions,  $\bar{E}_X^{\circ}$  can be obtained from the temperature dependence of the limiting partial molar ionic volumes of the respective anions given in Table 4. The calculated values of  $\bar{E}_X^{\circ}$  amount to  $(0.15 \pm 0.02) \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  for the saccharin nitran ion and  $(0.141 \pm 0.010) \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  for the acesulfame nitranion at 298.15 K. The two values of the partial molar ionic expansibility for saccharin and acesulfame ions obtained by the described procedures are within experimental uncertainty equal and so in further calculation we used their average values, i. e.  $(0.16 \pm 0.02) \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  for the saccharin nitranion and  $(0.137 \pm 0.019) \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  for the acesulfame nitranion.

The limiting partial molar ionic expansibility,  $\bar{E}_{\text{ion}}^{\circ}$ , can be obtained by differentiation of Eq. (8) with respect to temperature at constant pressure:

$$\bar{E}_{\text{ion}}^{\circ} = \bar{E}_{\text{int}}^{\circ} + \bar{E}_{\text{elect}}^{\circ} + \bar{E}_{\text{disord}}^{\circ} + \bar{E}_{\text{caged}}^{\circ} \quad (20)$$

where  $\bar{E}_{\text{int}}^{\circ}$  is the intrinsic expansibility,  $\bar{E}_{\text{elect}}^{\circ}$  is the electrostriction expansibility,  $\bar{E}_{\text{disord}}^{\circ}$  is the disordered expansibility, and  $\bar{E}_{\text{caged}}^{\circ}$  is the caged expansibility.

$\bar{E}_{\text{int}}^{\circ}$  is dictated mostly by the expansibility of covalent bonds, and as a first approximation, due to the narrow temperature range studied, can be neglected. The investigated nitranions do not greatly differ in electrostriction expansibility. This component in relation (20) describes the volume change due to changes in the electrostriction region which is proportional to  $Z^2/r$ . Since this ratio for both nitranions is nearly equal, 0.30 for saccharin and 0.32 for the acesulfame nitranion, we may expect that  $\bar{E}_{\text{elect}}^{\circ}$  for both anions is equal and small. The disorder expansibility,  $\bar{E}_{\text{disord}}^{\circ}$  depends on temperature and the magnitude of the electrostriction region, i. e. on  $Z^2/r$ . For ions with a small electrostriction region (small  $Z^2/r$ ), this region is very important. The  $\bar{E}_{\text{caged}}^{\circ}$  and  $\bar{E}_{\text{disord}}^{\circ}$  terms in Eq. (20) are responsible for the large and positive value of  $\bar{E}_{\text{ion}}^{\circ}$  of the investigated nitranions of saccharin-Na and acesulfame-K. These terms depend primarily on the ratio of the hydrophilic and hydrophobic surface of the nitranion. However, the exact form of the  $\bar{E}_{\text{ion}}^{\circ}$  due to the structure of water for various ions is quite complicated, and so the division of  $\bar{E}_{\text{ion}}^{\circ}$  or  $\bar{V}_{\text{ion}}^{\circ}$  into various components may be entirely arbitrary.<sup>37</sup>

The limiting apparent molar expansibility of aspartame can be explained by an approach given by Chalikian et al.<sup>33</sup> Assuming that the temperature dependence of the hydration number,  $n_h$ , is negligible and that the intrinsic expansibility of solute can be neglected, the limiting partial molar expansibility is given by

$$\Phi_{2,E}^{\circ} = \bar{E}_2^{\circ} = n_h (\bar{E}_h^{\circ} - \bar{E}_1^{\circ}) \quad (21)$$

where  $\bar{E}_h^{\circ} = (\partial \bar{V}_h^{\circ} / \partial T)_p$  and  $\bar{E}_1^{\circ} = (\partial \bar{V}_1^{\circ} / \partial T)_p$  are the partial molar expansibilities of water in the hydration shell of the solute ( $\bar{E}_h^{\circ}$ ) and the bulk state ( $\bar{E}_1^{\circ}$ ). Thus, from relation (21) it is possible to calculate the difference in the expansibility of water in the hydration shell and in the bulk state from the known hydration number. The hydration number of aspartame,  $n_h = 17.68$ , was estimated at 293.15 K.<sup>6</sup> From Eq. (21) it follows that the difference  $(\bar{E}_h^{\circ} - \bar{E}_1^{\circ})$  is  $0.0097 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ . The expansibility of bulk water at 293.15 K,  $\bar{E}_1^{\circ} = \alpha_0 \bar{V}_1^{\circ}$ , was calculated from the density and expansibility of water,<sup>17</sup> and amounts to  $0.003732 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ . So, the expansibility of water in the hydration shell of aspartame is  $0.0135 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  which is considerably greater than that in pure water. From this it follows that water molecules in the hydration shell are less tightly bound than in the bulk state, since water molecules are under the influence of the strong electrostatic field in the vicinity of charged groups.<sup>37</sup>

The coefficient of thermal expansion of solutions,  $\alpha$  ( $\text{K}^{-1}$ ), is defined by the relation

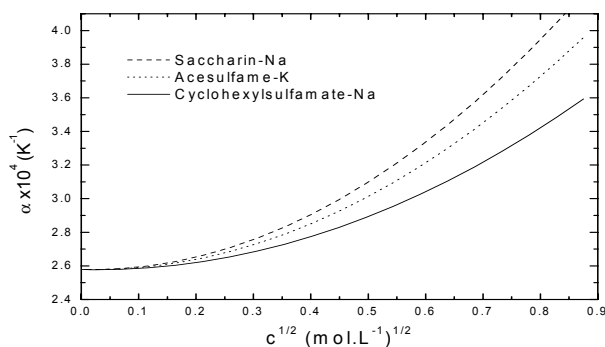
$$\alpha = -\frac{1}{d} \left( \frac{\partial d}{\partial T} \right)_{P,m} \quad (22)$$

For the investigated electrolyte solutions  $\alpha$  ( $\text{K}^{-1}$ ) can be calculated from relation (23) as a function of concentration in the following form<sup>14</sup>

$$\alpha = \alpha_0 + \left[ \frac{\phi_E^{\circ} - \alpha_0 V_{2,\Phi}^{\circ}}{1000} \right] c + \left[ \frac{A_E - \alpha_0 A_v}{1000} \right] c^{3/2} - \left[ \frac{\alpha_0 B_v}{1000} \right] c^2 - \left[ \frac{\alpha_0 D_v}{1000} \right] c^{5/2} \quad (23)$$

where  $\alpha_0$  ( $\text{K}^{-1}$ ) is the coefficient of thermal expansion of pure water and  $A_E = (\partial A_v / \partial T)_p$ . The coefficient of the  $c^{3/2}$  term according to the theory of Debye-Hückel is common to all strong electrolytes of the same valence type in a given solvent at definite temperature. At 298.15 K its value for a 1:1 electrolyte amounts to  $1.710 \times 10^{-5} \text{ cm}^3 \cdot \text{L}^{1/2} \cdot \text{K}^{-1}$ . On the other hand, the coefficients of the  $c$ ,  $c^2$  and  $c^{5/2}$  terms are characteristic of a given solute. In the calculation of  $\alpha$  we used  $\alpha_0$  value given by Kell,<sup>17</sup>

and for  $A_E$  a value of  $(0.01757 \pm 0.00005) \text{ cm}^3 \cdot \text{L}^{1/2} \cdot \text{mol}^{-3/2} \cdot \text{K}^{-1}$  obtained from the temperature dependence of  $A_V$  values.<sup>16</sup> The last term of relation (23) was omitted in calculation of  $\alpha$  for acesulfame-K. Fig. 1 shows the dependence of the coefficient of thermal expansion on the square root of concentration,  $c^{1/2} (\text{mol} \cdot \text{L}^{-1})^{1/2}$  at 298.15 K for aqueous solutions of some sweeteners, such as saccharin-Na acesulfame-K and cyclohexylsulfamate-Na.<sup>36</sup> From Fig.1 it can be seen that the coefficient of thermal expansion increases with increasing concentration and that  $\alpha$  of an aqueous solution of saccharin-Na at definite concentration is higher than that of acesulfame-K and that the latter is higher than that of cyclohexylsulfamate-Na.



**Figure 1.** Coefficient of thermal expansion of aqueous solutions of saccharin-Na, acesulfame-K and cyclohexylsulfamate-Na at 298.15 K.

The density of an aqueous solution of aspartame at a given temperature can be fitted to an equation of the type

$$d = d_0 + A_1 c \quad (24)$$

where  $d_0$  is the density of pure water<sup>17</sup> and  $A_1$  is a coefficient which depends on solute, solvent and temperature. The least-squares values of the coefficient  $A_1$  are listed in Table 7 together with the standard error of estimate,  $s$ .

**Table 7.** Coefficient  $A_1$  of relation (24) and standard error of the estimate,  $s$ , at the indicated temperatures.

$T(\text{K})$	$A_1 (\text{g} \cdot \text{L}^{1/2} \cdot \text{mol}^{-1} \cdot \text{cm}^{-3})$	$s \times 10^4$
293.15	0.07978	3
298.15	0.07890	2
303.15	0.07825	2
313.15	0.07692	2
323.15	0.07595	2
333.15	0.07476	0.9

The coefficient of thermal expansion of an aqueous solution of aspartame was obtained by differentiating the expression for density (24) with respect to temperature at constant pressure and molality, and by

dividing the obtained derivative with  $d$ . The following relation results

$$\alpha = \alpha_0 - b_1 c \quad (25)$$

where  $b_1 = (\partial A_1 / \partial T) \cdot (1/d_0)$ . The dependence of the coefficient  $A_1$  of Eq.(24) on temperature was expressed by a relation identical to (17) and for  $\partial A_1 / \partial T$  a value of  $-(1.444 \pm 0.087) \times 10^{-4} \text{ g} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-3} \cdot \text{K}^{-1}$  at 298.15 K was estimated. The value of  $b_1$  amounts to  $-(1.448 \pm 0.087) \times 10^{-4} \text{ L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ . Owing to the low solubility of aspartame in water, the coefficient of thermal expansion of its aqueous solution at the highest concentration studied is only  $2.668 \times 10^{-4} \text{ K}^{-1}$ , which is about four percent higher than that of pure water.<sup>17</sup>

The thermal expansion coefficient,  $\alpha^*$  ( $\text{K}^{-1}$ ), defined as<sup>38</sup>

$$\alpha^* = \frac{1}{V_{2,\Phi}^0} \left( \frac{\partial V_{2,\Phi}^0}{\partial T} \right)_p \quad (26)$$

was calculated for the investigated solutes and sodium cyclohexylsulfamate.<sup>36</sup> The results are collected in Table 8. Analysis of these data shows that values of  $\alpha^*$  of electrolyte solutes are greater than that of aspartame, which behaves as a non-electrolyte. Furthermore, the  $\alpha^*$  values of ionic solutes decrease linearly with increasing temperature with  $\partial \alpha^* / \partial T = -2.52 \times 10^{-5}$ ,  $-2.73 \times 10^{-5}$  and  $-1.50 \times 10^{-6} \text{ K}^{-2}$  for saccharin-Na, acesulfame-K and Na-cyclohexylsulfamate, respectively, while  $\alpha^*$  of aspartame shows a slight linear increase with temperature with  $\partial \alpha^* / \partial T = 1.01 \times 10^{-6} \text{ K}^{-2}$ . The values of  $\alpha^*$  of the investigated ionic compounds are comparable with  $\alpha^*$  values of inorganic salts such as ammonium chloride, ammonium acetate or ammonium propionate, which decrease with increasing temperature.<sup>38</sup> On the contrary,  $\alpha^*$  of aspartame is lower than that of diglycine and triglycine; this dipeptide and tripeptide also show a negative value of  $\partial \alpha^* / \partial T$ .<sup>38</sup> The complexity of the  $\alpha^*$  functions highlights the strong dependence of the expansibility upon structure features, such as electrical charge, size, type of ion, as well as the relative proportions of the hydrophilic or hydrophobic parts of the molecule.

**Table 8.** Thermal expansion coefficient,  $\alpha^*$  (rel. 26) of saccharin-Na, acesulfame-K, aspartame and Na-cyclohexylsulfamate<sup>10</sup> at the indicated temperatures.

Compound	$\alpha^* \times 10^3$ at $T(\text{K})$					
	293.15	298.15	303.15	313.15	323.15	333.15
Saccharin-Na	1.99	1.85	1.72	1.46	1.22	0.98
Acesulfame-K	1.96	1.81	1.67	1.39	1.12	0.86
Aspartame	0.80	0.81	0.81	0.82	0.83	0.84
Cyclohexylsulfamate-Na	1.24	1.24	1.23	1.21	1.20	-



Because apparent molar volumes and apparent molar expansibilities provide an important insight into the interactions of sweet solutes with water and perturbation effects on the structure of water, we correlated these parameters with the relative sweetness,  $RS$ , of the sweeteners investigated and some other alternatives (Table 9). The following equation, which relates  $\log RS$  to  $V_{2,\Phi}^{\circ}$  and  $\Phi_{2,E}^{\circ}$ , was derived :

$$\log RS = (1.47 \pm 0.61) \times 10^{-3} V_{2,\Phi}^{\circ} + (1.8 \pm 0.5) \Phi_{2,E}^{\circ} \quad (27)$$

where  $r = 0.996$  and  $s = 0.069$ .

**Table 9.** Relative sweetness,  $RS$ , limiting apparent molar volume,  $V_{2,\Phi}^{\circ}$  and limiting apparent molar expansibility  $\Phi_{2,E}^{\circ}$  of some sweeteners at 298.15 K.

Solute	$RS$	$V_{2,\Phi}^{\circ}$ ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )	$\Phi_{2,E}^{\circ}$ ( $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ )
Saccharin-Na	300 <sup>3</sup>	113.19	0.209
Acesulfame-K	200 <sup>3</sup>	107.58	0.195
Aspartame	180 <sup>3</sup>	216.37	0.174
Cyclohexylsulfamic acid	46 <sup>40</sup>	123.8 <sup>36</sup>	0.126 <sup>42</sup>
Cyclohexylsulfamate-K	39.8 <sup>41</sup>	122.05 <sup>36</sup>	0.151 <sup>36</sup>
Cyclohexylsulfamate-NH <sub>4</sub>	39.6 <sup>41</sup>	141.88 <sup>43</sup>	0.135 <sup>43</sup>

### 3. Conclusions

In summary we extended our knowledge of the volumetric properties of some alternative sweeteners on the basis of density measurements. Water stabilizes, solvates, and transports tastant molecules to receptors, and the investigated solution properties such as the apparent molar volume and the apparent molar expansibility, and especially their limiting values, clearly illustrate differences between solutes; the data can be related to the taste behaviour of sweeteners.

### 4. Experimental

#### 4.1. Materials

All the substances investigated were commercial products, e. g. saccharin-Na (dihydrate, Merck), acesulfame-K (Fluka), cyclohexylsulfamate-Na (Sigma) and aspartame (Fluka) and were used without further purification. The purity of the compounds was checked by analysis of the elements C, H and N (Perkin Elmer, 2400 Series II CHNS/O Analyzer) and for cyclohexylsulfamate-Na also by ion exchange of the cation of the salt with the hydrogen ion (DOWEX, Type 50 WX8); a purity of 99.5% at least (aspartame) or better, e. g. 99.9% for the potassium salt and sodium salts was determined. The salts were kept in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub> while aspartame was stored in a refrigerator at 277 K.

The investigated solutions were prepared on a molal concentration scale by precise weighing, using a digital balance (Mettler Toledo, model AT201, Switzerland) accurate to within  $\pm 1 \times 10^{-5}$  g. Before use the solutions were degassed by ultrasound (ultrasonic bath, Bandelin Sonorex, type TK 52, Berlin, Germany).

#### 4.2. Density Measurements

The density,  $d$ , of aqueous solutions of all sweeteners was measured by a vibrating-tube density meter (Anton Paar, model DMA 60, Graz, Austria) equipped with a measuring cell (Anton Paar, type 602) and a digital thermometer (Anton Paar, DT 100-20) with a precision of  $\pm 0.01$  K. The apparatus was calibrated with doubly distilled water<sup>17</sup> and dry air<sup>39</sup> at each investigated temperature at atmospheric pressure. The temperature in the measuring cell was regulated to better than  $\pm 0.01$  K, using an external bath circulator (Haake, DC3-B3, Karlsruhe, Germany). The uncertainty of the density measurements was  $\pm 2 \times 10^{-5}$  g·cm<sup>-3</sup>.

### 5. References

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## Povzetek

Na osnovi merjenja gostote vodnih raztopin nekaterih nadomestnih sladil pri različnih temperaturah smo določili njihove volumenske lastnosti. Razlike v navideznem molskem volumnu ter navidezni molski ekspanzibilnosti preiskovanih topljencev, zlasti njihove limitne vrednosti, kažejo na vpliv narave in velikosti topljenca; fizikalno kemijske lastnosti raztopin različnih topljencev so v korelaciji z njihovim okusom.