

Osmotic coefficients of aqueous solutions of potassium acesulfame, sodium saccharin, and ammonium and tetramethylammonium cyclohexylsulfamates at the freezing point of solutions

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Abstract The osmotic coefficients of aqueous solutions of potassium acesulfame (0.67 mol kg^{-1}), sodium saccharin (0.75 mol kg^{-1}), and tetramethylammonium (0.55 mol kg^{-1}) and ammonium (0.35 mol kg^{-1}) cyclohexylsulfamates were determined up to the molality indicated in parentheses. The osmotic coefficients were fitted to the Pitzer equation, and the ion interaction parameters α_1 , $\beta^{(0)}$, and $\beta^{(1)}$ were evaluated. The mean ionic activity coefficients of the solutes were calculated, and the non-ideal behaviour of the systems investigated were characterized by calculation of the excess Gibbs energy of the solution and the respective partial molar functions of solute and solvent. The partial molar excess Gibbs energies of the solutes are negative, as also are the corresponding excess Gibbs energies of their solutions, and the partial molar excess Gibbs energies of the solvent are positive and increase slightly with increasing concentrations of the solutes. The solvation ability of water was calculated from differences between the Gibbs energy of solution of water in the aqueous solutions and that of pure water, and are positive and small for all the solutes investigated, throughout the concentration ranges studied.

Keywords Osmotic coefficients · Mean ionic activity coefficients · Alternative sweeteners · Aqueous solution

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Introduction

Potassium acesulfame and sodium saccharin are two of the most widely used artificial sweetening agents in foods, beverages, and pharmaceuticals, and ammonium and tetramethylammonium cyclohexylsulfamates are interesting new potential sweetening agents. Synthetic sweeteners are considered to be non-nutritive sweeteners, because they are not metabolised by the human body and therefore do not contribute energy to the diet.

Chemoreception of sweet tastes originates in the loose and temporary binding of a sweet substance with a putative receptor [1, 2]. In such a process, weak hydrophilic forces, such as hydrogen bonds and/or hydrophobic forces are involved. The exceptional role of water in the sweetness mechanism was first recognized by Mathlouthi et al., who took into account the solute–solvent interactions in aqueous solutions of sweeteners, and the effects of sweetener molecules or ions on water structure [3]. In the past, many solution properties of aqueous artificial sweeteners have been used to interpret the ease of access of sweetener molecules or ions to the receptor site. It has been shown that the hydrophilic and hydrophobic balance and steric aspects of the molecules or ions of a sweetener can affect the mobility of water in the surroundings of the solute. Access to and orientation of a sweetener molecule or ion in the receptor microenvironment are aspects of chemoreception that need to be explained by the approaches of solution chemistry.

Accurate prediction of the thermodynamic properties of aqueous solutions has an important role in many fields, for example biological, pharmaceutical, and food-processing studies. In the past, a number of models have been developed to describe electrolyte properties, for example the Pitzer equations [4], the Bromley model [5, 6], the

Table 1 The freezing point data, osmotic coefficients, and mean ionic activity coefficients of aqueous solutions of potassium acesulfame, sodium saccharin, and tetramethylammonium and ammonium cyclohexylsulfamates at the freezing point of the solution

Acesulfame-K				Saccharin-Na			
m (mol kg ⁻¹)	θ (K)	ϕ_m	$-\ln \gamma_{\pm}$	m (mol kg ⁻¹)	θ (K)	ϕ_m	$-\ln \gamma_{\pm}$
0.02188	0.078	0.954	0.14577	0.03383	0.117	0.930	0.20846
0.05056	0.176	0.935	0.21076	0.08586	0.284	0.889	0.33058
0.12925	0.434	0.903	0.31769	0.16119	0.508	0.847	0.46304
0.30259	0.961	0.854	0.46840	0.21824	0.662	0.816	0.54169
0.46423	1.413	0.818	0.57766	0.30194	0.878	0.782	0.64068
0.51335	1.532	0.802	0.60799	0.38743	1.082	0.751	0.72903
0.59384	1.735	0.785	0.65570	0.45136	1.237	0.737	0.78870
0.66885	1.920	0.772	0.69836	0.53393	1.421	0.716	0.85883
				0.59262	1.551	0.704	0.90486
				0.66747	1.706	0.687	0.95967
				0.75215	1.874	0.670	1.10171
Tetramethylammonium cyclohexylsulfamate				Ammonium cyclohexylsulfamate			
m (mol kg ⁻¹)	θ (K)	ϕ_m	$-\ln \gamma_{\pm}$	m (mol kg ⁻¹)	θ (K)	ϕ_m	$-\ln \gamma_{\pm}$
0.05766	0.213	0.993	0.05956	0.05683	0.206	0.975	0.09090
0.10087	0.371	0.989	0.07022	0.08496	0.306	0.968	0.11074
0.15164	0.552	0.979	0.08337	0.11236	0.400	0.957	0.12701
0.20520	0.745	0.976	0.09545	0.14672	0.523	0.958	0.14356
0.25417	0.917	0.970	0.10416	0.17664	0.625	0.951	0.15500
0.30992	1.125	0.976	0.11137	0.20308	0.720	0.953	0.16312
0.35608	1.286	0.971	0.11531	0.23291	0.827	0.955	0.17043
0.40594	1.468	0.972	0.11771	0.26173	0.923	0.948	0.17585
0.46888	1.704	0.977	0.11834	0.30629	1.087	0.954	0.18161
0.55989	2.041	0.980	0.11518	0.35714	1.265	0.952	0.18497

NRTL model [7], and the SIT model [8]. Among these, the Pitzer model is the most widely used semi-empirical model, and it takes into account short-range interactions between ions.

In this study, the Pitzer ion interaction parameters have been evaluated from osmotic coefficient data of aqueous solutions of potassium acesulfame, sodium saccharin, and ammonium and tetramethylammonium cyclohexylsulfamates at the freezing point of solutions. From the results obtained, the non-ideal behaviour of the solutions investigated was characterized by calculation of the excess Gibbs energies of the solutions, and those of the solutes and solvent. Furthermore, differences between the Gibbs energy of solvation of water in the solutions and that of pure water were estimated.

Results and discussion

The molalities m (mol kg⁻¹) and the freezing-point depression θ (K) of the aqueous solutions investigated are

given in Table 1. The osmotic coefficient on a molality basis ϕ_m was calculated from the freezing point data by use of the relationship shown in Eq. 1 where the higher terms were omitted because of the uncertainty of the osmotic coefficient [9] (see below):

$$\phi_m = \frac{\Delta_{\text{fus}}H_{T_m}^{\theta}}{vmM_{\text{H}_2\text{O}}RT_m^2}\theta \quad (1)$$

where $M_{\text{H}_2\text{O}}RT_m^2/\Delta_{\text{fus}}H_{T_m}^{\theta} = 1.8598 \text{ K kg mol}^{-1}$, is the ideal freezing point depression constant, and v is the number of ions into which the electrolyte dissociates. The osmotic coefficients ϕ_m are given in Table 1. The uncertainties of the osmotic coefficient $\delta\phi_m$ were evaluated by use of Eq. 2, and seen to be smaller than 0.003:

$$(\delta\phi_m)^2 = \left(\frac{1}{1.8598vm}\right)^2 (\delta\theta)^2 \quad (2)$$

From Table 1, it can be seen that the osmotic coefficients ϕ_m of sodium saccharin and potassium acesulfame solutions are relatively low, and decrease with increasing molality, whereas the osmotic coefficients of tetramethylammonium

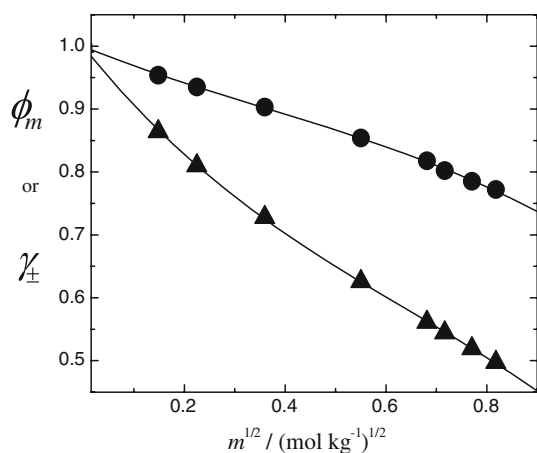


Fig. 1 Osmotic coefficients of aqueous solutions of potassium acesulfame (filled circles) and mean ionic activity coefficient of potassium acesulfame (filled triangles) at the freezing point of the solution. The full lines are drawn on the basis of Eqs. 3 and 7

and ammonium cyclohexylsulfamates are high, and at the higher concentrations they increase with increasing concentrations. As an example, Fig. 1 shows the concentration dependence of the osmotic coefficient of an aqueous solution of potassium acesulfame.

From conductometric data, it follows that the solutes under investigation are strong 1:1 electrolytes [10, 11]. The adjustable parameters of the Pitzer equation [4], which for dilute aqueous solutions of 1:1 electrolytes takes the form shown in Eq. 3, were fitted to experimentally obtained osmotic coefficients.

$$\phi_m = 1 + f^{(\phi_m)} + mB^{(\phi_m)} \quad (3)$$

where:

$$f^{(\phi_m)} = -A^{(\phi_m)} \frac{m^{1/2}}{1 + bm^{1/2}} \quad (4)$$

and:

$$B^{(\phi_m)} = \beta^{(0)} + \beta^{(1)} \exp(-\alpha_1 m^{1/2}) \quad (5)$$

In Eq. 4, $A^{(\phi_m)}$ is the Debye–Hückel constant, and b is a parameter of $1.2 \text{ (kg mol}^{-1}\text{)}^{1/2}$ for aqueous solutions. The $B^{(\phi_m)}$ term in Eq. 5 is a slowly varying function of molality that takes into account short-range ion–ion interactions. The constant $\beta^{(0)}$ in Eq. 5 is often correlated with structure-making and structure-breaking effects. The parameters $\beta^{(0)}$, $\beta^{(1)}$, and α_1 are obtained from experimental data.

In fitting procedures of osmotic coefficients with Eq. 3, we used a value of $A^{(\phi_m)} = 0.37642 \text{ (kg mol}^{-1}\text{)}^{1/2}$ for the Debye–Hückel constant [12], and $b = 1.2 \text{ (kg mol}^{-1}\text{)}^{1/2}$ for a temperature-independent parameter [13] which was proposed by Pitzer and Mayogra [4] for aqueous 1:1 electrolyte solutions. We obtained parameters $\beta^{(0)}$, $\beta^{(1)}$, and

Table 2 Parameters $\beta^{(0)}$, $\beta^{(1)}$, and α_1 of Eq. 5 for aqueous solutions of sodium saccharin (Sac-Na), potassium acesulfame (Ace-K), and tetramethylammonium ((CH₃)₄NCy) and ammonium cyclohexylsulfamate (NH₄Cy)

Solute	$\beta^{(0)}$ (kg mol ⁻¹)	$\beta^{(1)}$ (kg mol ⁻¹)	α_1 (kg mol ⁻¹) ^{1/2}	s
Ace-K	-0.153 ± 0.008	0.34 ± 0.05	2.59	0.005
Sac-Na	-1.34 ± 0.08	0.93 ± 0.07	-0.2	0.004
(CH ₃) ₄ NCy	0.204 ± 0.004	4.45 ± 0.05	6.69	0.002
NH ₄ Cy	0.226 ± 0.001	5.38 ± 0.09	9.46	0.003

s , Standard deviation at the freezing point of the solutions

α_1 in Eq. 5 by optimizing fitting equation parameters to the experimental data. The values obtained are given in Table 2. The value of parameter α_1 is substantially higher than 2.0, which was the value used for simple 1:1 electrolyte solutions [14]. As was pointed out by Pitzer [14], the value of parameter α_1 can be adjusted for each substance, if desired. The parameter $\beta^{(0)}$ is negative for potassium acesulfame and sodium saccharin, in agreement with their structure-breaking effects [15], whereas for tetramethylammonium and ammonium cyclohexylsulfamate, the parameter $\beta^{(0)}$ is positive, because of their effects on the structure of water [16]. The $\beta^{(1)}$ parameter is relatively small for potassium acesulfame and sodium saccharin, whereas for tetramethylammonium and ammonium cyclohexylsulfamate it is high.

The overall quality of the fit was expressed as the corresponding standard deviation shown in Eq. 6:

$$s = \pm \left[\frac{(\phi_{m(\text{exp})} - \phi_{m(\text{cal})})}{n} \right]^{1/2} \quad (6)$$

where $\phi_{m(\text{exp})}$ and $\phi_{m(\text{cal})}$ denote the experimental and calculated osmotic coefficients, and n is the number of experimental data. The standard deviation of the fit is given in Table 2. For the fit of the data of potassium acesulfame and sodium saccharin, the standard deviation is about two standard deviations of the experimental values of ϕ_m , whereas for tetramethylammonium and ammonium cyclohexylsulfamates the standard deviations are the same as those for their experimental data. Marshall et al. [17] showed that for a small molality range the experimental data by the Pitzer relationship [4] provides the best fit although the parameters obtained for small molality ranges do not necessarily result in good prediction at higher molality.

The mean ionic activity coefficient of the solute γ_{\pm} was calculated from Eq. 7 [4]:

$$\ln \gamma_{\pm} = f^{(\gamma)} + mB^{(\gamma)} \quad (7)$$

where:

$$f^{(\gamma)} = -A^{(\phi_m)} \left[\frac{m^{1/2}}{1 + bm^{1/2}} + \frac{2}{b} \ln(1 + bm^{1/2}) \right] \quad (8)$$

and:

$$B^{(\gamma)} = 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha_1^2 m} \left[1 - \exp(-\alpha_1 m^{1/2}) \left(1 + \alpha_1 m^{1/2} - \frac{1}{2} \alpha_1^2 m \right) \right] \quad (9)$$

The calculated values of $\ln \gamma_{\pm}$ are given in Table 1, and for potassium acesulfame they are illustrated in Fig. 1. The $\ln \gamma_{\pm}$ values decrease with increasing solute molality, and show similar concentration dependence to that seen for the osmotic coefficients. The values for tetramethylammonium and ammonium cyclohexylsulfamates are low, whereas the values for potassium acesulfame and sodium saccharin are substantially higher.

The non-ideal behaviour of the aqueous solutions of the salts investigated was further characterized according to the excess Gibbs energy of solution G^E . From the mean ionic activity coefficient and osmotic coefficient, the excess Gibbs energy of solution per kilogram of solvent is given by Eq. 10 [14]:

$$G^E = 2mRT(1 - \phi_m + \ln \gamma_{\pm}) = RT \left(f^{(G^E)} + 2m^2 B^{(G^E)} \right) \quad (10)$$

where:

$$f^{(G^E)} = -A^{(\phi_m)} \left(\frac{4m}{b} \right) \ln(1 + bm^{1/2}) \quad (11)$$

and:

$$B^{(G^E)} = \beta^{(0)} + \frac{2\beta^{(1)}}{\alpha_1^2 m} \left[1 - \exp(-\alpha_1 m^{1/2}) \left(1 + \alpha_1 m^{1/2} \right) \right] \quad (12)$$

Table 3 Excess Gibbs energies of solution, partial specific excess Gibbs energies of the solvent and the solute, and the differences in the Gibbs energy of solvation of water molecules at the freezing point of the solution

Acesulfame-K					Saccharin-Na				
m (mol kg ⁻¹)	$-G^E$ (J kg ⁻¹)	$n_1 G_1^E$ (J kg ⁻¹)	$-m G_2^E$ (J kg ⁻¹)	$\Delta \Delta G_1^*$ (J mol ⁻¹)	m (mol kg ⁻¹)	$-G^E$ (J kg ⁻¹)	$n_1 G_1^E$ (J kg ⁻¹)	$-m G_2^E$ (J kg ⁻¹)	$\Delta \Delta G_1^*$ (J mol ⁻¹)
0.02188	10	5	15	-5	0.03383	21	11	32	0.3
0.05056	34	15	48	-0.3	0.08586	85	44	129	13
0.12925	130	57	187	12	0.16119	224	115	339	33
0.30259	443	201	644	41	0.21824	355	183	537	47
0.46423	828	390	1,218	67	0.30194	579	299	879	69
0.51335	960	458	1,418	75	0.38743	846	437	1,283	91
0.59384	1,191	578	1,769	88	0.45136	1,067	550	1,617	107
0.66885	1,422	700	2,122	101	0.53393	1,367	707	2,083	128
					0.59262	1,610	825	2,436	143
					0.66747	1,927	982	2,910	161
					0.75215	2,596	1,168	3,764	183
Tetramethylammonium cyclohexylsulfamate					Ammonium cyclohexylsulfamate				
m (mol kg ⁻¹)	$-G^E$ (J kg ⁻¹)	$n_1 G_1^E$ (J kg ⁻¹)	$-m G_2^E$ (J kg ⁻¹)	$\Delta \Delta G_1^*$ (J mol ⁻¹)	m (mol kg ⁻¹)	$-G^E$ (J kg ⁻¹)	$n_1 G_1^E$ (J kg ⁻¹)	$-m G_2^E$ (J kg ⁻¹)	$\Delta \Delta G_1^*$ (J mol ⁻¹)
0.05766	14	2	16	14	0.05683	17	7	24	
0.10087	26	6	32	31	0.08496	30	12	43	
0.15164	44	13	57	51	0.11236	43	22	65	
0.20520	66	23	89	71	0.14672	68	28	96	
0.25417	88	32	120	89	0.17664	85	39	124	
0.30992	116	41	157	109	0.20308	107	43	151	
0.35608	139	47	187	126	0.23291	133	48	180	
0.40594	166	51	217	144	0.26173	147	62	209	
0.46888	200	52	252	166	0.30629	189	64	253	
0.55989	248	45	293	198	0.35714	222	78	300	

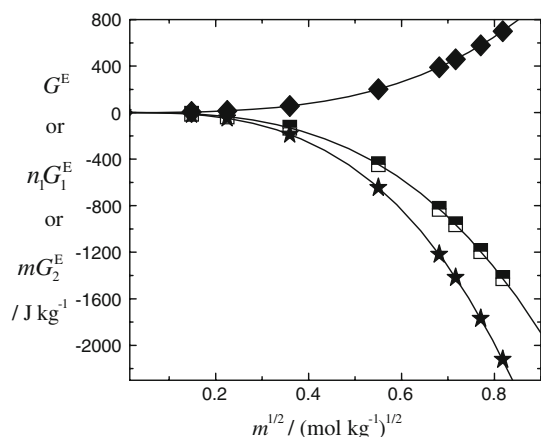


Fig. 2 The excess Gibbs energy of an aqueous solution of potassium acesulfame (white and black squares), and the partial excess Gibbs energy of water (filled rhombuses) and of potassium acesulfame (filled stars) at the freezing point of the solution

The calculated values of G^E are given in Table 3, and are shown in Fig. 2 as an example for an aqueous solution of potassium acesulfame. As can be seen, the values of G^E are negative and show the same tendency for non-ideal behaviour as the osmotic and mean ionic activity coefficients. The negative sign of the excess Gibbs energy comes from non-structural interactions through hydrophobic interactions of anions of the salts investigated, which are largely responsible for this behaviour.

The excess Gibbs energy of solution can also be given by Eq. 13 [18]:

$$G^E = n_1 G_1^E + m G_2^E \quad (13)$$

where n_1 represents the number of moles of solvent per kilogram of solvent, M_1 (g mol^{-1}) is the molar mass of the solvent, G_1^E (J mol^{-1}) is the partial specific excess Gibbs energy of the solvent, and G_2^E (J mol^{-1}) is the partial molar excess Gibbs energy of the solute. G_2^E can be calculated according to Eq. 14 [18, 19]:

$$G_2^E = \left(\frac{\partial G^E}{\partial m} \right)_{n_1, T, p} = 2RT \ln \gamma_{\pm} = 2RT [f^{(\gamma)} + mB^{(\gamma)}] \quad (14)$$

and G_1^E according to Eq. 15:

$$G_1^E = 2M_1 m RT (1 - \phi_m) = -2M_1 m RT [f^{(\phi_m)} + mB^{(\phi_m)}] \quad (15)$$

The values of the products $n_1 G_1^E$ and $m G_2^E$ are given in Table 3, and as an example for aqueous solutions of potassium acesulfame they are shown in Fig. 2. From the collected data in Table 3 it can be seen that the $m G_2^E$ values are negative for all of the solutes, like G^E , i.e. they decrease with the increasing molality of the solute. In contrast, the $n_1 G_1^E$ values are positive and low, and increase with the increasing molality of the solute.

The solvation ability of water can be obtained by the approach of Ben-Naim [20]. The difference between the Gibbs energy of solvation of water molecules in solution and that of pure water $\Delta \Delta G_1^*$ (J mol^{-1}) is given by Eq. 16:

$$\Delta \Delta G_1^* = \Delta G_1^{*1} - \Delta G_1^{*p} = RT \ln \left(\frac{\rho_1^p a_1}{\rho_1^l} \right) \quad (16)$$

where ΔG_1^{*1} and ΔG_1^{*p} are the Gibbs energies of solution 1 and of pure water, p , ρ_1^p is the number density of water in the pure solvent (molecules/cm^3), ρ_1^l is the number density of water, and a_1 is the activity of water in solution. The term ρ_1^p/ρ_1^l was obtained from the respective densities and expansibility of water [21] and aqueous solutions of sodium saccharin and potassium acesulfame [15], and for tetramethylammonium cyclohexylsulfamate from Refs. [22, 23]. The values of $\ln a_1$ were calculated from Eq. 17:

$$\ln a_1 = -\nu m M_1 \phi_m \quad (17)$$

where $\nu = 2$.

The calculated values of $\Delta \Delta G_1^*$ (J mol^{-1}) are given in Table 3, except for ammonium cyclohexylsulfamate. From Table 3, it follows that the $\Delta \Delta G_1^*$ values are positive and small, and increase with increasing concentrations of the solute. However, there are significant differences between $\Delta \Delta G_1^*$ for the solutes investigated. For example, at $m^{1/2} = 0.600$ (mol kg^{-1})^{1/2}, the values of $\Delta \Delta G_1^*$ are presented in Table 4, together with the values of the osmotic coefficients and the excess Gibbs energies of the solvent.

According to Ben-Naim [20], it is not possible to state categorically whether the observed effects on $\Delta \Delta G_1^*$ are because of direct solute–solvent interactions or indirect changes in the structure of the solvent environment that are induced by addition of the solute. Because the ΔG_1^{*p} of water as a pure liquid at 0 °C is negative, $\Delta G_1^{*p} = -27.792$ kJ mol^{-1} [20], we can conclude that the addition of one of the solutes under investigation makes the Gibbs energy of solvation of water in solution, ΔG_1^{*1} , less negative than in pure water. The major reason for this seems to be the overall weakening of the average binding energy of water molecules to their surroundings when one of the solutes under investigation is added to the solvent.

Table 4 Differences between the Gibbs energy of solvation of water molecules, the osmotic coefficients, and the partial specific Gibbs energies of water at molality $m^{1/2} = (0.600 \text{ mol kg}^{-1})^{1/2}$ at the freezing point of the solutions

Solute	$\Delta \Delta G_1^*$ (J mol^{-1})	ϕ_m	ΔG^E (J mol^{-1})
NH_4Cy	–	0.956	1.4
$(\text{CH}_3)_4\text{NCy}$	127.4	0.972	0.8
Ace-K	49.9	0.837	5.2
Sac-Na	83.5	0.761	7.1

From Table 4 it can be seen that ammonium and tetramethylammonium cyclohexylsulfamates differ in all of the thermodynamic parameters investigated from those of potassium acesulfame and sodium saccharin. The differences observed can be explained by the structure of the ions. The short-range solvating properties of the anions investigated can be considered according to the sign of the difference between the partial molar ionic volume $\bar{V}_{\text{ion}}^{\circ}$ and the van der Waals volume of the ion V_W [24]. When this difference is negative, the ion is classified as an electrostatic “positive-solvating ion”, and when this difference is positive, the ion is classified as a “negative-solvating ion”. This quantity, i.e. $(\bar{V}_{\text{ion}}^{\circ} - V_W)$, is positive for saccharin and acesulfame nitranions, which means that both of these ions are negative solvating ions [15]. In contrast, for the cyclohexylsulfamate ion, the difference is negative, as $(\bar{V}_{\text{ion}}^{\circ} - V_W) = -(4.4 \pm 0.7) \text{ cm}^3 \text{ mol}^{-1}$ [22, 23], and the cyclohexylsulfamate ion is therefore classified as a “positive-solvating ion”.

According to this view, the nitranions of saccharin and acesulfame disorganize the bulk water structure while organizing a portion of the solvent water by attraction of the nitranions of the water molecules. It has been shown that the average hydration number of the nitranions investigated is about 2.0, i.e. two molecules of water are bound for each 3-oxo-3H-benzisothiazolyl group [15]. The cyclohexylsulfamate ion is weakly hydrated because of its hydrophobicity [23]. The interaction with water molecules of this ion, which has a large hydrophobic surface and its negative charge distributed unequally over the whole group, as just over three oxygen atoms, proceeds as a subtle balance between the hydrophobic and hydrophilic characteristics of the ion.

Experimental

Materials

Potassium acesulfame was obtained from Fluka (Acesulfame-K, Ace-K, puriss, $\geq 99.0\%$) and used without further purification. Sodium saccharin (Saccharin-Na, Sac-Na) was purchased from Merck (dehydrate purum, $\geq 99.0\%$). By thermogravimetric analysis (Mettler Toledo TGA/SDTA 851e), the amount of water of crystallization in the Saccharin-Na was 1.55 ± 0.01 . Ammonium cyclohexylsulfamate (NH_4Cy) and tetramethylammonium cyclohexylsulfamate ($(\text{CH}_3)_4\text{NCy}$) were obtained by careful neutralization of cyclohexylsulfamic acid (purchased from Sigma) with the corresponding bases (Fluka). After repeated recrystallization from water, the purities of the cyclohexylsulfamates were checked by analysis of the elements C, H, and N (Perkin-Elmer, 2400 Series II CHNS/O Analyzer) and also by ion

exchange of the cations of the salts with the hydrogen ion (Dowex, Type 50 WX8). Purity 99.9 % was determined. The salts were kept in a vacuum desiccator over P_2O_5 .

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

Freezing point measurements

Freezing point depression was measured with a Knauer cryoscopic unit (model 731240000, equipped with a strip chart recorder, Knauer Model 733.41). The solvent and the solutions were supercooled and the formation of ice crystals was initiated by internal vibrations. Freezing-point depression was recorded as the difference between the resistance of the thermistor Δr (arbitrary scale) for solvent and solution. The reproducibility of these Δr measurements was better than 0.5% of the measurement scale. The instrument was calibrated with sodium chloride solutions [25] of accurately known molality over the same freezing-point range as for the solutions investigated, and the calibration was checked before and after each run. The freezing-point data of the sodium chloride solution were smoothed using the Lagrange interpolation method. The relationship obtained was: $\theta = k \cdot \Delta r$, where θ is the freezing point depression and k is the calibration constant. The overall accuracy of the freezing-point depression of sodium chloride solution was $\pm 0.005 \text{ K}$.

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