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Volumetric properties and compressibilities of alkyltrimethylammonium bromides and sodium alkylsulphates in aqueous solution

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ABSTRACT: Density and sound velocity data for aqueous solutions at 298.2 K containing alkyltrimethylammonium bromides and sodium alkylsulphates were analysed to yield partial molar volumes and isentropic compressions. The calculated contributions of methylene groups to the properties of alkyltrimethylammonium cations and alkylsulphate anions show no dependence on position in the alkyl chains and a common contribution to the ionic partial molar volumes over the range methyl \( n \)-octyl for the sulphates and \( n \)-propyl \( n \)-hexyl for the alkyltrimethylammonium ions. However, a switch in head group from trimethylammonium to sulphate changes the contribution of methylene groups to estimated partial molar isentropic compressibilities. The reasons for this sensitivity are discussed in terms of hydration characteristics.

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KEYWORDS: alkyltrimethylammonium bromides; sodium alkylsulphates; partial molar volumes; partial molar isentropic compressibilities; hydration

INTRODUCTION

The hydration of solute molecules in aqueous solution is determined by a subtle balance between the hydrophobic and hydrophilic characteristics of groups within a given solute molecule. Kinetic data for well characterized reactions can be used to comment on this balance by reference to the effect of added solutes on, for example, the dependence of rate constants for hydrolysis of an ester. Recently, we showed that for added organic solutes having the general formula RX, the pattern of the dependence of rate constants on solutes having a constant hydrophilic group X can be understood in terms of incremental contributions from the CH₂ groups in the alkyl group R. For another series having a different hydrophilic group X, the patterns formed by the dependence of the rate constant on the molality of the added solute RX can be understood again in terms of incremental contributions. However, the pattern is not identical because the hydrophilic characteristics of alkyl groups R are sensitive to the nature of the polar head group. These conclusions were reached on the basis of kinetic data and are therefore open to criticism that such data probe indirectly the hydration characteristics of added solute RX by virtue of added solute–kinetic probe interactions.

EXPERIMENTAL

Materials. The alkyltrimethylammonium salts and sodium alkylsulphates were prepared using the methods described previously. All solutions were prepared by
weight using doubly distilled water. The same solutions were used in the measurements of density and sound velocity. The molalities of the solutions covered the range 0.04–0.16 mol kg⁻¹.

**Densities and partial molar volumes.** Densities⁷,⁸ were measured using a Paar Model DMA 60 digital densitometer. The error in these density measurements was estimated to be ±3×10⁻⁴ g cm⁻³. The measurements were made on solutions at 25.00 ± 0.05 °C, the density of water being taken as 0.9970429 g cm⁻³. The apparent molar volume of a solute j in aqueous solution (at 298.2 K and ambient pressure) having molality m_j and density ρ (aq) was calculated using the equation

\[ \Phi (V_j; \text{aq}) = [m_j \rho (\text{aq}) \rho_1^+ (l)]^{-1} \left[ \rho_1^+ (l) - \rho (\text{aq}) \right] + M_j / \rho (\text{aq}) \]  

(1)

Where \( \rho_1^+ (l) \) is the density of water at the same temperature and pressure and \( M_j \) is the molar mass of solute j. Equation (1) yields \( \Phi (V_j; \text{aq}) \) for solute j at molality \( m_j \).

**Sound velocities and isentropic compressions.** The speed of sound in the aqueous salt solutions was measured using the ‘sing-around’ technique.⁸,⁹,¹⁰ The solutions were placed in a gold-plated brass cylinder of length 4 cm through which passed the ultrasonic pulses. The frequency of these pulses was measured using a Philips PM6666 timer counter, averaging over periods of 10 s. The La Place equation relates the (equilibrium) isentropic compressibility \( \kappa_S (\text{aq}) \) of an aqueous solution to the measured (low-frequency) sound velocity \( u \) and the density \( \rho (\text{aq}) \):

\[ \kappa_S (\text{aq}) = \frac{1}{u^2 \rho (\text{aq})} \]  

(2)

The isentropic compressibility of water (at 298.2 K and ambient pressure), 4.4774 × 10⁻⁵ bar⁻¹, was calculated using the sound velocity reported by Del Grosso and Mader¹¹. The corresponding isentropic compressibility of water is 8.17 × 10⁻⁴ m³ mol⁻¹ bar⁻¹. For dilute aqueous solutions at 298.2 K (and ambient pressure), the apparent molar isentropic compressibility \( \phi (\kappa_S j; \text{aq}) \) for solute j is conventionally given by

\[ \phi (\kappa_S j; \text{aq}) = [m_j \rho (\text{aq}) \rho_1^+ (l)]^{-1} \left[ \kappa_S (\text{aq}) - \kappa_{S1}^+ (l) \right] + \kappa_S (\text{aq}) \phi (V_j; \text{aq}) \]  

(3)

**RESULTS**

**Apparent molar volumes, \( \phi (V_j; \text{aq}) \)**

The measured densities for sodium alkylsulphates (aq), RSO₃⁻Na⁺, where R = Me, Et, n-propyl, n-butyl, n-pentyl, n-heptyl and n-octyl, and for alkyltrimethylammonium bromides, RMe₃N⁺Br⁻, where R = n-propyl, n-butyl, n-pentyl and n-hexyl, were used in conjunction with equation (1) to yield the corresponding apparent molar volumes \( \phi (V_j; \text{aq}) \) at molarity \( m_j \). For these 1:1 salts, the Debye–Hückel limiting law (DHL) predicts a linear dependence of \( \phi (V_j; \text{aq}) \) on \( 1 / (c_j / c) \)¹²,¹³, where \( c_j \) is the concentration of salt given by the product \( m_j \rho (\text{aq}) \) and \( c = 1 \) mol dm⁻³. The slope of this predicted linear dependence, \( S_V \), for aqueous solutions of 1:1 salts at 298.2 K and ambient pressure is 1.868 mol dm⁻³. The dependences of \( \phi (V_j; \text{aq}) \) on molarity \( m_j \) were fitted to the equation

\[
[\phi (V_j; \text{aq}) - S_V (C_j / c)^{1/2}] = \phi (V_j; \text{aq})^\infty + V_{ij} \left( m_j / m^* \right)
\]  

(4)

where \( \phi (V_j; \text{aq})^\infty \) is the limiting apparent molar volume of salt j [ (V_j; \text{aq})^\infty] and \( V_{ij} \) is a volumetric interaction parameter describing the extent to which the properties of these solution differ from those defined by \( \phi (V_j; \text{aq})^\infty \) and the DHL. The results are summarised in Table 1.

### Table 1. Limiting partial molar volumes and compressions for sodium alkylsulphates (aq) and alkyltrimethylammonium bromides (aq) at 298.2 K

<table>
<thead>
<tr>
<th>Compounds</th>
<th>R</th>
<th>( \phi (V_j; \text{aq})^\infty ) (cm³ mol⁻¹)</th>
<th>( V_{ij} ) (cm³ mol⁻¹)</th>
<th>( \phi (\kappa_S j; \text{aq})^\infty ) (cm³ mol⁻¹ bar⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium alkylsulphates</td>
<td>Me</td>
<td>63.4 ± 0.3</td>
<td>-5.7 ± 3.0</td>
<td>-39.1 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>Et</td>
<td>78.2 ± 0.1</td>
<td>-1.5 ± 0.8</td>
<td>-46.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>n-Pr</td>
<td>94.7 ± 0.1</td>
<td>-0.8 ± 1.2</td>
<td>-47.4 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>n-Bu</td>
<td>111.8 ± 0.1</td>
<td>-3.8 ± 1.7</td>
<td>-46.3 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>n-Pe</td>
<td>127.5 ± 0.1</td>
<td>-2.2 ± 1.0</td>
<td>-49.1 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>n-Pentyl</td>
<td>157.1 ± 0.1</td>
<td>-1.0 ± 0.7</td>
<td>-55.3 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>n-Oct</td>
<td>169.8 ± 0.2</td>
<td>9.0 ± 2.0</td>
<td>-60.7 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>n-Pr</td>
<td>146.0 ± 0.1</td>
<td>-2.0 ± 1.0</td>
<td>-6.5 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>n-Bu</td>
<td>161.9 ± 0.1</td>
<td>-2.3 ± 0.9</td>
<td>-7.5 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>n-Pe</td>
<td>177.3 ± 0.3</td>
<td>-0.8 ± 2.0</td>
<td>-9.3 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>n-Hex</td>
<td>194.2 ± 0.4</td>
<td>-6.9 ± 3.2</td>
<td>-7.7 ± 1.0</td>
</tr>
<tr>
<td>Alkyltrimethylammonium bromides</td>
<td>n-Pr</td>
<td>146.0 ± 0.1</td>
<td>-2.0 ± 1.0</td>
<td>-6.5 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>n-Bu</td>
<td>161.9 ± 0.1</td>
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<td>-7.7 ± 1.0</td>
</tr>
</tbody>
</table>
Apparent molar isentropic compressibilities, \( \phi(\kappa_S; \text{aq}) \)

The dependence of \( \phi(\kappa_S; \text{aq}) \) on concentration \( c_j \) followed the general pattern

\[
\phi(\kappa_S; \text{aq}) = \phi(\kappa_S; \text{aq})^\infty + A' (c/c_1)^{1/2} \tag{5}
\]

where \( A' \) is dependent on the solute. \(^{14,15}\) The dependence of \( \phi(\kappa_S; \text{aq}) \) on concentration \( c_i \) was fitted to equation (5), for each salt the aim being to estimate the quantity \( \phi(\kappa_S; \text{aq})^\infty \). For all systems reported here equation (5) accounted for the results satisfactorily, leading to the results summarized in Table 1.

DISCUSSION

There is merit in considering the volumetric and compressibility data separately. In both cases, however, we concentrate attention on the limiting properties \( \phi(V; \text{aq})^\infty \) and \( \phi(\kappa_S; \text{aq})^\infty \) because, as described in the Introduction, the aim of this study was to probe the impact of hydrophilic head groups on the properties of the linked hydrophobic alkyl chains. This series of solutes was chosen in order to highlight possible differences between the roles of anionic and cationic head groups. \(^{16}\)

The limiting partial molar volumes of the alkyl sulphates were related to the number of methylene groups in the alkyl chain using the equation

\[
\phi(V; \text{aq})^\infty = [\kappa — I — \text{OSO}_3^- \text{Na}^+] + nV[\text{CH}_2] \tag{6}
\]

The symbol I—I represents a terminal hydrogen to the hydrophobic alkyl chain in order to contrast it with, for example, the H atom in the hydrogen sulphate anion \( \text{HOSO}_3^- \) and the H atoms attached to the cation in, for example, monomethylammonium bromide, \( \text{MeH}_3\text{N}^+\text{Br}^- \). Thus, for \( R = \text{Me} n = 1 \), for \( R = \text{Et} n = 2 \), etc. Inspection of the data in Table 1 shows that this pattern is not closely followed by the longer chain alkyl sulphates. Nevertheless, a least-squares analysis based on equation (6) and the data in Table 1 yielded the values for \( V[\text{CH}_2] = 15.2 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1} \) with \( V[\text{CH}_2] = 15.2 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1} \); this estimate is consistent with previously reported volumetric data. \(^{17}\)

A similar analysis showed that each methylene group in \( V[\text{I— I — \text{OSO}_3^- \text{Na}^+] = 48.8 \pm 2.3 \text{ cm}^3 \text{ mol}^{-1} \) with \( V[\text{CH}_2] = 15.2 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1} \); this estimate is consistent with previously reported volumetric data. \(^{17}\)

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methylene group. In contrast, partial molar compressibilities are a more direct measure of the hydration characteristics. Then, in these terms, we conclude that the switch from $\text{OSO}_3^-$ to $\text{NMe}_3^+$ head groups has a profound influence on the hydration of linked hydrophobic alkyl groups.

Acknowledgement

Analysis of volumetric and compressibility data was undertaken by M.J.B. as Visiting Professor at the University of Groningen.

REFERENCES