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

Cveto Klofutar, Jaka Horvat and Darja Rudan-Tasič*

Biotechnical Faculty, University of Ljubljana, Jamnikarjeva 101, 1000 Ljubljana, Slovenia

* Corresponding author: E-mail: darja.rudan.tasic@bf.uni-lj.si

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†Dedicated to Prof. Dr. Jože Škerljane 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.

Keywords: Density data, partial molar volume, expansibility, cyclohexylsulfamates, aqueous solutions

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. 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., 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. 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.

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. 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. With this in mind, we determined some volumetric properties of tetra-n-alkylammonium cyclohexylsulfamates...
mulates 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, \( \Phi_V \) (dm\(^3\) mol\(^{-1}\)), of a solute with molar mass, \( M_2 \) (kg mol\(^{-1}\)), was calculated from the relation\(^{11}\)

\[
\Phi_V = \frac{\left( \frac{d_\phi - d}{cd_\phi} \right) + M_2}{d_\phi}
\]  

(1)

where \( d_\phi \) is the density of pure water (kg dm\(^{-3}\)) and \( c \) is the concentration of the salt (mol dm\(^{-3}\)) calculated from \( c = \frac{md(1 + nM_2)}{1000} \). In calculation of the uncertainty of the apparent molar volume, \( \delta \Phi_V \) only the uncertainty in density measurement was taken into account since \( \Phi_V \) is not seriously influenced by errors in molarity:

\[
(\delta \Phi_V)^2 = \left( \frac{-1}{cd_\phi} \right)^2 (\delta d)^2
\]  

(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 \( \Phi_V \) of Et\(_4\)NCy are plotted against \( c^{1/2} \) at 293.15, 313.15 and 333.15 K; the values of \( \Phi_V \) of the other salts give similar plots. From Fig. 1 it can be seen that deviations in \( \Phi_V \) are more pronounced at lower temperature. In dilute solutions \( \Phi_V \) 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 \( \Phi_V \) against \( c^{1/2} \) show negative slopes, indicating a type of behaviour not normally associated with 1:1 electrolytes.\(^{12}\)

The dependence of \( \Phi_V \) on the square root of molarity at a definite temperature was fitted with an equation of the type where \( \Phi_V \) represents the apparent molar volume of the salt at infinite dilution, equal to the limiting partial molar volume of the salt, \( \Phi_V^o \) (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 \( \Phi_V \) values calculated from the sum of the limiting conventional partial molar ionic volumes of the tetra-n-alkylammonium ions at the relevant temperatures. The \( \Phi_V \) values for temperatures other than 273.15 K, 298.15 K and 323.15 K were obtained by analytical interpolation to Millero’s data\(^{7}\) and the cyclohexylsulfamate ion from ref.\(^{7}\). For n-Pr\(_4\)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 \( \Phi_V^o \) and \( \Phi_V^o \), is given in Table 2.

To represent the experimental data adequately for Et\(_4\)N\(^+\)Cycl we used three and for the other salts only two empirical constants in rel. (3). The regression values of \( \Phi_V \) and the empirical constants of rel. (3), together with the standard error of the estimate, \( s_d \), 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\(_4\)N\(^+\)Cy 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\(_4\)N\(^+\)Cy, n-Pr\(_4\)N\(^+\)Cy and n-Bu\(_4\)N\(^+\)Cy, while for n-Pe\(_4\)N\(^+\)Cy it is positive.

In recent years many investigators have studied the \( \Phi_V \) 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 \( \Phi_V \) values of some tetra-n-alkylammonium salts in dilute aqueous solutions and showed that \( \Phi_V \) 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 \( \Phi_V^o \) 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)

\[
d = d_\phi + \left( M_2 - \Phi_V^o d_\phi \right) c - A_1 d_\phi c^{3/2} - A_2 d_\phi c + A_3 d_\phi c^{5/2}
\]  

(4)

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

\[
s_d = \pm \sqrt{\frac{\sum (d_\text{exp} - d_\text{calc})^2}{n-1}}
\]  

(5)

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

The partial molar volume of solute, \( \Phi_2 \) (dm\(^3\) mol\(^{-1}\)) and solvent, \( \Phi_1 \) (dm\(^3\) mol\(^{-1}\)) were computed from \( \Phi_V \) by the following relations:\(^{11}\)

\[
\Phi_2 = \Phi_V + \left[ \frac{1 - c \Phi_V}{2 + c^{3/2} (\delta \Phi_V / \delta c)^{1/2}} \right] c^{1/2} (\delta \Phi_V / \delta c)^{1/2}
\]  

(6)

and

\[
\Phi_1 = \left[ \frac{2}{2 + c^{3/2} (\delta \Phi_V / \delta c)^{1/2}} \right] \Phi_V
\]  

(7)
where \( V_1^0 \) is the molar volume of water and \( \partial V_\phi / \partial c^{1/2} \) according to rel. (3), is given as

\[
\frac{\partial V_\phi}{\partial c^{1/2}} = A_1 + 2A_2c^{1/2} + 3A_3c
\]  

(8)

where the last term of (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 \( 1 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \) for \( V_2 \) and \( 5 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \) for \( V_1 \) 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

\[
\bar{V}_2 = V_1^0 + 1.5A_1c^{1/2} + 2.0A_2c + 2.5A_3c^{3/2}
\]

(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\(^{-3}\).

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 \( \pm 5 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \). The \( V_1 \) values of some
tetra-n-alkylammonium bromides in aqueous solution have been determined previously by Schiavo et al.\textsuperscript{17} They found that for a relatively high concentration of the salts \(2.5\,\text{mol dm}^{-3}\), \(V_\text{norm}^{-1}\) increased with increasing concentration of solute and temperature.

Conway et al.\textsuperscript{13} found that in aqueous solution \(V_\Phi^o\) of tetra-n-alkylammonium halides is a linear function of the cation molecular weight, \(M_{R^4N^+}\) where \(V_\Phi^o\) is the limiting partial molar ionic volume of the anion and \(w\) is the slope of the Conway plot.\textsuperscript{13} The dependence of the limiting partial molar volume of the tetra-n-alkylammonium cyclohexylsulfamates, together with \(\text{Me}_4\text{NCy}^+\) on the molecular weight of \(R^4N^+\) 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. \(V_\text{norm}^{-1}\), are within experimental uncertainties equal to those given in ref.\textsuperscript{7} though with a higher error of about \(2.5 \times 10^{-3}\,\text{dm}^3\,\text{mol}^{-1}\). A relatively high scatter of \(V_\Phi^o\) was also observed earlier on studying the partial molar volumes of tetra-n-alkylammonium hydroxides in aqueous solution\textsuperscript{8} or even of tetra-n-alkylammonium perchlorates in non-aqueous solutions.\textsuperscript{19} The slope \(w\) of rel. \(10\) slightly increases with increasing temperature (see Table 4), from \((1.13 \pm 0.1)\,\text{dm}^3\,\text{kg}^{-1}\) at 293.15 K to \((1.194 \pm 0.005)\,\text{dm}^3\,\text{kg}^{-1}\) at 333.15 K, with a positive value of \(\partial w/\partial t = (7.4 \pm 1.3)\times 10^{-4}\,\text{dm}^3\,\text{kg}^{-1}\,\text{K}^{-1}\). This increase of the slope \(w\) with temperature was also observed by Krumgalz earlier.\textsuperscript{5}

<table>
<thead>
<tr>
<th>Solute</th>
<th>(V_\Phi^o \times 10^3) (dm(^3) mol(^{-1}))</th>
<th>(A_1 \times 10^3) (dm(^{9/2}) mol(^{-3/2}))</th>
<th>(A_2 \times 10^3) (dm(^6) mol(^{-2}))</th>
<th>(A_3 \times 10^3) (dm(^{15/2}) mol(^{-5/2}))</th>
<th>(s_v \times 10^3) (dm(^3) mol(^{-1}))</th>
<th>(s_d \times 10^6) (kg dm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Et}_4\text{NCy})</td>
<td>271.96 ± 0.07</td>
<td>–38.9 ± 1.8</td>
<td>99.7 ± 12</td>
<td>–96.6 ± 23</td>
<td>0.09</td>
<td>4.4</td>
</tr>
<tr>
<td>(\text{n-Pr}_4\text{NCy})</td>
<td>337.05 ± 0.03</td>
<td>–1.4 ± 0.7</td>
<td>7.3</td>
<td>0.04</td>
<td>337.7 ± 0.4</td>
<td>7.3</td>
</tr>
<tr>
<td>(\text{n-Bu}_4\text{NCy})</td>
<td>460.85 ± 0.06</td>
<td>–1.4 ± 1.0</td>
<td>7.7</td>
<td>0.08</td>
<td>337.7 ± 0.4</td>
<td>7.7</td>
</tr>
<tr>
<td>(\text{n-Pe}_4\text{NCy})</td>
<td>463.71 ± 0.06</td>
<td>–1.4 ± 1.0</td>
<td>7.7</td>
<td>0.08</td>
<td>337.7 ± 0.4</td>
<td>7.7</td>
</tr>
</tbody>
</table>

\(V_\text{norm}^{-1} \times 10^3\) (dm\(^3\) mol\(^{-1}\)) | 272.67 ± 0.11                                | –49.3 ± 2.7                                    | 192.3 ± 18                                    | –267.4 ± 35                                   | 0.13                                           | 5.0                                           |
| \(V_\Phi^o \times 10^3\) (dm\(^3\) mol\(^{-1}\)) | 273.38 ± 0.23                                | –52.7 ± 5.8                                    | 232.3 ± 39                                    | –346.2 ± 75                                   | 0.29                                           | 8.5                                           |
| \(V_\Phi^o \times 10^3\) (dm\(^3\) mol\(^{-1}\)) | 275.61 ± 0.17                                | –51.0 ± 4.2                                    | 214.6 ± 29                                    | –307.1 ± 55                                   | 0.21                                           | 6.6                                           |
| \(V_\Phi^o \times 10^3\) (dm\(^3\) mol\(^{-1}\)) | 277.86 ± 0.15                                | –60.9 ± 3.9                                    | 279.5 ± 24                                    | –412.1 ± 50                                   | 0.19                                           | 8.8                                           |
| \(V_\Phi^o \times 10^3\) (dm\(^3\) mol\(^{-1}\)) | 280.43 ± 0.06                                | –52.4 ± 1.6                                    | 209.0 ± 11                                    | –282.0 ± 21                                   | 0.08                                           | 7.2                                           |

Table 2. Limiting apparent molar volume, \(V_\Phi^o\), 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, \(V_{\text{n-Pe}^4\text{NCy}}^{-1}\) as a function of temperature.
The average value of the slope in different organic solvents was established to be 1.235 dm$^3$ kg$^{-1}$ at 298.15 K.\textsuperscript{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$^{-1}$,\textsuperscript{18} and from aqueous solutions of different ions or tetra-n-alkylammonium perchlorates in non-aqueous solutions,\textsuperscript{5} which varies from $w = 1.162$ dm$^3$ kg$^{-1}$ to $w = 1.199$ dm$^3$ kg$^{-1}$.\textsuperscript{19} The Conway method was criticized by Hefter and Marcus\textsuperscript{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:\textsuperscript{3}

$$V_0^q = V_{R,N}^q + V_{C}^q$$ \hspace{1cm} (11)

The conventional values of $V_{R,N}^q$ and $V_{C}^q$ take the standard partial molar ionic values of hydrogen ion to be zero at all temperatures. The absolute partial molar ionic value, $V_{\text{abs}}^q$ of any ion $i$ of charge $z_i$ can be obtained from\textsuperscript{5}

$$V_{\text{abs}}^q = V_{\text{con}}^q + z_i V^q(H^+_{\text{abs}})$$ \hspace{1cm} (12)

where $V^q(H^+_{\text{abs}})$ was suggested by Conway\textsuperscript{21} to be $-5.5 \times 10^{-3}$ dm$^3$ mol$^{-1}$, $-(4.9 \times 10^{-3} \pm 7 \times 10^{-4})$ dm$^3$ mol$^{-1}$ by King\textsuperscript{22} and $-5.4 \times 10^{-3}$ dm$^3$ mol$^{-1}$ by Zana and Yeager\textsuperscript{23} at 298.15 K. The $V_{\text{abs}}^q$ values of the investigated ions, $n$-Pr$_4$N$^+$, n-Bu$_4$N$^+$, n-Pe$_4$N$^+$, and n-Pe$_4$NCy, are given in Tables 3 and 4.

### Table 3: Partial molar volume, $V_2^q$, of tetraethyl-, tetra-n-propyl-, tetra-n-butyl-, and tetra-n-pentylammonium cyclohexylsulfamates in aqueous solutions at indicated molalities and temperatures.

<table>
<thead>
<tr>
<th>Ion</th>
<th>m (mol kg$^{-1}$)</th>
<th>$V_2 \times 10^3$ (dm$^3$ mol$^{-1}$) at T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et$_4$NCy</td>
<td>0.00499</td>
<td>268.8, 269.1, 272.1, 273.8, 276.8</td>
</tr>
<tr>
<td></td>
<td>0.01036</td>
<td>267.8, 268.4, 271.5, 273.3, 276.0</td>
</tr>
<tr>
<td></td>
<td>0.01498</td>
<td>267.4, 268.2, 269.1, 273.2, 275.8</td>
</tr>
<tr>
<td></td>
<td>0.02026</td>
<td>266.8, 268.0, 269.0, 273.2, 275.7</td>
</tr>
<tr>
<td></td>
<td>0.02506</td>
<td>266.6, 267.9, 269.1, 273.2, 275.7</td>
</tr>
<tr>
<td></td>
<td>0.03037</td>
<td>266.6, 267.9, 269.1, 273.2, 275.7</td>
</tr>
<tr>
<td></td>
<td>0.05074</td>
<td>266.2, 267.9, 269.3, 273.9, 275.9</td>
</tr>
<tr>
<td></td>
<td>0.06100</td>
<td>266.1, 267.8, 269.2, 273.9, 275.9</td>
</tr>
<tr>
<td></td>
<td>0.07128</td>
<td>266.0, 267.7, 268.9, 273.8, 275.9</td>
</tr>
<tr>
<td></td>
<td>0.07514</td>
<td>266.0, 267.6, 268.9, 273.8, 275.8</td>
</tr>
<tr>
<td></td>
<td>0.08124</td>
<td>265.9, 267.9, 269.1, 271.2, 273.2</td>
</tr>
<tr>
<td>n-Pr$_4$NCy</td>
<td>0.02635</td>
<td>335.3, 336.6, 338.0, 340.6, 343.5</td>
</tr>
<tr>
<td></td>
<td>0.05031</td>
<td>334.5, 335.9, 337.3, 340.1, 343.0</td>
</tr>
<tr>
<td></td>
<td>0.07657</td>
<td>333.8, 335.2, 336.7, 339.6, 342.7</td>
</tr>
<tr>
<td></td>
<td>0.10035</td>
<td>333.2, 334.7, 336.2, 339.3, 342.5</td>
</tr>
<tr>
<td></td>
<td>0.12618</td>
<td>332.7, 334.2, 335.8, 339.2, 342.3</td>
</tr>
<tr>
<td></td>
<td>0.14773</td>
<td>332.2, 333.7, 335.3, 338.7, 342.2</td>
</tr>
<tr>
<td></td>
<td>0.17753</td>
<td>331.7, 333.3, 334.9, 338.5, 342.1</td>
</tr>
<tr>
<td></td>
<td>0.19408</td>
<td>331.5, 333.0, 334.7, 338.3, 342.1</td>
</tr>
<tr>
<td></td>
<td>0.22877</td>
<td>330.9, 332.4, 334.0, 338.2, 342.1</td>
</tr>
<tr>
<td></td>
<td>0.25226</td>
<td>330.6, 332.2, 333.9, 337.9, 341.9</td>
</tr>
</tbody>
</table>

### Table 4: Dependence of intercept, $V_{\text{abs}}^q$, and slope, $w$, of rel. (10) on temperature, linear correlation coefficient, $r$, and standard error of estimate, $s$.

<table>
<thead>
<tr>
<th>Ion</th>
<th>T (K)</th>
<th>$V_{\text{abs}}^q \times 10^3$ (dm$^3$ mol$^{-1}$)</th>
<th>$w$ (dm$^3$ kg$^{-1}$)</th>
<th>$r$</th>
<th>$s \times 10^3$ (dm$^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>293.15</td>
<td>125.0 ± 2.7</td>
<td>1.13 ± 0.01</td>
<td>0.9997</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>298.15</td>
<td>125.5 ± 2.6</td>
<td>1.13 ± 0.01</td>
<td>0.9997</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>303.15</td>
<td>126.0 ± 2.6</td>
<td>1.14 ± 0.01</td>
<td>0.9997</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>313.15</td>
<td>127.0 ± 2.5</td>
<td>1.15 ± 0.01</td>
<td>0.9997</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>323.15</td>
<td>127.0 ± 2.5</td>
<td>1.17 ± 0.01</td>
<td>0.9997</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>333.15</td>
<td>125.0 ± 1.1</td>
<td>1.194 ± 0.005</td>
<td>0.9997</td>
<td>1.1</td>
</tr>
</tbody>
</table>

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together with Me₄N⁺ and NH₄⁺ ions, are given in Table 5 where for $\overline{V}_i^o (H_{\text{hydr}}^+)$ a value of $-5.5 \times 10^{-3}$ dm³ mol⁻¹ was used. The $V_{\text{cal}}^o$ 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 model5 which involves a hydration shell of specified thickness, where $V_{\text{hydr}}^i$ is the volume of a hydrated ion when not electrostricted, $V_{\text{el}1}^i$ is the electrostriction caused by the charge in the hydration shell, $V_{\text{el}2}^i$ is the electrostriction caused in the water surrounding this shell and $V_{\text{str}}^i$ is the volume increment which is a consequence of the structuring of water molecules around hydrophobic ions:

$$
\overline{V}_i^o = V_{\text{hydr}}^i + V_{\text{el}1}^i + V_{\text{el}2}^i + V_{\text{str}}^i
$$

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

$$
n_i = \frac{A}{\rho} \left[ \frac{z_i}{r_i} \right]
$$

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 volumes22 while the ionic radius of the cyclohexylsulfamate ion was determined from X-ray structural data previously24. 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 $\Delta r$ is the thickness of the unelectrostricted hydration shell, obtained from (16) where $d = 276$ pm is the diameter of a water molecule.

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

molecule. From the results collected in Table 5 it can be seen that $V_{\text{hydr}}^i$ contributes a fraction of about 0.75 of the partial molar ionic volume of Me₄N⁺, 0.72 of the Et₄N⁺ ion and then a constant value of 0.68 for higher members of the series of R₄N⁺ ions. A relatively high value, of 2.1 was obtained for the NH₄⁺ 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

$$
V_{\text{el}1}^i = -59.27 \left[ \frac{z_i}{\rho} \Delta r / (r_i + \Delta r) \right]
$$

and given in Table 5. Except for the NH₄⁺ ion, $V_{\text{el}1}^i$ 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

$$
V_{\text{el}2}^i = -417.5 \left[ \frac{z_i}{\rho} \left[ 1 / (r_i + \Delta r) \right] \right]
$$

given in Table 5. Like $V_{\text{el}1}^i$, the values of $V_{\text{el}2}^i$ are small and negative and increase from the Me₄N⁺ ion to the n-Pe₄N⁺ 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 $V_{\text{str}}^i$. It was found4 that if $V_{\text{str}}^i$ was assigned a value of $6.1 \times 10^{-3}$ dm³ mol⁻¹ per CH₃-group and $5.4 \times 10^{-3}$ dm³ mol⁻¹ per –CH₂-group, the value of $V_{\text{str}}^i$ for hydrophobic R₄N⁺ ions can be determined. The calculated values of $V_{\text{str}}^i$ of R₄N⁺ ions are presented in Table 5. The sum of the various contributions to the partial molar ionic volumes given by rel. (13), i.e. $V_{\text{cal}}^o$ are presented in Table 5, from which it follows that the adopted model satisfactorily describes the behaviour of highly hydrophobic R₄N⁺ ions. The greatest difference between $V_{\text{cal}}^o$ and $V_{\text{obs}}^o$ was observed for the Et₄N⁺ ion (= 2.5 %), while for the other ions this difference was smaller than one per cent.

The $V_{\text{cal}}^o$ values of NH₄⁺ and Cy⁺ ions were obtained as the difference between $V_{\text{obs}}^o$ and the other ionic volume contributions. Surprisingly $V_{\text{str}}^i$ 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 $23.3 \times 10^{-3}$ dm³ mol⁻¹ was assigned.23 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 R₄N⁺ ions, given by Robinson and Stokes25 are substantially larger than those given in Table 5. As commented on by Marcus5 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 R₄N⁺ 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 by28 are given

$$
d_p = \frac{V_{\text{vdW}}}{V_{\text{obs}}}
$$

where $V_{\text{vdW}}$ 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 second derivative of positive coefficient for the temperature term means that

given in Table 6 together with the standard error of the estimate, \( s \).

\[
V^{o}_{\Phi} = a_0 + a_1 (T - T_o) + a_2 (T - T_o)^2 \tag{20}
\]

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 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 expansibility of the investigated ions, \( E_{R_4N}^{o} \) and \( E_{Cy}^{o} \), the limiting partial molar expansibility of the salts can be calculated from\(^{31}\) (22) the \( E_{R_4N}^{o} \) values were obtained from the temperature dependence of \( V^{o}_{\Phi} \) at 298.15 K on the molecular weight of the salts is given and where the corresponding data on \( NH_4Cy \) and \( Me_4NCy \) are included. The 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, \( \Phi^{o}_{\omega} = (\partial V^{o}_{\Phi} / \partial T)_p \), was calculated from the temperature dependence of \( V^{o}_{\Phi} \) given as where \( a_0 \), \( a_1 \) and \( a_2 \)

\[
T \left( \frac{\partial^2 V^{o}_{\Phi}}{\partial T^2} \right)_p = - \left( \frac{\partial \Delta C^{o}_p}{\partial P} \right)_T \tag{21}
\]

where \( \Delta C^{o}_p \) 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, \( NH_4Cy \) and \( Me_4NCy \) having a negative coefficient for the temperature term with a negative second derivative of \( V^{o}_{\Phi} \) 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 \( \Phi^{o}_{\omega} \) at 298.15 K on the molecular weight of the salts is given and where the corresponding data on \( NH_4Cy \) and \( Me_4NCy \) 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.

<table>
<thead>
<tr>
<th>Solute</th>
<th>( a_0 \times 10^3 ) (dm(^3) mol(^{-1}))</th>
<th>( a_1 \times 10^3 ) (dm(^3) mol(^{-1}) K(^{-1}))</th>
<th>( a_2 \times 10^3 ) (dm(^3) mol(^{-1}) K(^{-2}))</th>
<th>( s \times 10^2 ) (dm(^3) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et_NCy</td>
<td>272.67 ± 0.06</td>
<td>0.165 ± 0.009</td>
<td>0.0017 ± 0.0003</td>
<td>0.12</td>
</tr>
<tr>
<td>n-Pr_NCy</td>
<td>338.26 ± 0.05</td>
<td>0.254 ± 0.007</td>
<td>0.0011 ± 0.0002</td>
<td>0.08</td>
</tr>
<tr>
<td>n-Bu_NCy</td>
<td>399.71 ± 0.13</td>
<td>0.402 ± 0.020</td>
<td>0.0014 ± 0.0006</td>
<td>0.24</td>
</tr>
<tr>
<td>n-Pe_NCy</td>
<td>462.73 ± 0.10</td>
<td>0.368 ± 0.015</td>
<td>0.0037 ± 0.0005</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Klofutar et al.: Apparent Molar Volume and Apparent Molar Expansibility of Tetraethyl-, Tetra-n-propyl-...
Table 7. Limiting partial molar ionic expansibility of some \( R_N^+ \), \( \text{NH}_4^+ \) and \( \text{Cy}^- \) ions at the indicated temperatures.

<table>
<thead>
<tr>
<th>Ion</th>
<th>( E_{\text{ion}}^o \times 10^3 ) (dm(^3) mol(^{-1})K(^{-1})) at T(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>293.15</td>
</tr>
<tr>
<td>( \text{NH}_4^+ )</td>
<td>0.0344</td>
</tr>
<tr>
<td>( \text{Me}_4N^+ )</td>
<td>0.0469</td>
</tr>
<tr>
<td>( \text{Et}_4N^+ )</td>
<td>0.0760</td>
</tr>
<tr>
<td>n-Pr(_4N^+ )</td>
<td>0.1070</td>
</tr>
<tr>
<td>n-Bu(_4N^+ )</td>
<td>0.2398</td>
</tr>
<tr>
<td>n-Pe(_4N^+ )</td>
<td>0.2116</td>
</tr>
<tr>
<td>( \text{Cy}^- )</td>
<td>0.1150</td>
</tr>
</tbody>
</table>

In Table 7 we included the corresponding data for \( \text{NH}_4^+ \) and \( \text{Cy}^- \) ions obtained in an analogous way previously.6,7 From the data collected in Table 7, it can be seen that \( E_{\text{NH}_4^+}^o \) linearly decreases with increasing temperature, \( E_{\text{Cy}^-}^o \) is constant at the indicated temperatures, while \( E_{\text{R}_4N^+}^o \) values linearly increase with temperature. In Fig. 4, \( E_{\text{R}_4N^+}^o \) the values are plotted versus \( M_{\text{R}_4N^+} \) of the ions at 298.15 K. From this plot it follows that the limiting partial molar ionic expansibility of \( R_N^+ \) and \( \text{NH}_4^+ \) ions gradually increases with increasing ionic molecular weight, with the exception of the n-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-Bu\(_4N\)Br with \( \partial V_{\text{n-Bu}_4N}/\partial T \) between \((0.2 – 0.5) \times 10^{-4} \) dm\(^3\) mol\(^{-1}\) K\(^{-1}\) at room temperature. According to Hepler30 (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 \( E_{\text{R}_4N^+}^o \) values on his plots fall on two straight lines with a point of intersection, showing that the specific hydrophobic hydration of \( R_N^+ \) ions begins to play a dominant role only starting from the n-Pr\(_4N^+ \) ion.

The calculated sum of rel. (22) at 298.15 K within experimental uncertainty for n-Pr\(_4\)NCy, n-Bu\(_4\)NCy and n-Pe\(_4\)NCy is equal to those given in Table 6, while for Et\(_4\)NCy it is higher by about three standard deviations (see Fig. 3).

### 3. Experimental

#### 3.1. Materials

All tetraalkylammonium salts investigated, i.e. tetraethyl- (Et\(_4\)NCy), tetra-n-propyl- (Pr\(_4\)NCy), tetra-n-butyl- (Bu\(_4\)NCy), and tetra-n-pentylammonium cyclohexylsulfamates (Pe\(_4\)NCy) 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\(_4\)NCy from ethyl methyl ketone, Pr\(_4\)NCy from ethyl methyl ketone, Bu\(_4\)NCy and Pe\(_4\)NCy 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\(_4\)NCy) or better, e.g. 99.9% for Bu\(_4\)NCy was determined. The salts were kept in a vacuum desiccator over P\(_2\)O\(_5\).

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](image3.png)  
**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 \( \text{NH}_4\)Cy and Me\(_4\)NCy are given in refs.7,4

![Figure 4](image4.png)  
**Figure 4.** Dependence of \( E_{\text{NH}_4^+}^o \) and \( E_{\text{R}_4N^+}^o \) on molecular weight of the cation at 298.15 K; the data are from ref.4
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 ±2 × 10\(^{-5} \) kg dm\(^{-3} \).

4. References


Povzetek

Na osnovi merjenja gostote vodnih raztopin nekaterih tetraalkilamonijevih soli cikloheksilsulfaminske kisline pri različnih temperaturah smo določili njihove volumenske lastnosti. Razlike v navideznem molskem volumenu ter navidezni molski ekspanzibilnosti preiskovanih topljencev, zlasti njihove limite vrednosti, kažejo na vpliv velikosti tetraalkilamonijevega kationa oz. naraščajočega hidrofobnega karakterja v izbrani homologni vrsti sintetičnih sladil.