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Apparent Molar Volume and Apparent Molar Expansibility of Tetraethyl-, Tetra-n-propyl-, Tetra-n-butyl-, and Tetra-n-pentylammonium Cyclohexylsulfamates in Aqueous Solution[†]

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[†]Dedicated to Prof. Dr. Jože Škerjanc on the occasion of his 70th birthday

Abstract

The apparent molar volume of tetraethyl-, tetra-n-propyl-, tetra-n-butyl, and tetra-n-pentylammonium cyclohexylsulfamates 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. From the apparent molar volume the partial molar volume of the salts and water was determined. The limiting apparent molar volume and apparent molar expansibility were apportioned into their ionic components. The limiting apparent molar volume of the salts was found to be a linear function of the cation molecular weight. The partial molar ionic volumes at infinite dilution were treated by a model proposed by *Marcus*. From the second derivative of the limiting apparent molar volume with temperature it was found that the investigated solutes behave as structure-making ones in water. The packing density of the ions in solution were evaluated and compared with the corresponding data for tetra-n-alkylammonium halides. The density of aqueous solutions of the investigated salts can be adequately represented by an equation derived by *Redlich*.

1. Introduction

Aqueous solutions of tetra-n-alkylammonium salts are of great interest because of their anomalous properties. Their physicochemical properties such as activity coefficients, partial molar volumes, viscosity, and electrical conductivity are quite different from those of most simple electrolytes.[1] It is well known that tetra-n-alkylammonium salts dissolved in water undergo hydrophobic hydration with the formation of a more ordered and rigid structure of water surrounding the ions. Therefore, tetra-n-alkylammonium salts have been and still are extensively used as model systems for the characterization of hydrophobic hydration and various types of interactions. From the valuable literature data, e. g.,[2–4] it follows that tetra-n-alkylammonium ions do not form strong hydrogen bonds with water molecules in solution, nor do they exhibit strong electrostatic interactions. Volumetric studies of such electrolyte solutions can provide useful information

concerning ion-solvent, ion-ion, and solvent-solvent interactions.[3] From a theoretical point of view, the most useful thermodynamic quantities are the limiting values of the apparent molar volume and the apparent molar expansibility since these values depend on the intrinsic size of the ion and on ion-solvent interactions. So, the ion-solvent interactions manifest themselves in all molar functions obtained by extrapolation to infinite dilution.[5]

The present work deals with the apparent molar volumes and expansibilities of dilute aqueous solutions of some lower numbers of the tetra-n-alkylammonium cyclohexylsulfamates, i. e. with salts where both of the ions, cation and anion, undergo hydrophobic hydration. Through this study we extended our knowledge of the volumetric properties of cyclohexylsulfamates as potential artificial sweeteners.[6,7] The partial molar and apparent molar volumes of various solutes have been used in the past in accessing drug potency and in sweet taste chemoreception, e. g.[8–10] With this in mind, we determined some volumetric properties of tetra-n-alkylammonium cyclohexylsulfa-

mates which can provide an important insight into the interactions of sweet solutes with water and perturbation effects on the structure of water.

2. Results and Discussion

The values of density, d (kg dm^{-3}) of all investigated salts are given in Table 1 as a function of the temperature-independent molalities, m (mol kg^{-1}). The apparent molar volume, V_Φ(dm^3 mol^{-1}), of a solute with molar mass, M_2 (kg mol^{-1}), was calculated from the relation[11]

$$V_\Phi = \frac{(d_o - d)}{cd_o} + \frac{M_2}{d_o} \tag{1}$$

where d_0 is the density of pure water (kg dm^{-3}) and c is the concentration of the salt (mol dm^{-3}) calculated from $c = md/(1 + mM_2)$. In calculation of the uncertainty of the apparent molar volume, δV_Φ, only the uncertainty in density measurement was taken into account since V_Φ is not seriously influenced by errors in molarity:

$$\left(\delta V_\Phi\right)^2 = \left(-\frac{1}{cd_o}\right)^2 \left(\delta d\right)^2 \tag{2}$$

The relative error of the apparent molar volume is about 1 per cent at the lowest concentration and 0.1 per cent at the highest concentration. In Fig. 1 the values of V_Φ of Et$_4$NCy are plotted against $c^{1/2}$ at 293.15, 313.15 and 333.15 K; the values of V_Φ of the other salts give similar plots. From Fig. 1 it can be seen that deviations in V_Φ are more pronounced at lower temperature. In dilute solutions V_Φ values of the salts investigated decrease at all temperatures with increase of the square root of the molar concentration. It has been established that, except for the tetramethylammonium salts, plots of V_Φ against $c^{1/2}$ show negative slopes, indicating a type of behaviour not normally associated with 1:1 electrolytes.[12]

The dependence of V_Φ on the square root of molarity at a definite temperature was fitted with an equation of the

$$V_\Phi = V_\Phi^o + A_1 c^{1/2} + A_2 c + A_3 c^{3/2} \tag{3}$$

type where V_Φ^o represents the apparent molar volume of the salt at infinite dilution, equal to the limiting partial molar volume of the salt, $\bar{V}_2^o$ (dm^3 mol^{-1}), A_1, A_2 and A_3 are empirical constants which depend on the salt, solvent and temperature. In calculation of the empirical constants we considered also the V_Φ^o values calculated from the sum of the limiting conventional partial molar ionic volumes of the tetra-n-alkylammonium ions at the relevant temperature. The V_Φ^o values for temperatures other than 273.15 K, 298.15 K and 323.15 K were obtained by analytical interpolation to *Millero*'s data[3] and the cyclohexylsulfamate ion from ref.[7] For n-Pe$_4$N$^+$ ion we used the average value

(0.3996 dm^3 mol^{-1}) at 298.15 K given in refs.[3, 12] The conventional limiting partial molar ionic volume of the n-Pe$_4$N$^+$ ion at other temperatures, calculated from the difference between V_Φ^o and $\bar{V}_{Cy^-}^o$, is given in Table 2.

To represent the experimental data adequately for Et$_4$NCy we used three and for the other salts only two empirical constants in rel. (3). The regression values of V_Φ^o and the empirical constants of rel. (3), together with the standard error of the estimate, s_v are given in Table 2. As can be seen from this Table, the sign of the limiting slope, A_1, is negative for all investigated salts. It is interesting to note that aqueous solutions of Me$_4$NCy studied previously[6] follow the limiting *Debye-Hückel* law. Furthermore, the limiting slope increases with increasing size of the R$_4$N$^+$ ion. However, the effect of temperature on the limiting slope is different. So, $\partial A_1/\partial T$ at 298.15 K is negative for Et$_4$NCy, n-Pr$_4$NCy and n-Bu$_4$NCy, while for n-Pe$_4$NCy it is positive. In recent years many investigators have studied the V_Φ values of tetra-n-alkylammonium salts in aqueous solution and they have shown that these salts have large negative deviations from the limiting slope, e. g. [12, 13, 14] On the contrary, *Franks* and *Smith*[15] determined V_Φ values of some tetra-n-alkylammonium salts in dilute aqueous solutions and showed that V_Φ values approach limiting behaviour (a positive limiting slope) in extremely dilute solutions in accordance with the *Debye-Hückel* law. From these it may be concluded that for such systems in extremely dilute range, c < 0.01 mol dm^{-3}, the initial slope being positive.

The values of V_Φ^o and the empirical constants of rel. (3) obtained were tested by a *Redlich* type of equation[16] which follows from the combination of rel.(1) and 3)

$$d = d_o + \left(M_2 - V_\Phi^o d_o\right)c - A_1 d_o c^{3/2} - A_2 d c^2 - A_3 d_o c^{5/2} \tag{4}$$

In calculation of the density via rel. (4), the last term was used only for Et$_4$NCy solutions. The calculated densities are, within experimental uncertainty, equal to those given in Table 1. From the standard deviation, s_d presented

$$s_d = \pm \left[\frac{\sum\left(d_{exp} - d_{cal}\right)^2}{n-1}\right]^{1/2} \tag{5}$$

in Table 2, it follows that the parameters (rel. 3) obtained correctly represent the experimental density data.

The partial molar volume of solute, $\bar{V}_2$ (dm^3 mol^{-1}) and solvent, $\bar{V}_1$ (dm^3 mol^{-1}) were computed from V_Φ by the following relations:[11]

$$\bar{V}_2 = V_\Phi + \left[\frac{1 - cV_\Phi}{2 + c^{3/2}\left(\partial V_\Phi / \partial c^{1/2}\right)}\right]c^{1/2}\left(\partial V_\Phi / \partial c^{1/2}\right) \tag{6}$$

and

$$\bar{V}_1 = \left[\frac{2}{2 + c^{3/2}\left(\partial V_\Phi / \partial c^{1/2}\right)}\right]V_1^o \tag{7}$$

Table 1. Density of aqueous solutions of tetraethyl- (Et$_4$NCy), tetra-n-propyl- (n-Pr$_4$NCy), tetra-n-butyl- (n-Bu$_4$NCy), and tetra-n-pentylammonium (n-Pe$_4$NCy) cyclohexylsulfamates at the indicated molalities and temperatures.

| m (mol kg^{-1})	d (kg dm^{-3}) at T (K)					
	293.15	298.15	303.15	313.15	323.15	333.15
	Et$_4$NCy					
0.00499	0.99840	0.99724	0.99584	0.99240	0.98822	0.98337
0,01036	0.99862	0.99746	0.99605	0.99261	0.98842	0.98357
0,01498	0.99881	0.99764	0.99624	0.99278	0.98859	0.98375
0,02026	0.99902	0.99786	0.99645	0.99299	0.98879	0.98392
0.02506	0.99923	0.99805	0.99664	0.99317	0.98897	0.98410
0.03037	0.99945	0.99827	0.99685	0.99338	0.98917	0.98429
0.05074	1.00028	0.99909	0.99766	0.99416	0.98992	0.98503
0.06100	1.00072	0.99950	0.99806	0.99454	0.99029	0.98539
0.07128	1.00114	0.99992	0.99847	0.99493	0.99067	0.98575
0.07514	1.00130	1.00007	0.99862	0.99508	0.99081	0.98589
0.08124	1.00156	1.00031	0.99885	0.99532	0.99104	0.98609
0.10049	1.00235	1.00109	0.99961	0.99604	0.99174	0.98679
0.12458	1.00332	1.00205	1.00055	0.99694	0.99261	0.98763
	n-Pr$_4$NCy					
0.02635	0.99897	0.99778	0.99636	0.99289	0.98867	0.98379
0.05031	0.99967	0.99847	0.99702	0.99352	0.98926	0.98434
0.07657	1.00046	0.99923	0.99776	0.99420	0.98990	0.98495
0.10035	1.00117	0.99991	0.99842	0.99481	0.99048	0.98549
0.12618	1.00194	1.00065	0.99914	0.99549	0.99110	0.98607
0.15169	1.00271	1.00139	0.99985	0.99614	0.99172	0.98664
0.17753	1.00348	1.00214	1.00056	0.99681	0.99233	0.98722
0.19408	1.00398	1.00260	1.00101	0.99721	0.99271	0.98757
0.25226	1.00568	1.00428	1.00262	0.99870	0.99405	0.98884
	n-Bu$_4$NCy					
0.02701	0.99885	0.99765	0.99621	0.99271	0.98846	0.98357
0.05166	0.99943	0.99820	0.99673	0.99316	0.98885	0.98391
0.07686	1.00003	0.99876	0.99726	0.99363	0.98926	0.98425
0.10195	1.00063	0.99932	0.99778	0.99409	0.98966	0.98459
0.12777	1.00126	0.99992	0.99833	0.99456	0.99006	0.98492
0.14773	1.00175	1.00037	0.99876	0.99493	0.99038	0.98519
0.17718	1.00246	1.00103	0.99937	0.99545	0.99081	0.98555
0.20069	1.00304	1.00156	0.99986	0.99587	0.99117	0.98585
0.22877	1.00374	1.00220	1.00046	0.99637	0.99159	0.98620
0.25358	1.00434	1.00276	1.00097	0.99680	0.99195	0.98649
0.28523	1.00512	1.00348	1.00162	0.99733	0.99238	0.98685
0.34975	1.00672	1.00493	1.00294	0.99842	0.99327	0.98757
	n-Pe$_4$NCy					
0.00450	0.99828	0.99711	0.99571	0.99227	0.98807	0.98322
0.01128	0.99840	0.99722	0.99581	0.99234	0.98813	0.98325
0.01567	0.99847	0.99729	0.99587	0.99239	0.98817	0.98328
0.02033	0.99855	0.99737	0.99594	0.99245	0.98820	0.98330
0.02709	0.99868	0.99748	0.99604	0.99252	0.98826	0.98333
0.03022	0.99874	0.99753	0.99609	0.99256	0.98829	0.98335
0.03494	0.99882	0.99761	0.99616	0.99261	0.98832	0.98338
0.04131	0.99895	0.99772	0.99625	0.99269	0.98838	0.98341
0.04795	0.99907	0.99783	0.99635	0.99277	0.98843	0.98344
0.05259	0.99917	0.99792	0.99643	0.99282	0.98847	0.98347
0.06193	0.99936	0.99808	0.99657	0.99293	0.98855	0.98351
0.06576	0.99943	0.99815	0.99663	0.99298	0.98858	0.98353
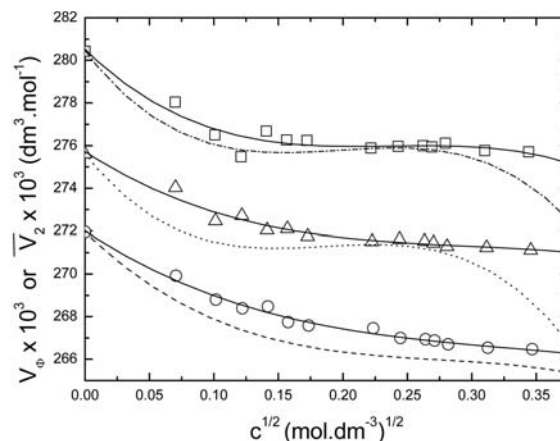
Figure 1. Dependence of apparent and partial molar volume of Et$_4$NCy on square root of molar concentration; apparent molar volume: 293.15 K –, 313.15 K 8, 333.15 K∀. The full lines are calculated using the rel. (3) and respective parameters given in Table 2; partial molar volume: 293.15 K – – – –, 313.15 K · · · · and 333.15 K – · – · –; the lines were calculated according to rel. (9) using the parameters given in Table 2.

where V_1^o is the molar volume of water and $\partial V_\Phi/\partial c^{1/2}$, according to rel. (3), is given as

$$\partial V_\Phi / \partial c^{1/2} = A_1 + 2A_2 c^{1/2} + 3A_3 c \qquad (8)$$

where the last term of rel. (8) was used only for Et$_4$NCy. The partial molar volumes of the salts are compiled in Table 3 as a function of temperature-independent molalities, m and presented in Fig. 1 for Et$_4$NCy at three temperatures. At low solute concentration the error caused by neglecting the concentration terms within the square brackets of rels. (6) and (7) is less than 1×10^{-4} dm^3 mol^{-1} for $\bar{V}_2$ and 5×10^{-5} dm^3 mol^{-1} for $\bar{V}_1$ and the values of square brackets are close to 0.5 (rel. 6) and 1.0 (rel. 7). Taking into account rels. (3), (6) and (8), the partial molar volume of solute can be given at low solute concentration as

$$\bar{V}_2 = V_\Phi^o + 1.5 A_1 c^{1/2} + 2.0 A_2 c + 2.5 A_3 c^{3/2} \qquad (9)$$

where the last term is used only for Et$_4$NCy. For the solutions investigated rel. (9) is valid over the entire concentration range used for Et$_4$NCy and n-Pe$_4$NCy, while for n-Pr$_4$NCy and n-Bu$_4$NCy the upper concentration at which rel. (9) can be used gradually increases with increasing temperature; at 293.15, 298.15 and 303.15 K the upper concentration is about 0.150 mol dm^{-3}, at 313.15 K it is 0.200 mol dm^{-3} and at 323.15 and 333.15 K rel. (9) is valid up to the maximal concentration used. For simple 1:1 electrolytes the upper limit of validity of rel. (9) is about 1.0 mol dm^{-3}.[11]

The partial molar volume of the solvent in the whole concentration and temperature range studied was found to be close to the molar volume of water at a definite temperature within $\pm 5 \times 10^{-5}$ dm^3 mol^{-1}. The $\bar{V}_1$ values of some

Table 2. Limiting apparent molar volume, V_Φ^o empirical constants of rel. (3), standard error of estimate, s_v, and standard deviation of density, s_d, of tetraethyl- (Et$_4$NCy), tetra-n-propyl-(n-Pr$_4$NCy), tetra-n-butyl- (n-Bu$_4$NCy), and tetra-n-pentylammonium (n-Pe$_4$NCy) cyclohexylsulfamates in aqueous solution, and the conventional partial molar volume of tetra-n-pentylammonium ion, $\bar{V}_{n\text{-Pe}_4N^+}^o$ as a function of temperature.

Solute		T (K)					
		293.15	298.15	303.15	313.15	323.15	333.15
Et$_4$NCy	$V_\Phi^o \times 10^3$ (dm^3 mol^{-1})	271.96 ± 0.07	272.67 ± 0.11	273.38 ± 0.23	275.61 ± 0.17	277.86 ± 0.15	280.43 ± 0.06
	$A_1 \times 10^3$ (dm$^{9/2}$ mol$^{-3/2}$)	−38.9 ± 1.8	−49.3 ± 2.7	−52.7 ± 5.8	−51.0 ± 4.2	−60.9 ± 3.9	−52.4 ± 1.6
	$A_2 \times 10^3$ (dm^6 mol^{-2})	99.7 ± 12	192.3 ± 18	232.3 ± 39	214.6 ± 29	279.5 ± 26	209.0 ± 11
	$A_3 \times 10^3$ (dm$^{15/2}$ mol$^{-5/2}$)	−96.6 ± 23	−267.4 ± 35	−346.2 ± 75	−307.1 ± 55	−412.1 ± 50	−282.0 ± 21
	$s_v \times 10^3$ (dm^3 mol^{-1})	0.09	0.13	0.29	0.21	0.19	0.08
	$s_d \times 10^6$ (kg dm^{-3})	4.4	5.0	8.5	6.6	8.8	7.2
n-Pr$_4$NCy	$V_\Phi^o \times 10^3$ (dm^3 mol^{-1})	337.05 ± 0.03	338.25 ± 0.03	339.56 ± 0.03	342.25 ± 0.04	345.41 ± 0.04	348.44 ± 0.05
	$A_1 \times 10^3$ (dm$^{9/2}$ mol$^{-3/2}$)	−6.6 ± 0.03	−8.0 ± 0.2	−5.9 ± 0.3	−7.0 ± 0.4	−9.3 ± 0.4	−8.1 ± 0.5
	$A_2 \times 10^3$ (dm^6 mol^{-2})	−4.1 ± 0.7	−4.2 ± 0.5	−3.3 ± 0.6	1.3 ± 0.7	7.0 ± 0.8	5.1 ± 0.9
	$s_v \times 10^3$ (dm^3 mol^{-1})	0.04	0.03	0.04	0.05	0.05	0.06
	$s_d \times 10^6$ (kg dm^{-3})	7.3	3.7	4.7	7.4	5.2	5.6
n-Bu$_4$NCy	$V_\Phi^o \times 10^3$ (dm^3 mol^{-1})	397.85 ± 0.07	399.57 ± 0.06	401.81 ± 0.02	405.86 ± 0.02	410.95 ± 0.02	415.42 ± 0.04
	$A_1 \times 10^3$ (dm$^{9/2}$ mol$^{-3/2}$)	−0.35 ± 0.54	−0.39 ± 0.5	−2.1 ± 0.1	−3.9 ± 0.2	−9.5 ± 0.2	−11.6 ± 0.4
	$A_2 \times 10^3$ (dm^6 mol^{-2})	−12,8 ± 0.9	−10.4 ± 0.8	−6.9 ± 0.2	−1.0 ± 0.3	8.5 ± 0.3	14.0 ± 0.8
	$s_v \times 10^3$ (dm^3 mol^{-1})	0.09	0.08	0.02	0.03	0.03	0.09
	$s_d \times 10^6$ (kg dm^{-3})	7.7	6.4	4.8	5.1	6.7	16.1
n-Pe$_4$NCy	$V_\Phi^o \times 10^3$ (dm^3 mol^{-1})	460.85 ± 0.06	462.99 ± 0.04	464.60 ± 0.03	469.03 ± 0.02	474.20 ± 0.01	480.11 ± 0.01
	$A_1 \times 10^3$ (dm$^{9/2}$ mol$^{-3/2}$)	−1.4 ± 1.0	−1.5 ± 0.6	−0.3 ± 0.4	−0.1 ± 0.4	−1.7 ± 0.2	−3.1 ± 0.3
	$A_2 \times 10^3$ (dm^6 mol^{-2})	−33.8 ± 4	−29.5 ± 2	−19.3 ± 2	−8.2 ± 2	1.8 ± 0.8	2.4 ± 1.0
	$s_v \times 10^3$ (dm^3 mol^{-1})	0.08	0.05	0.03	0.03	0.02	0.02
	$s_d \times 10^6$ (kg dm^{-3})	2.8	1.3	0.9	1.5	0.5	0.6
	$\bar{V}_{n\text{-Pe}_4N^+}^0 \times 10^3$ (dm^3 mol^{-1})	337.7 ± 0.4	339.6 ± 0.4	340.2 ± 0.5	343.5 ± 0.6	347.6 ± 0.6	352.3 ± 0.9

tetra-n-alkylammonium bromides in aqueous solution have been determined previously by *Schiavo* et al.[17] They found that for a relatively high concentration of the salts (2.5 mol dm^{-3}), $\bar{V}_1$ increased with increasing concentration of solute and temperature.

Conway et al.[13] found that in aqueous solution V_Φ^o of tetra-n-alkylammonium halides is a linear function of the cation molecular weight, $M_{R_4N^+}$ where $\bar{V}_{X^-}^o$ is the limiting

$$V_\Phi^o = \bar{V}_{X^-}^o + wM_{R_4N^+} \qquad (10)$$

partial molar ionic volume of the anion and w is the slope of the *Conway* plot.[13] The dependence of the limiting partial molar volume of the tetra-n-alkylammonium cyclohexylsulfamates, together with Me$_4$NCy[5] on the molecular weight of R$_4$N$^+$ cation is presented in Fig. 2 at 298.15 K, from which it is evident that a linear correlation exists. This linear relation (10) was also obtained at other temperatures studied. The intercepts and slopes of rel. (10) are given in Table 4 together with the linear correlation coefficient and the standard error of the estimate. The values of the intercept, i. e. $\bar{V}_{Cy^-}^o$, are within experimental uncertainties equal to those given in ref.[7] though with a higher error of about 2.5×10^{-3} dm^3 mol^{-1}. A relatively high scatter of $\bar{V}_{X^-}^o$ was also observed earlier on studying the partial molar volumes of tetra-n-alkylammonium hydroxides in aqueous solution[8] or even of tetra-n-alky-

lammonium perchlorates in non-aqueous solutions.[19] The slope w of rel. (10) slightly increases with increasing temperature (see Table 4), from (1.13 ± 0.1) dm^3 kg^{-1} at 293.15 K to (1.194 ± 0.005) dm^3 kg^{-1} at 333.15 K, with a positive value of $\partial w/\partial t = (7.4 ± 1.3)10^{-4}$ dm^3 kg^{-1} K^{-1}. This increase of the slope w with temperature was also observed by *Krumgalz* earlier.[5]
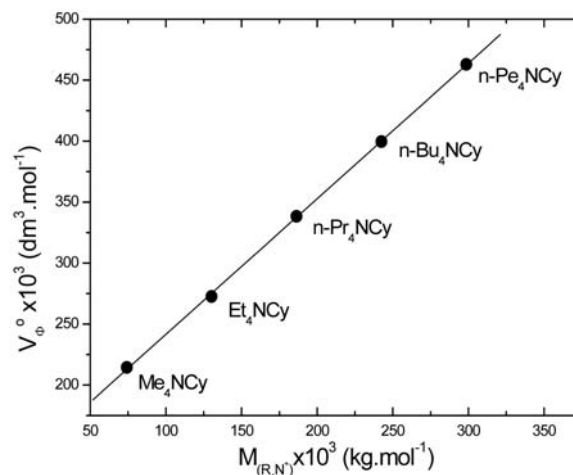

Figure 2. Dependence of the limiting apparent molar volume V_Φ^o f some tetra-n-alkylammonium cyclohexylsulfamates in aqueous solution on the molecular weight of the R$_4$N$^+$ ion at 298.15 K; the V_Φ^o value of Me$_4$NCy is given in ref.[5]

Table 3. Partial molar volume, $\bar{V}_2$ of tetraethyl-, tetra-n-propyl-, tetra-n-butyl-, and tetra-n-pentylammonium cyclohexylsulfamates in aqueous solutions at indicated molalities and temperatures.

m (mol kg^{-1})	$\bar{V}_2 \times 10^3$ (dm^3 mol^{-1}) at T (K)					
	293.15	298.15	303.15	313.15	323.15	333.15
			Et$_4$NCy			
0.00499	268.8	269.1	269.8	272.1	273.8	276.7
0,01036	267.8	268.4	269.2	271.5	273.3	276.0
0,01498	267.4	268.2	269.1	271.3	273.2	275.8
0,02026	267.0	268.0	269.0	271.2	273.2	275.7
0.02506	266.8	267.9	269.1	271.2	273.3	275.7
0.03037	266.6	267.9	269.1	271.2	273.4	275.7
0.05074	266.2	267.9	269.3	271.4	273.9	275.9
0.06100	266.1	267.8	269.2	271.3	273.9	275.9
0.07128	266.0	267.7	268.9	271.2	273.8	275.9
0.07514	266.0	267.6	268.9	271.1	273.7	275.8
0.08124	265.9	267.4	268.7	270.9	273.5	275.7
0.10049	265.8	266.8	267.7	270.2	272.6	275.4
0.12458	265.7	265.5	265.9	268.8	270.7	274.2
			n-Pr$_4$NCy			
0.02635	335.3	336.6	338.0	340.6	343.5	346.8
0.05031	334.5	335.9	337.3	340.1	343.0	346.3
0.07657	333.8	335.2	336.7	339.6	342.7	345.9
0.10035	333.2	334.7	336.2	339.3	342.5	345.7
0.12618	332.7	334.2	335.8	339.2	342.3	345.5
0.15169	332.2	333.7	335.3	338.7	342.2	345.4
0.17753	331.7	333.3	334.9	338.5	342.1	345.2
0.19408	331.5	333.0	334.7	338.3	342.1	345.2
0.25226	330.6	332.2	333.9	337.9	341.9	345.0

m (mol kg^{-1})	$\bar{V}_2 \times 10^3$ (dm^3 mol^{-1}) at T (K)					
	293.15	298.15	303.15	313.15	323.15	333.15
			n-Bu$_4$NCy			
0.02701	397.1	398.9	400.9	404.9	409.1	413.3
0.05166	396.5	398.4	400.4	404.5	408.6	412.9
0.07686	395.8	397.9	400.0	404.1	408.4	412.8
0.10195	395.2	397.4	399.5	403.9	408.2	412.7
0.12777	394.6	396.9	399.1	403.6	408.1	412.8
0.14773	394.2	396.5	398.8	403.5	408.0	412.8
0.17718	393.5	396.0	398.4	403.2	408.0	413.0
0.20069	393.1	395.6	398.0	403.1	408.0	413.1
0.22877	392.5	395.1	397.6	402.9	408.0	413.3
0.25358	391.9	394.7	397.3	402.7	408.1	413.4
0.28523	391.4	394.2	396.9	402.5	408.1	413.6
0.34975	390.2	393.3	396.2	402.2	408.3	414.2
			n-Pe$_4$NCy			
0.00450	460.4	462.6	464.4	468.9	474.0	479.8
0.01128	459.9	462.1	464.1	468.8	473.9	479.7
0.01567	459.5	461.8	463.9	468.8	473.9	479.6
0.02033	459.2	461.5	463.8	468.7	473.9	479.6
0.02709	458.7	461.1	463.5	468.6	473.9	479.5
0.03022	458.5	460.9	463.4	468.5	473.9	479.5
0.03494	458.2	460.6	463.2	468.4	473.9	479.4
0.04131	457.7	460.2	463.0	468.3	473.9	479.4
0.04795	457.3	459.8	462.7	468.2	473.8	479.3
0.05259	456.9	459.5	462.5	468.2	473.8	479.3
0.06193	456.3	459.0	462.2	468.0	473.8	479.3
0.06576	456.1	458.7	462.1	468.0	473.8	479.3

The average value of the slope in different organic solvents was established to be 1.235 dm^3 kg^{-1} at 298.15 K.[5] This value is higher than values obtained earlier from the partial molar volumes of tetra-n-alkylammonium hydroxides in aqueous solution, where $w = (1.107 \pm 0.012)$ dm^3 kg^{-1},[18] and from aqueous solutions of different ions or tetra-n-alkylammonium perchlorates in non-aqueous solutions,[5] which varies from $w = 1.162$ dm^3 kg^{-1} to $w = 1.199$ dm^3 kg^{-1}.[19] The *Conway* method was criticized by *Hefter* and *Marcus*[20] since extrapolation (rel. 10) neglects the solvent exclusion volume which depends on the size of the solvent and on the electrostriction caused by charge.

The limiting apparent molar volume can be separated into the individual volumes for the cation and anion:[3]

$$V_\Phi^o = \bar{V}_{R_4N^+}^o + \bar{V}_{Cy^-}^o \qquad (11)$$

The conventional values of $\bar{V}_{R_4N^+}^o$ and $\bar{V}_{Cy^-}^o$ take the standard partial molar ionic values of hydrogen ion to be zero at all temperatures. The absolute partial molar ionic value, $\bar{V}_{i,abs}^o$ of any ion i of charge z_i can be obtained from[5]

$$\bar{V}_{i,abs}^o = \bar{V}_{i,conv}^o + z_i \bar{V}^o \left(H_{abs}^+ \right) \qquad (12)$$

where $\bar{V}^o(H_{abs}^+)$ was suggested by *Conway*[21] to be -5.5×10^{-3} dm^3 mol^{-1}, $-(4.9 \times 10^{-3} \pm 7 \times 10^{-4})$ dm^3 mol^{-1} by *King*[22] and -5.4×10^{-3} dm^3 mol^{-1} by *Zana* and *Yeager*[23] at 298.15 K. The $\bar{V}_{i,abs}^o$ values of the investigated ions,

Table 4. Dependence of intercept, $\bar{V}_{x^-}^o$, and slope, w, of rel. (10) on temperature, linear correlation coefficient, r, and standard error of estimate, s.

Ion	T(K)					
	293.15	298.15	303.15	313.15	323.15	333.15
$\bar{V}_{Cy^-}^o \times 10^3$ (dm^3 mol^{-1})	125.0 ± 2.7	125.5 ± 2.6	126.0 ± 2.6	127.0 ± 2.5	127.0 ± 2.5	125.0 ± 1.1
w (dm^3 kg^{-1})	1.13 ± 0.01	1.13 ± 0.01	1.14 ± 0.01	1.15 ± 0.01	1.17 ± 0.01	1.194 ± 0.005
r	0.9997	0.9997	0.9997	0.9997	0.9997	0.9999
$s \times 10^3$ (dm^3 mol^{-1})	3.4	3.3	3.3	3.3	3.1	1.1

together with Me_4N^+ and NH_4^+ ions, are given in Table 5 where for $\bar{V}^o(H_{abs}^+)$ a value of -5.5×10^{-3} dm^3 mol^{-1} was used. The $\bar{V}_{i,abs}^o$ values of cations are within experimental error equal to those given in ref.[4]

The standard partial molar ionic volumes at 298.15 K were treated by a model[4] which involves a hydration shell of specified thickness, where $V_{i,hydr}$ is the volume of a hydrated ion when not electrostricted, $V_{i,el\,1}$ is the electrostriction caused by the charge in the hydration shell, $V_{i,el\,2}$ is the electrostriction caused in the water surrounding this shell and $V_{i,str}$ is the volume increment which is a consequence of the structuring of water molecules around hydrophobic ions:

$$\bar{V}_i^o = V_{i,hydr} + V_{i,el\,1} + V_{i,el\,2} + V_{i,str} \tag{13}$$

In the adopted model it was supposed that the hydration shell of the ion contains n_i molecules of water, given by

$$n_i = A|z_i|/r_i \tag{14}$$

where r_i is the ionic radius (pm) and $A = 360$ pm a constant. The values of ionic radii, given in Table 5 were calculated from *King*'s *van der Waals* volumes[22] while the ionic radius of the cyclohexylsulfamate ion was determined from X-ray structural data previously[24]. The number of water molecules bound in the hydration shell of ions (see Table 5) is approximately one molecule of water per ion. Previously we found that n_i for the cyclohexylsulfamate ion is about 0.54.[24]

The molar volume of the hydrated ion was calculated from (15) where N_A is *Avogadro*'s constant and Δr is the

$$V_{i,hydr} = (N_A 4\pi/3)(r_i + \Delta r_i)^3 \tag{15}$$

thickness of the unelectrostricted hydration shell, obtained from (16) where $d = 276$ pm is the diameter of a water

$$n_i \pi d^3/6 = (4\pi/3)\left[(r_i + \Delta r_i)^3 - r_i^3\right] \tag{16}$$

molecule. From the results collected in Table 5 it can be seen that $V_{i,hydr}$ contributes a fraction of about 0.75 of the partial molar ionic volume of Me_4N^+, 0.72 of the Et_4N^+ ion and then a constant value of 0.68 for higher members of the series of R_4N^+ ions. A relatively high value, of 2.1 was obtained for the NH_4^+ ion and 1.13 part of cyclohexylsulfamate ion.

The electrostriction contribution to the ionic volume, i. e. diminution of the volume within the hydration shell was calculated by

$$V_{i,el\,1} = -59.27|z_i|\Delta r_i/(r_i + \Delta r_i) \tag{17}$$

and given in Table 5. Except for the NH_4^+ ion, $V_{i,el\,1}$ contributes a minor and negative value to the absolute partial molar ionic volume. The electrostriction contribution in

the surroundings of the hydrated ion was calculated by and

$$V_{i,el2} = -417.5|z_i|\left[1/(r_i + \Delta r_i)\right] \tag{18}$$

given in Table 5. Like $V_{i,el\,1}$, the values of $V_{i,el\,2}$ are small and negative and increase from the Me_4N^+ ion to the n-Pe_4N^+ ion. The rest of the partial molar ionic volume was ascribed to the volume increment caused by the structuring of water molecules around hydrophobic ions with an open, clathrate-like structure, yielding a positive value of $V_{i,str}$. It was found[4] that if $V_{i,str}$ was assigned a value of 6.1×10^{-3} dm^3 mol^{-1} per CH_3-group and 5.4×10^{-3} dm^3 mol^{-1} per $-CH_2$-group, the value of $V_{i,str}$ for hydrophobic R_4N^+ ions can be determined. The calculated values of $V_{i,str}$ of R_4N^+ ions are presented in Table 5. The sum of the various contributions to the partial molar ionic volumes given by rel. (13), i. e. $\bar{V}_{i,cal}^o$, are presented in Table 5, from which it follows that the adopted model satisfactorily describes the behaviour of highly hydrophobic R_4N^+ ions. The greatest difference between $\bar{V}_{i,obs}^o$ and $\bar{V}_{i,cal}^o$ was observed for the Et_4N^+ ion ($\approx 2.5\%$), while for the other ions this difference was smaller than one per cent.

The $\bar{V}_{i,str}^o$ values of NH_4^+ and Cy^- ions were obtained as the difference between $\bar{V}_{i,obs}^o$ and the other ionic volume contributions. Surprisingly $V_{i,str}$ of the cyclohexylsulfamate ion is negative in spite of the fact that it contains a cyclohexyl entity which causes structural effects on water molecules like the phenyl group, to which a positive value of 23.3×10^{-3} dm^3 mol^{-1} was assigned.[4] It seems that a theory which can satisfactorily describe the behaviour of large hydrophobic ions in an aqueous environment is at present beyond reach. Some difficulties arise from the inadequacy of the values of radii assigned to the ions. Thus, for example, the ionic radii of R_4N^+ ions, given by *Robinson* and *Stokes*[25] are substantially larger than those given in Table 5. As comented on by *Marcus*[4] the inadequacy of the ionic radii is possibly the main reason for the observed discrepancies. The second reason arises from the charge of the ion. Recent quantum mechanical ab initio calculations show that the positive charge of the R_4N^+ ion is distributed on the α and β methylene carbon atoms rather than on the nitrogen atom.[26, 27] Similarly, in the case of the cyclohexylsulfamate ion, the charge is distributed along the three oxygen atoms and the hydrocarbon portion of the ion.[7, 24] As a consequence the charge density of such ions may be low because electron delocalization and its polarizing effect on water molecules could be unusually small.

In the last column in Table 5, the packing density of the investigated ions in solution, defined by[28] are given

$$d_p = \frac{V_{vdW}}{\bar{V}_{i,obs}^o} \tag{19}$$

where V_{vdW} is *van der Waals* volume of the ion. This represents the fraction of the partial molar ionic volume occupied by the ions of the solute in solution at infinite dilution. The

Table 5. Partial molar ionic volumes, ionic radii, hydration numbers, various volume increments of partial molar ionic volumes (rel. 13), calculated partial molar ionic volumes and packing densities of some R_4N^+ ions, NH_4^+ and Cy^- ions at 298.15 K.

Ion	$\bar{V}^o_{i,obs} \times 10^3$ (dm³ mol⁻¹)	r_i (pm)	n_i	$V_{i,hydr} \times 10^3$ (dm³ mol⁻¹)	$-V_{i,el\,1} \times 10^3$ (dm³ mol⁻¹)	$-V_{i,el\,2} \times 10^3$ (dm³ mol⁻¹)	$V_{i,str} \times 10^3$ (dm³ mol⁻¹)	$\bar{V}^o_{i,cal} \times 10^3$ (dm³ mol⁻¹)	$\bar{V}_{i,vdW}/\bar{V}^o_{i,obs}$
NH_4^+	12.6 ± 0.4[a]	168[d]	2.1	25.8	13.7	1.9	2.4	12.6	0.944
Me_4N^+	85.1 ± 0.5[b]	280[d]	1.3	64.1	2.8	1.4	24.4	84.3	0.650
Et_4N^+	143.4 ± 0.4	337[d]	1.0	103.6	1.4	1.2	46.0	147.0	0.671
$n\text{-}Pr_4N^+$	209.0 ± 0.4	379[d]	0.9	142.9	0.8	1.1	67.6	208.6	0.656
$n\text{-}Bu_4N^+$	270.3 ± 0.4	413[d]	0.9	184.3	0.7	1.0	89.2	271.8	0.659
$n\text{-}Pe_4N^+$	333.7 ± 0.4[a]	443[d]	0.8	225.3	0.5	0.9	110.8	334.7	0.656
Cy^-	118.3 ± 0.4[c]	370[e]	1.0	134.1	0.9	1.1	−13.8	118.3	1.084

a) Ref.[4] b) Ref.[6] c) Ref.[7] d) Ref.[22] e) Ref.[24]

V_{vdW} values of the NH_4^+ ion and R_4N^+ ions were taken from[22] and for the cyclohexylsulfamate ion from.[24] The average value of the packing density, considering all the investigated R_4N^+ ions, is 0.658 ± 0.008, which is in good agreement with the value 0.655 ± 0.003 given by *King*,[22] with a plateau density of 0.660.[28] The packing density of the cyclohexylsulfamate ion is greater than unity. It seems that molecules of water are packed more tightly around R_4N^+ ions than around the cyclohexylsulfamate or NH_4^+ ion.

The temperature derivative of the limiting apparent molar volume, $\Phi^o_E = (\partial V^o_\Phi / \partial t)_P$, was calculated from the temperatre dependence of V^o_Φ given as where a_0, a_1 and a_2

$$V^o_\Phi = a_0 + a_1 (T - T_o) + a_2 (T - T_o)^2 \qquad (20)$$

are empirical constants depending on salt and solvent, and $T_o = 298.15$ K. Rel. (20) is a quadratic function 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*.[29] The values of the constants of relation (20) are given in Table 6 together with the standard error of the estimate, s. From relation (20) it follows that Φ^o_E is a linear function of temperature and that $\Phi^o_E = a_1$ at 298.15 K. From the results collected in Table 6 it follows that Φ^o_E at other temperatures studied increases with temperature. The fact that Φ^o_E is a linear function of temperature with a positive coefficient for the temperature term means that the second derivative of $\bar{V}^o_\Phi$ with respect to temperature is also positive. As *Hepler*[30] has pointed out that

$$T \left(\frac{\partial^2 V^o_\Phi}{\partial T^2} \right)_P = - \left(\frac{\partial \Delta C^o_p}{\partial P} \right)_T \qquad (21)$$

where ΔC^o_P is the partial molar isobaric heat capacity of aqueous electrolyte at infinite dilution and P is a pressure, a negative value of $(\partial \Delta C^o_P / \partial P)_T$ is evidence that the investigated ionic solutes behave as structure-making solutes in water over the experimental temperature range studied. On the other hand, NH_4Cy[7] and Me_4Ncy,[6] having a negative coefficient for the temperature term with a negative second derivative of V^o_Φ with respect to temperature, may be classified as structure-breaking solutes in water. This difference with respect to other ionic R_4NCy solutes can be explained by the different solvation behaviour of NH_4^+ and Me_4N^+ ions, e. g.[4,6,13]

In Fig. 3 the dependence of Φ^o_E at 298.15 K on the molecular weight of the salts is given and where the corresponding data on NH_4Cy[7] and Me_4NCy[6] are included. From the plot it can be seen that the limiting partial molar expansibility at 298.15 K increases with increasing molecular weight of the salts.

From the limiting partial molar ionic expansibility of the investigated ions, $\bar{E}^o_{R_4N^+}$ and $\bar{E}^o_{Cy^-}$, the limiting partial molar expansibility of the salts can be calculated from[31] (22) the $\bar{E}^o_{R_4N^+}$ values were obtained from the temperature

$$\Phi^o_E = \bar{E}^o_{R_4N^+} + \bar{E}^o_{Cy^-} \qquad (22)$$

dependence of $\bar{V}^o_{R_4N^+}$ values using *Millero*'s data[3] at 273.15, 298.15 and 323.15 K for Et_4N^+, $n\text{-}Pr_4N^+$ and $n\text{-}Bu_4N^+$ ions, while for the $n\text{-}Pe_4N^+$ ion we used an average value of $\bar{V}^o_{R_4N^+}$ ion at 298.15 K obtained from,[3,12] while for other temperatures the $\bar{V}^o_{R_4N^+}$ values given in Table 2 were used. The temperature dependence of $\bar{V}^o_{R_4N^+}$ was expressed by rel. (20). The values of $\bar{E}^o_{R_4N^+}$ at various temperatures are given in Table 7.

Table 6. Values of the constants a_i of relation (20) and the standard error of the estimate, s.

Solute	$a0 \times 10^3$ (dm³ mol⁻¹)	$a_1 \times 10^3$ (dm³ mol⁻¹ K⁻¹)	$a_2 \times 10^3$ (dm³ mol⁻¹ K⁻²)	$s \times 10^3$ (dm³ mol⁻¹)
Et_4NCy	272.67 ± 0.06	0.165 ± 0.009	0.0017 ± 0.0003	0.12
$n\text{-}Pr_4NCy$	338.26 ± 0.05	0.254 ± 0.007	0.0011 ± 0.0002	0.08
$n\text{-}Bu_4NCy$	399.71 ± 0.13	0.402 ± 0.020	0.0014 ± 0.0006	0.24
$n\text{-}Pe_4NCy$	462.73 ± 0.10	0.368 ± 0.015	0.0037 ± 0.0005	0.17

Table 7. Limiting partial molar ionic expansibility of some R_4N^+, NH_4^+ and Cy^- ions at the indicated temperatures.

| Ion	$\bar{E}^o_{ion} \times 10^3$ (dm³ mol⁻¹K⁻¹) at T(K)					
	293.15	298.15	303.15	313.15	323.15	333.15
NH_4^+	0.0344	0.0325	0.0307	0.0269	0.0233	0.0196
Me_4N^+	0.0469	0.0522	0.0574	0.0678	0.0782	0.0886
Et_4N^+	0.0760	0.0826	0.0892	0.1025	0.1158	0.1291
$n\text{-}Pr_4N^+$	0.1070	0.1274	0.1478	0.1886	0.2294	0.2702
$n\text{-}Bu_4N^+$	0.2398	0.2780	0.3162	0.3927	0.4692	0.5457
$n\text{-}Pe_4N^+$	0.2116	0.2487	0.2857	0.3598	0.4338	0.5079
Cy^-			0.1150			

In Table 7 we included the corresponding data for NH_4^+ and Cy^- ions obtained in an analoguous way previously.[6,7]

From the data collected in Table 7, it can be seen that $\bar{E}^o_{NH_4^+}$ linearly decreases with increasing temperature, $\bar{E}^o_{Cy^-}$ is constant at the indicated temperatures, while $\bar{E}^o_{R_4N^+}$ values linearly increase with temperature. In Fig. 4 $\bar{E}^o_{R_4N^+}$ the values are plotted versus $\bar{M}_{R_4N^+}$ of the ions at 298.15 K. From this plot it follows that the limiting partial molar ionic expansibility of R_4N^+ and NH_4^+ ions gradually increases with increasing ionic molecular weight, with the exception of the $n\text{-}Bu_4N^+$ ion whose different solvation behaviour from other ions was pointed out by *Wen* and *Saito*.[12] They proposed a clathrate-like structure for $n\text{-}Bu_4NBr$ with $\partial\bar{V}^o_{n\text{-}Bu_4N^+}/\partial T$ between $(0.2 - 0.5) \times 10^{-4}$ dm³ mol⁻¹ K⁻¹ at room temperature. According to *Hepler*[30] (see rel. 21) the investigated cations are structure-making in water, while the cyclohexylsulfamate anion according to this view is neither a structure-making nor structure-breaking ion. The large cyclohexylsulfamate ion causes structural effects which are different from those of simple
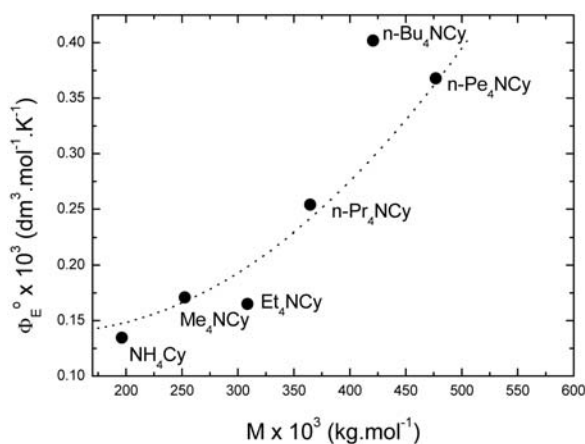
monovalent ions.[7] A similar plot to those given in Fig. 4 was obtained earlier by *Krumgalz*.[5] $\bar{E}^o_{R_4N^+}$ values on his plots fall on two straight lines with a point of intersection, showing that the specific hydrophobic hydration of R_4N^+ ions begins to play a dominant role only starting from the $n\text{-}Pr_4N^+$ ion.

The calculated sum of rel. (22) at 298.15 K within experimental uncertainty for $n\text{-}Pr_4NCy$, $n\text{-}Bu_4NCy$ and $n\text{-}Pe_4NCy$ is equal to those given in Table 6, while for Et_4NCy it is higher by about three standard deviations (see Fig. 3).
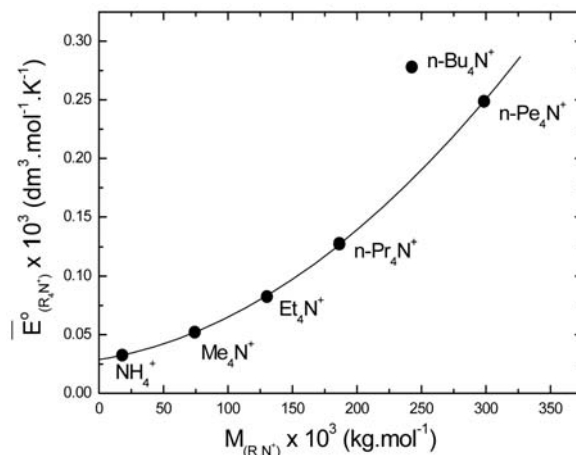
Figure 4. Dependence of $\bar{E}^o_{NH_4^+}$ and $\bar{E}^o_{R_4N^+}$ on molecular weight of the cation at 298.15 K; the data are from ref.[3]

3. Experimental

3. 1. Materials

All tetraalkylammonium salts investigated, i. e. tetraethyl- (Et_4NCy), tetra-n-propyl- (Pr_4NCy), tetra-n-butyl- (Bu_4NCy), and tetra-n-pentylammonium cyclohexylsulfamates (Pe_4NCy) were obtained by careful neutralization of cyclohexylsulfamic acid (purchased from Sigma) with the corresponding base (Fluka). The purity of the salts were checked after recrystallization from various organic solvents (Et_4NCy from ethyl methyl ketone, Pr_4NCy from ethyl acetate, Bu_4NCy and Pe_4NCy from cyclohexane) by analysis of the elements C, H and N (Perkin Elmer, 2400 Series II CHNS/O Analyzer) and also by ion exchange of the cation of the salt by the hydrogen ion (DOWEX, Type 50 WX8); a purity of 99.7 % at least (Et_4NCy) or better, e. g. 99.9% for Bu_4NCy was determined. The salts were kept in a vacuum desiccator over P_2O_5.

The solutions investigated were prepared on a molal concentration scale by precise weighing, using a digital balance (Mettler Toledo, model AT201, Switzerland) accurate to within $\pm 1 \times 10^{-8}$ kg. Before use the solutions were degassed by ultrasound (ultrasonic bath, Bandelin Sonorex, type TK 52, Berlin, Germany).

Figure 3. Dependence of the limiting partial molar expansibility of some tetra-n-alkylammonium and ammonium cyclohexylsulfamates in aqueous solution on molecular weight at 298.15 K; the dotted line was calculated using rel. (22) and corresponding data given in Table 7; the data for NH_4Cy and Me_4NCy are given in refs.[7,6]

3. 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 ± 0.01 K. The apparatus was calibrated with doubly distilled water[32] and dry air[33] at each investigated temperature at atmospheric pressure. The temperature in the measuring cell was regulated to better than ± 0.01 K, using an external bath circulator (Haake, DC3-B3, Karlsruhe, Germany). The uncertainty of the density measurements was $\pm 2 \times 10^{-5}$ kg dm^{-3}.

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Povzetek

Na osnovi merjenja gostote vodnih raztopin nekaterih tetraalkilamonijevih soli cikloheksilsulfaminske kisline 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 velikosti tetraalkilamonijevega kationa oz. naraščajočega hidrofobnega karakterja v izbrani homologni vrsti sintetičnih sladil.