

# The Electric Conductivities of Aqueous Solutions of Rubidium and Cesium Cyclohexylsulfamates, Potassium Acesulfame and Sodium Saccharin<sup>†</sup>

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## Abstract

The electric conductivities of aqueous solutions of rubidium and cesium salts of cyclohexylsulfamic acid, potassium acesulfame and sodium saccharin were measured from 5 °C to 35 °C (in steps of 5 °C) in the concentration range  $0.0003 < c/\text{mol dm}^{-3} < 0.01$ . Data analysis based on the chemical model of electrolyte solutions yielded the limiting molar conductivity  $\Lambda^\infty$  and the association constant  $K_A$ . Using the known data of the limiting conductivities of rubidium, cesium, sodium and potassium ions the limiting conductivities of the cyclohexylsulfamate, acesulfame and saccharin ions were evaluated. Total dissociation of the investigated salts in water and negligible hydration of anions are evident.

**Key words:** electrolyte conductivity, electrolyte solution, cyclohexylsulfamates, acesulfame, saccharin, chemical model

## 1. Introduction

Saccharin, potassium acesulfame and the salts of cyclohexylsulfamic acid are widely used as non-caloric sweetening agents in foods, beverages and pharmaceuticals.<sup>1</sup> In our previous study the conductivity<sup>2</sup> of aqueous solutions of some cyclohexylsulfamates was studied. It has been found that cyclohexylsulfamates as salts are completely dissociated in water solutions. The cyclohexylsulfamate anion turned out as weakly hydrated due to its hydrophobicity, whereas the hydration of cations depends on their charge densities. The obtained results were in agreement with the volumetric properties<sup>3</sup> and viscosities<sup>4</sup> and confirmed the suggestion that sweetness is a complex interplay of structural and solution properties.

On the other hand, it was recognized, that the sulfamate function is essential for cyclamate sweetness although the cation seems to have some effect on the sweet taste.<sup>5, 6</sup> The behaviour of an ion in a solvent depends on the ion-ion and ion-solvent interactions. It is to be expected that the taste of a sweet substance could be interpreted by an understanding of these interactions in the medium. Because there is a lack of the literature information on the properties of

acesulfame and saccharin anion in the solutions we extended our investigations with precise conductivity measurements on potassium acesulfame and sodium saccharin dilute aqueous solutions. However, aqueous rubidium and cesium cyclohexylsulfamate solutions were also investigated in order to complete the series of the mentioned salts of monovalent cations.

The obtained data were treated in the framework of the low concentration chemical model (lcCM).<sup>7</sup>

## 2. Experimental

### 2.1 Materials

Rubidium (RbCy) and cesium cyclohexylsulfamate (CsCy) were obtained by careful neutralization of cyclohexylsulfamic acid (HCy, purchased from Sigma) with the corresponding base (Fluka or Merck). The purity of the salts was checked after repeated recrystallizations from water by analysis of the elements C, H and N (Perkin Elmer, 2400 Series II CHNS/O Analyzer) and also by the ion exchange of the cations with the hydrogen ion (DOWEX, Type 50 WX8); a purity of 99.9% for all the salts was determined.

Sodium saccharin (Sacharin-Na, Sac-Na) was purchased from Merck (dihydrate purum, ≥ 99.0%).

By thermogravimetric analysis (Mettler Toledo TGA/SDTA 851e) the amount of crystal water  $1.55 \pm 0.01$  H<sub>2</sub>O in the Sac-Na was found.

The Fluka product potassium acesulfame (Acesulfame-K, Ace-K, puriss, ≥ 99.0%) was used without further purification.

The salts were kept in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub>.

Demineralized water was distilled in a quartz bidistillation apparatus (Destmat Bi18E, Heraeus). The final product with specific conductance of less than  $6 \cdot 10^{-7}$  S cm<sup>-1</sup> was distilled into a flask permitting storage and transfer of the solvent into the measuring cell under an atmosphere of nitrogen. The stock solutions were prepared by weighing salt and water.

## 2.2 Thermostat

The high precision thermostat used in the laboratory experiments has been described previously.<sup>8</sup> It can be set to each temperature of a temperature programme with a reproducibility of less than 0.003 °C.

## 2.3 Conductivity Measurement

The conductivities of dilute solutions were determined with the help of a three-electrode measuring cell, described elsewhere.<sup>9</sup> The cell was calibrated with dilute potassium chloride solutions.<sup>10</sup> At the beginning of every measuring cycle the cell was filled with a weighed amount of water. After measurement of the solvent conductivity at all temperatures of the programme, a weighed amount of a stock solution was added using a gas-tight syringe and the temperature programme was repeated.

From the weights and the corresponding solution densities  $d$ , the molar concentrations  $c$  were determined. A linear change of  $d$  with increasing salt content for diluted solutions was assumed,  $d = d_s + D\tilde{m}$ , where  $d_s$  is the density of the solvent (water) and  $\tilde{m}$  is the molality of the electrolyte (moles of electrolyte per kilogram of solution). The densities of the solutions were determined by the method of Kratky et al.<sup>11</sup> by use of a Paar densimeter (DMA 60, DMA 601 HT) at 25 °C combined with a precision thermostat. As usual the density gradient  $D$  is considered to be independent of temperature, see Table 1.

The measuring procedure, including corrections and the extrapolation of the sample conductivity to infinite frequency, is described in the literature.<sup>10</sup> The measured conductivity data of all investigated salts are given in Table 1 as a function of the temperature independent molonomies. They can be converted to the temperature-dependent molarities by use of the relationship  $c = \tilde{m}d$ . Taking into account the sources of error (calibration, titration, measurements, impurities), the specific conductivities are accurate to within 0.1%.

## 3. Data Analysis

The analysis of conductivity data in the framework of the low concentration chemical model (lcCM) given in Ref. (7) and the literature quoted there, uses the set of equations

$$\frac{\Lambda}{\alpha} = \Lambda^\infty - S\sqrt{ac} + Eac \ln(ac) + J_1 ac + J_2 (ac)^{\frac{3}{2}} \quad (1)$$

$$K_A = \frac{1-\alpha}{c\alpha^2 y_\pm^2}; \quad y'_\pm = \exp\left(-\frac{\kappa q}{1+\kappa R}\right); \quad (2a-b)$$

$$\kappa^2 = 16\pi N_A qac; \quad q = \frac{e_o^2}{8\pi\epsilon\epsilon_o kT} \quad (2c-d)$$

$$K_A = 4\pi N_A \int_a^R r^2 \exp\left[\frac{2q}{r} - \frac{W^*}{kT}\right] dr \quad (3)$$

where  $\Lambda$  and  $\Lambda^\infty$  are the molar conductivities at molarity  $c$  and infinite dilution,  $(1-\alpha)$  is the fraction of oppositely charged ions acting as ion pairs, and  $K_A$  is the equilibrium constant of the lcCM with an upper association limit  $R$ ;  $y'_\pm$  is the corresponding activity coefficient of the free ions,  $(y'_\pm)^2 = y'_+ y'_-$ ,  $k$  is the Debye parameter,  $e_o$  is the proton charge,  $\epsilon$  is the relative permittivity of the solvent,  $\epsilon_o$  is the permittivity of a vacuum and  $T$  the absolute temperature. The other symbols have their usual meaning.  $W^*$  is a step function for the potential of mean force between cation and anion due to non-Coulombic interactions.

The coefficients of Eq. (1) are given in Ref. (7). The limiting slope  $S$  and the parameter  $E$  are evaluable when the solvent data are available. The coefficients  $J_1$  and  $J_2$  are functions of the distance parameter  $R$ , representing the distance to which oppositely charged ions can approach as freely moving particles in solution.

Analysis of the conductivity data of associated electrolytes are carried out by setting the coefficients  $S$ ,  $E$  and  $J_1$  of Eq. (1) to their calculated values<sup>7</sup> and then usually using three-parameter fits to obtain the limiting values of molar conductivity  $\Lambda^\infty$ , the association  $K_A$  and the coefficient  $J_2$  by non-linear least squares iterations. A three-parameter evaluation is reduced to a two-parameter procedure for non-associating electrolytes,<sup>9</sup> where usually the coefficient  $J_2$  is also fixed. The input data for the calculation of the coefficients are the known solvent properties used in the literature<sup>12</sup> and the distance parameter  $R$ . The lower limit  $a$  of the association integral is the distance of closest approach of cation and anion (contact distance)  $a = a_+ + a_-$  calculated from the ionic radii of the cations<sup>7</sup>  $a_+ = 0.098, 0.133, 0.149$  and  $0.165$  nm for Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> respectively. Cyclohexylsulfamate, saccharin

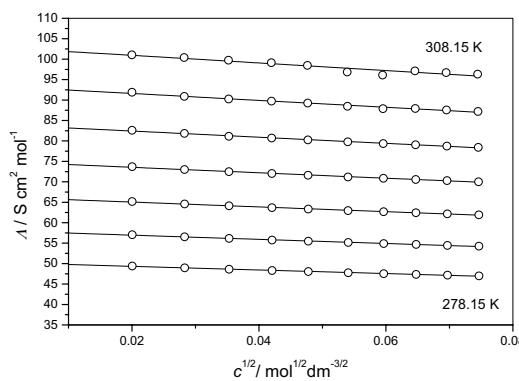
and acesulfame anions have a shape far from spherical. The radii for saccharin and acesulfame anions were estimated from van der Waals radii of the atoms given by Bondi.<sup>13</sup> Obtained values 0.327 and 0.315 nm for saccharin and acesulfame anion respectively are in good agreement with radii from X-ray diffraction measurements (0.355 nm for saccharin and 0.339 nm for acesulfame anion). The later ones were used in the further procedure.

For cyclohexylsulfame anion we used the value of  $a_- = 0.176$  nm which was estimated for sulfamic acid assuming that the cyclohexyl radical does not change its interionic distance between the proton and the basic oxygen atom in the zwitterion structure of sulfamic acid.<sup>14</sup>

From extended investigations of electrolyte solutions in amphiprotic hydroxylic solvents (water, alcohols) it is known that the upper limit of association is given by an expression of the type  $R = a + n \cdot s$ , where  $s$  is the length of an oriented solvent molecule,  $n$  is an integer,  $n = 0, 1, 2, \dots$ . Here,  $s$  is the length of an OH-group,  $d_{\text{OH}}$  and  $s = d_{\text{OH}} = 0.28$  nm. In our previous work only slightly dependence of the association constants by the choice of the distance parameter  $R$  was observed. Here for all the systems investigated  $n = 2$  was chosen in order to encompass three types of ion pairs: contact, solvent shared and solvent separated ion pairs.

## 4. Results and Discussion

Figure 1 shows a comparison of the experimental data for the sodium saccharin aqueous solutions given in Table 1 and the results of the lcCM calculations executed using Eqs. (1-5) under the assumption  $n = 2$  for Eqs. (4 and 5), encompassing three types of ion pairs: contact ion pairs, solvent-shared and solvent-separated ion pairs. All other investigated systems show similar dependence. In Figure 2 the conductivity data for sodium saccharine, potassium acesulfame together with rubidium and cesium cyclohexylsulfamate aqueous solutions at 298.15 K are presented.



**Figure 1.** Molar conductivities of aqueous solutions of sodium saccharin from 278.15 K to 308.15 K (in steps of 5 K) in the concentration range  $0.0003 < c/\text{mol dm}^{-3} < 0.01$ ; full lines: lcCM calculations.

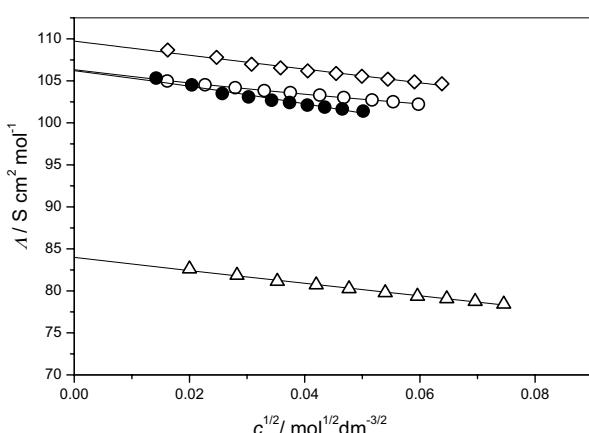
**Table 1:** Experimental molar conductivities of the investigated sweeteners in water<sup>a</sup>

T	278.15	283.15	288.15	293.15	298.15	303.15	308.15
$10^3 \times \tilde{m}$							
<i>A</i>							
<i>RbCy, D = 0.1290</i>							
0.26123	65.808	75.011	84.623	94.612	104.987	115.668	126.577
0.51673	65.487	74.656	84.254	94.230	104.535	115.221	126.181
0.78251	65.253	74.418	83.965	93.921	104.198	114.824	125.780
1.09083	65.061	74.178	83.705	93.610	103.852	114.468	125.408
1.41094	64.921	74.011	83.510	93.379	103.603	114.198	125.121
1.82113	64.717	73.800	83.255	93.097	103.309	113.859	124.729
2.19430	64.552	73.598	83.036	92.847	103.031	113.543	124.372
2.67868	64.375	73.396	82.810	92.595	102.727	113.227	124.018
3.07203	64.253	73.242	82.625	92.387	102.512	112.971	123.654
3.57864	64.084	73.065	82.422	92.133	102.226	112.707	123.352
<i>CsCy, D = 0.1690</i>							
0.20232	65.911	75.064	84.567	94.578	105.327	115.542	125.283
0.41746	65.470	74.593	84.098	94.038	104.528	114.266	125.183
0.66172	65.097	74.164	83.625	93.459	103.498	113.602	124.045
0.91796	64.766	73.779	83.166	92.858	103.088	113.428	124.201
1.17636	64.531	73.490	82.793	92.533	102.696	113.000	123.749
1.40136	64.313	73.254	82.583	92.301	102.424	112.694	123.408
1.64177	64.127	73.040	82.345	92.041	102.124	112.384	123.043
1.89557	63.985	72.881	82.148	91.837	101.880	112.136	122.762
2.17077	63.849	72.710	81.975	91.614	101.656	111.888	122.090
2.52123	63.688	72.542	81.781	91.385	101.407	111.385	121.483

**Table 1:** Contuned

T $10^3 \times \tilde{m}$	278.15	283.15	288.15	293.15	298.15	303.15	308.15
<b>Ace-K, <math>D = 0.0949</math></b>							
0.26345	67.704	77.274	87.356	97.833	108.673	119.822	130.854
0.61191	67.097	76.610	86.635	97.008	107.805	118.611	130.044
0.94979	66.571	76.050	86.029	96.339	106.985	117.902	129.022
1.28621	66.313	75.754	85.652	95.899	106.544	117.520	128.851
1.64720	66.076	75.509	85.338	95.587	106.191	117.147	128.447
2.07266	65.863	75.237	85.071	95.286	105.878	116.785	128.018
2.49919	65.661	74.821	84.837	94.992	105.550	116.426	127.623
2.97005	65.469	74.831	84.558	94.717	105.206	116.056	127.226
3.49614	65.275	74.569	84.288	94.420	104.878	115.701	126.619
4.08285	65.079	74.378	84.101	94.193	104.654	115.111	125.631
<b>Sac-Na, <math>D = 0.0936</math></b>							
0.40135	49.407	57.070	65.170	73.697	82.603	91.902	101.048
0.80063	48.960	56.556	64.575	73.015	81.849	90.888	100.391
1.24622	48.628	56.159	64.125	72.498	81.138	90.251	99.746
1.76948	48.303	55.748	63.687	72.028	80.715	89.738	99.147
2.28232	48.053	55.491	63.351	71.611	80.256	89.279	98.475
2.92215	47.767	55.158	62.962	71.183	79.786	88.480	97.672
3.55777	47.539	54.904	62.681	70.855	79.360	87.893	97.161
4.19230	47.351	54.687	62.431	70.564	79.068	87.927	97.129
4.85544	47.167	54.442	62.179	70.289	78.747	87.569	96.729
5.57112	46.981	54.263	61.917	70.008	78.426	87.218	96.337

<sup>a</sup>Units:  $\tilde{m}$ , mol kg<sup>-1</sup>;  $T$ , K;  $\Lambda$ , S cm<sup>2</sup> mol<sup>-1</sup>;  $D$ , kg<sup>2</sup> dm<sup>-3</sup> mol<sup>-1</sup>



**Figure 2.** Molar conductivities of the rubidium (○) and cesium (●) cyclohexylsulfamate, potassium acesulfame (◇) and sodium saccharin (△) in water at 25 °C.

In Table 2 the limiting conductivities and association constants calculated by using the lcCM are gathered. The values of the association constants are very low:  $K_A = 5\text{--}6$  for aqueous solutions of the cesium cyclohexylsulfamate and  $K_A = 2\text{--}3$  in all other systems investigated. All the investigated salts could be regarded as completely dissociated in water solutions (“strong-electrolytes”). Whereas the temperature coefficient

$dK_A/dT$  is usually positive for the alkali salts water solutions, no evidence for the temperature dependence of the association process in the investigated systems was found.

**Table 2.** Limiting molar conductivities  $\Lambda^\infty$  and association constants  $K_A$  of rubidium and cesium cyclohexylsulfamates, sodium saccharin and potassium acesulfame in water<sup>a</sup>

T	$\Lambda^\infty$	$K_A$		$\Lambda^\infty$	$K_A$		
		RbCy					
		R = 0.885	CsCy				
278.15	$66.55 \pm 0.02$	$1.0 \pm 0.7$	$66.54 \pm 0.06$	$6.2 \pm 0.8$			
283.15	$75.89 \pm 0.02$	$1.3 \pm 0.5$	$75.81 \pm 0.06$	$6.1 \pm 0.7$			
288.15	$85.65 \pm 0.03$	$1.0 \pm 0.6$	$85.46 \pm 0.07$	$5.8 \pm 0.6$			
293.15	$95.82 \pm 0.03$	$2.0 \pm 0.7$	$95.55 \pm 0.09$	$5.9 \pm 0.8$			
298.15	$106.33 \pm 0.02$	$0.9 \pm 0.4$	$106.21 \pm 0.17$	$6.8 \pm 1.2$			
303.15	$117.18 \pm 0.08$	$1.0 \pm 0.4$	$116.46 \pm 0.15$	$4.5 \pm 1.0$			
308.15	$128.42 \pm 0.18$	$3.3 \pm 0.3$	$127.13 \pm 0.19$	$3.3 \pm 1.2$			
Sac-Na							
$R = 1.014$							
278.15	$50.23 \pm 0.03$	$3.0 \pm 0.3$	$68.27 \pm 0.09$	$3.5 \pm 0.6$			
283.15	$58.02 \pm 0.04$	$3.0 \pm 0.3$	$77.96 \pm 0.10$	$3.1 \pm 0.7$			
288.15	$66.27 \pm 0.05$	$3.1 \pm 0.3$	$88.18 \pm 0.09$	$3.0 \pm 0.5$			
293.15	$74.94 \pm 0.05$	$3.1 \pm 0.3$	$98.76 \pm 0.10$	$2.8 \pm 0.7$			
298.15	$83.99 \pm 0.07$	$3.1 \pm 0.3$	$109.74 \pm 0.12$	$2.7 \pm 0.7$			
303.15	$93.37 \pm 0.14$	$3.2 \pm 0.6$	$120.99 \pm 0.11$	$2.6 \pm 0.5$			
308.15	$102.90 \pm 0.14$	$3.1 \pm 1.0$	$132.57 \pm 0.14$	$2.8 \pm 0.6$			
Ace-K							
$R = 1.032$							

<sup>a</sup> Units:  $T$ , K;  $\Lambda^\infty$ , S cm<sup>2</sup> mol<sup>-1</sup>;  $K_A$ , dm<sup>3</sup> mol<sup>-1</sup>;  $R$ , nm

Combining the limiting ion conductivities  $\Lambda^\infty$  of Table 2 and the known limiting values of cations<sup>15</sup>  $\lambda^\infty(M^+)$ ,  $M^+ = \text{Na}^+, \text{K}^+, \text{Rb}^+$  and  $\text{Cs}^+$  (Table 3)

$$\lambda^\infty(T, A^-) = \Lambda^\infty(T, \text{MA}) - \lambda^\infty(T, M^+) \quad (4)$$

yields the limiting anion conductivities  $\lambda^\infty(A^-)$  for cyclohexylsulfate, saccharin and acesulfame anions and their temperature dependence; see Table 4.

**Table 3.** Densities and viscosities of pure water and limiting conductance of ions in water<sup>a</sup>

T	$d_s$ <sup>b</sup>	$10^3 \times \eta$ <sup>b</sup>	$\lambda^\infty(\text{Na}^+)$ <sup>c</sup>	$\lambda^\infty(\text{K}^+)$ <sup>c</sup>	$\lambda^\infty(\text{Rb}^+)$ <sup>c</sup>	$\lambda^\infty(\text{Cs}^+)$ <sup>c</sup>
278.15	0.99997	1.5192	30.30	46.72	50.12	50.00
283.15	0.99970	1.3069	34.88	53.03	56.63	56.47
288.15	0.99910	1.1382	39.72	59.61	63.44	63.18
293.15	0.99821	1.002	44.81	66.44	70.51	70.12
298.15	0.99704	0.8903	50.15	73.50	77.81	77.26
303.15	0.99565	0.7975	55.72	80.76	85.30	84.59
308.15	0.99404	0.7195	61.53	88.20	92.94	92.10

<sup>a</sup> Units: T, K;  $d_s$ , kg dm<sup>-3</sup>;  $\eta$ , Pa s;  $\lambda^\infty$ , S cm<sup>2</sup> mol<sup>-1</sup>

<sup>b</sup> Ref.<sup>12</sup>

<sup>c</sup> Ref.<sup>15</sup>

**Table 4.** Limiting conductances of cyclohexylsulfamate, saccharin and acesulfame ion in water as a function of temperature<sup>a</sup>

T	$\lambda^\infty(\text{Cy})$		$\lambda^\infty(\text{Sac}^-)$			$\lambda^\infty(\text{Ace}^-)$	
	RbCy	CsCy	Literature <sup>2</sup>	Sac-Na	Ace-K		
278.15	16.44	16.54	16.25	19.93	21.54		
283.15	19.26	19.34	19.08	23.14	24.93		
288.15	22.21	22.28	22.05	26.55	28.57		
293.15	25.31	25.43	25.21	30.13	32.32		
298.15	28.52	28.95	28.47	33.84	36.24		
303.15	31.88	31.87	31.86	37.64	40.23		
308.15	35.48	35.03	35.37	41.44	44.37		

<sup>a</sup> Units: T, K;  $\lambda^\infty$ , S cm<sup>2</sup> mol<sup>-1</sup>

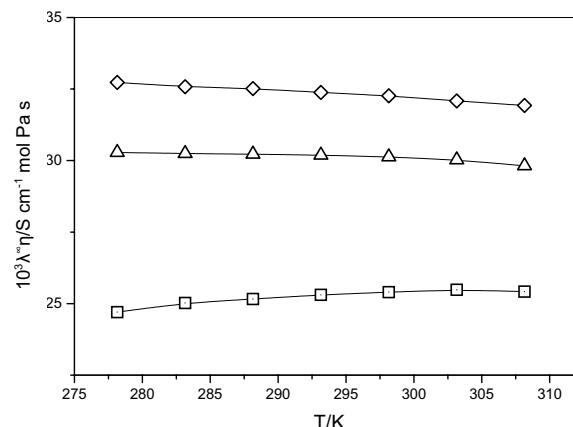
The values obtained from the measurements on the rubidium and cesium cyclohexylsulfamate solutions are in good agreement with the data published recently<sup>2</sup> whereas for saccharin and acesulfame anions no reported data were found in the literature.

From the Walden rule<sup>7</sup>

$$\lambda^\infty(T)\eta(T) = \frac{Fe_o|z|}{6\pi r} \quad (5)$$

the hydrodynamic radii  $r$  could be estimated ( $F$  is the Faraday constant and  $z$  the ionic charge). Figure 3 represents the corresponding Walden products  $\lambda^\infty(T)\eta(T)$  as a function of temperature for all investigated ions. All hydrodynamic radii are collected in Table 5.

As already discussed<sup>2,16</sup> comparison of the values of the hydrodynamic radii and the crystal radii of cations shows large differences for  $\text{Li}^+$  and  $\text{Na}^+$  ions, whereas the ion-size parameters of  $\text{K}^+$  are close together.  $\text{Cs}^+$  and  $\text{Rb}^+$  ions, however, exhibit perceivable lower values of the hydrodynamic radii. An inspection of the Table 5



**Figure 3.** The temperature dependence of the Walden products of cyclohexylsulfamate (□), acesulfame (◇) and saccharin anion (△) in water.

**Table 5.** Hydrodynamic radii,  $r$ , of ions in water from Walden's rule as a function of temperature<sup>a</sup>

T	$r$						
	$\text{Na}^+$	$\text{K}^+$	$\text{Rb}^+$	$\text{Cs}^+$	$\text{Cy}^-$ <sup>b</sup>	$\text{Sac}^-$	$\text{Ace}^-$
278.15	0.178	0.115	0.107	0.108	0.332	0.270	0.250
283.15	0.180	0.118	0.111	0.111	0.328	0.271	0.251
288.15	0.181	0.121	0.113	0.114	0.326	0.271	0.252
293.15	0.182	0.123	0.116	0.117	0.324	0.271	0.253
298.15	0.183	0.125	0.118	0.119	0.323	0.272	0.254
303.15	0.184	0.127	0.120	0.121	0.322	0.273	0.255
308.15	0.185	0.129	0.122	0.124	0.322	0.275	0.257

<sup>a</sup> Units: T, K;  $r$ , nm

<sup>b</sup> Ref.<sup>2</sup>

reveals, together with the published data for  $\text{Li}^+$ , a well known and unequivocal order of hydration values for monovalent cations  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$  although there is considerable disagreement over the actual values.<sup>17</sup>

As shown before<sup>2</sup> the obtained hydrodynamic radii for the cyclohexylsulfamate anion are in reasonable agreement with the reported crystal radius of the anion ( $r_{cy} = 0.37$  nm) and with the value obtained from volumetric properties,  $r_h = 0.334$  nm at 298.15 K<sup>4</sup> and no explicit hydration could be assumed. On the other hand the obtained radii for saccharin and acesulfame anions are distinctly different from their van der Waals and crystal radii:  $a/r = 1.20$  and 1.24 for saccharin and acesulfame anion at 298 K respectively. Similar was observed for the smaller tetraalkylammonium ions ( $a/r = 1.69, 1.42, 1.15$  for  $\text{Me}_4\text{N}^+$ ,  $\text{Et}_4\text{N}^+$ ,  $\text{Pr}_4\text{N}^+$  respectively<sup>7</sup>).

Thus, the hydrophobicity of the organic anions seems to predominate in their intrinsic hydrophilic/hydrophobic balance.

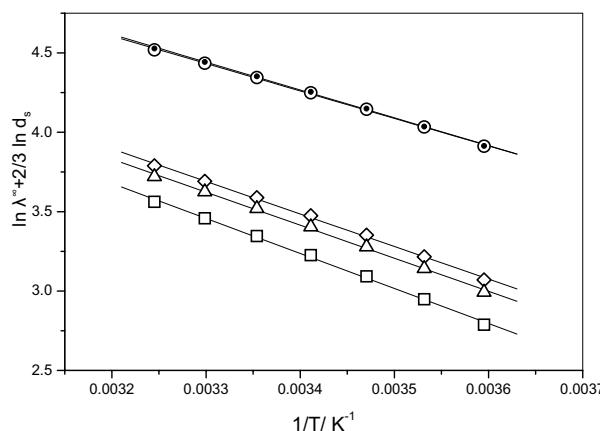
Walden rule treats the ionic migration as a movement of a rigid spherical ion through viscous continuum therefore no further information on the molecular scale transport process could be estimated.

The temperature dependence of limiting conductivity yields Eyring's enthalpy of activation of charge transport<sup>18</sup>

$$\ln \lambda^\infty + \frac{2}{3} \ln d_s = -\frac{\Delta H^*}{RT} + B \quad (6)$$

where  $B$  is the integration constant.

Values  $\Delta H^* = 16.76^2, 14.98^2, 14.568, 14.395, 18.34^2, 17.356$  and  $17.051$  kJ/mol for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Cy}^-$ ,  $\text{Sac}^-$  and  $\text{Ace}^-$  respectively (Figure 4) show that the molar ionic enthalpy of activation for the anions of all sweeteners are higher than the values for the cations.



**Figure 4.** Plot of  $\ln \lambda^\infty + \frac{2}{3} \ln d_s$  as a function of  $1/T$  for  $\text{Cs}^+$  and  $\text{Rb}^+$  ( $\circ$ ), cyclohexylsulfamate ( $\square$ ), acesulfame ( $\diamond$ ) and saccharin anion ( $\triangle$ ). From the slope the activation energy of the ionic movement,  $\Delta H^*$ , is obtained.

It has been shown that the ionic migration in a non-structures solvent is a solvent property mainly and that the difference in the mobilities of ions is simply the result of different ion sizes.<sup>19</sup> The observed differences in the Eyring's enthalpy of activation of charge transport in the investigated systems could be also ascribed to the differences in the ion sizes. In water additional strong hydrophobic interactions are presented, resulting not only in the size parameters. Therefore it could be assumed that, for the jump of the cyclohexylsulfamate, saccharinate and acesulfame anions to a prepared vacancy in the solvent - or to produce such a vacancy – a higher energy is required than for the cations investigated in this work. This could be explained by the repulsion of water molecules by the hydrophobic sites of the anions.

The observed order of the molar ionic enthalpy of activation for the cations  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$  agrees with the order of hydration values for these cations and could be explained by the energy needed for the desolvation and rearrangement of water molecules in the vicinity of the ion and it depends on the expressed hydration.

## 5. Conclusion

Investigated sweeteners, i.e. rubidium and cesium cyclohexylsulfamates, potassium acesulfame and sodium saccharin are completely dissociated in water solutions. The anions are weakly hydrated due to its hydrophobicity, whereas the hydration of cations depends on their charge densities.

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## Povzetek

Izmerili smo električno prevodnost razredčenih vodnih raztopin rubidijevega in cezijevega cikloheksilsulfamata, natrijevega saharina in kalijevega acesulfama v temperaturenem območju med 5 in 35 °C v območju koncentracij med  $0.0003 \leq c / \text{mol dm}^{-3} \leq 0.01$ . Na osnovi kemijskega modela smo določili vrednosti molskih prevodnosti pri neskončnem razredčenju,  $\Lambda^\infty$ , ter konstante asociacije ionov,  $K_a$ , v posameznem sistemu. S pomočjo znanih vrednosti limitnih prevodnosti kationov smo ocenili limitne prevodnosti cikloheksilsulfamatnega, saharinovega in acesulfamovega aniona. Ugotovili smo, da je delež ionskih parov v raztopini zanemarljiv in preiskovanim elektrolitom v vodnih raztopinah lahko pripšemo popolno disociacijo v celotnem obravnavanem temperaturnem območju ter zanemarljivo hidratacijo anionov.