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

Rixt Buwalda,[1] Jan B. F. N. Engberts,[1] Harald Høiland[2] and Michael J. Blandamer[3]*

[1]Department of Organic and Molecular Inorganic Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
[2]Department of Chemistry, University of Bergen, N-5014, Bergen, Norway
[3]Department of Chemistry, University of Leicester, University Road, Leicester, LE1 7RH, UK

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 $\leq$ n-octyl for the sulphates and n-propyl $\leq$ 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. © 1998 John Wiley & Sons, Ltd.

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

INTRODUCTION

The hydration of solute molecules in aqueous solution[1] 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[2] 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[3,4] in terms of incremental contributions from the CH_2 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.[5] However, the pattern is not identical because the hydrophobic 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.

The kinetic data and possible criticisms indicated above prompted the study reported here. We measured the densities of and (low frequency ultrasonic) sound velocities in aqueous solutions containing either alkyltrimethylammonium bromides (**I**) or sodium alkylsulphates (**II**).

$$R—N^+Me_3 \ Br^- \quad \textbf{I}$$

$$R—OSO_3^- \ Na^+ \quad \textbf{II}$$
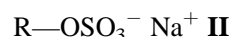
The aim was to compare the impact of a change from head group $—NMe_3^+$ to head group $—OSO_3^-$ on the properties of alkyl chains in aqueous solution in the cation (**I**) and anion (**II**). We show that the increment in limiting partial molar volume $V(RX;aq)^\infty$ per CH_2 group is surprisingly insensitive but that the increment in calculated limiting partial molar isentropic compressibility $\kappa_S (RX;aq)^\infty$ is sensitive to the hydrophilic head group X. Nevertheless, within each set of properties the dependences on the number of hydrophobic CH_2 groups form relatively simple patterns with constant increments per additional methylene group.

EXPERIMENTAL

Materials. The alkyltrimethylammonium salts and sodium alkylsulphates were prepared using the methods described previously.[6] All solutions were prepared by

Correspondence to: M. J. Blandamer, Department of Chemistry, University of Leicester, University Road, Leicester, LE1 7RH, UK.

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

Compounds	R	$\phi(V_j; aq)^\infty$ ($cm^3\ mol^{-1}$)	V_{jj} ($cm^3\ mol^{-1}$)	$\phi(\kappa_{Sj}; aq)^\infty$ ($cm^3\ mol^{-1}\ bar^{-1}$)
Sodium alkylsulphates	Me	63.4 ± 0.3	-5.7 ± 3.0	-39.1 ± 0.4
	Et	78.2 ± 0.1	-1.5 ± 0.8	-46.2 ± 0.2
	n-Pr	94.7 ± 0.1	-0.8 ± 1.2	-47.4 ± 0.4
	n-Bu	111.8 ± 0.1	-3.8 ± 1.7	-46.3 ± 0.9
	n-Pe	127.5 ± 0.1	-2.2 ± 1.0	-49.1 ± 0.6
	n-Hep	157.1 ± 0.1	-1.0 ± 0.7	-55.3 ± 0.6
	n-Oct	169.8 ± 0.2	9.0 ± 2.0	-60.7 ± 0.4
Alkyltrimethylammonium bromides	*n*-Pr	146.0 ± 0.1	-2.0 ± 1.0	-6.5 ± 1.0
	n-Bu	161.9 ± 0.1	-2.3 ± 0.9	-7.5 ± 0.3
	n-Pe	177.3 ± 0.3	-0.8 ± 2.0	-9.3 ± 0.9
	n-Hex	194.2 ± 0.4	-6.9 ± 3.2	-7.7 ± 1.0

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. Densities[7,8] were measured using a Paar Model DMA 60 digital densitometer. The error in these density measurements was estimated to be $\pm 3 \times 10^{-6}$ g cm^{-3}. The measurements were made on solutions at $25.00 \pm 0.05\ ^\circ$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

$$\Phi\ (V_j; aq) = [m_j\ \rho\ (aq)\ \rho_1^*\ (l)]^{-1}\ [\rho_1^*\ (l) - \rho\ (aq)]$$
$$+ M_j / \rho\ (aq) \qquad (1)$$

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 $\phi(V_j; aq)$ 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 *ca* 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 κ_S(aq) of an aqueous solution to the measured (low-frequency) sound velocity u and the density ρ(aq):

$$\kappa_S(aq) = [u^2\ \rho\ (aq)]^{-1} \qquad (2)$$

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

Mader[11]. The corresponding isentropic compressibility of water[8] is 8.17×10^{-4} m^3 mol^{-1} bar^{-1}. For dilute aqueous solutions at 298.2 K (and ambient pressure), the apparent molar isentropic compressibility $\phi(\kappa_{Sj}; aq)$ for solute j is conventionally given by

$$\phi(\kappa_{Sj}; aq) = [m_j\ \rho(aq)\ \rho_1^*\ (l)]^{-1}\ [\kappa_S\ (aq) - \kappa_{S1}^*\ (l)]$$
$$+ \kappa_{Sj}\ (aq)\ \phi(V_j; aq) \qquad (3)$$

RESULTS

Apparent molar volumes, $\phi(V_j; aq)$

The measured densities for sodium alkylsulphates (aq), $RSO_3^-Na^+$, where R = Me, Et, *n*-propyl, *n*-pentyl, *n*-heptyl and *n*-octyl, and for alkyltrimethylammonium bromides, $RMe_3N^+Br^-$, 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 $\phi(V_j; aq)$ at molarity m_j. For these 1:1 salts, the Debye–Hückel limiting law (DHLL) predicts a linear dependence of $\phi(V_j; aq)$ on $(c_j/c_r)^{1/2}$, is where c_j is the concentration of salt given by the product $m_j\ \rho\ (aq)$ and $c_r = 1$ mol dm^{-3}. The slope[12,13] 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 $\phi(V_j; aq)$ on molarity m_j were fitted to the equation

$$[\phi(V_j; aq) - S_V\ (C_j / c_r)^{1/2}] = \phi(V_j; aq)^\infty$$
$$+ V_{jj}(m_j/m^o) \qquad (4)$$

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

Apparent molar isentropic compressibilities, $\phi(\kappa_{Sj};$ aq)

The dependence of $\phi(\kappa_{Sj};$ aq) on concentration c_j followed the general pattern

$$\phi(\kappa_{Sj};\text{ aq}) = \phi(\kappa_{Sj};\text{ aq})^{\infty} + A'\,(c_j/c_r)^{1/2} \qquad (5)$$

where A' is dependent on the solute.[14,15] The dependence of $\phi(\kappa_{Sj};$ aq) on concentration c_j was fitted to equation (5), for each salt the aim being to estimate the quantity $\phi(\kappa_{Sj};$ 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 $\phi(V_j;$ aq)$^{\infty}$ and $\phi(\kappa_{Sj};$ 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

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

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 hydrogensulphate anion HOSO_3^- and the H atoms attached to the onium ion in, for example, monomethylammonium bromide, $\text{MeH}_3\text{N}^+\text{Br}^-$. Thus, for R = Me $n = 1$, for R = Et $n = 2$, etc. Inspection of the data in Table 1 shows that this pattern is not closely followed by the longer chain alkylsulphates. Nevertheless, a least-squares analysis based on equation (6) and the data in Table 1 yielded the $V[\text{I—I} \cdots \text{OSO}_3^-\text{Na}^+] = 48.8 \pm 2.3$ cm^3 mol^{-1} with $V[\text{CH}_2] = 15.2 \pm 0.2$ cm^3 mol^{-1}; this estimate is consistent with previously reported volumetric data.[17] A similar analysis showed that each methylene group in $V[\text{I—I} \cdots \text{NMe}_3^+\text{Br}^-]$ contributes 16.0 cm^3 mol^{-1} to the salt partial molar volumes (see also [Ref. 18]). A comparison is possible with the contributions[15] made by CH$_2$ groups to the limiting partial molar volumes for monoalkylammonium bromides in aqueous solutions, $\text{RNH}_3^+\text{Br}^-$. For example,[15] $[V(\text{EtNH}_3^+\text{Br}^-;$ aq)$^{\infty}$ − $V(\text{MeNH}_3^+\text{Br}^-;$ aq)$^{\infty}]$ equals 16.81 cm^3 mol^{-1}. The average increment per methylene group over the range from $\text{MeNH}_3^+\text{Br}^-$ to $n\text{-C}_8\text{H}_{17}\text{NH}_3^+\text{Br}^-$ is 16.1 cm^3 mol^{-1}. In the case of tetraalkylammonium ions,[6] the mean increment per methylene group is 15.4 cm^3 mol^{-1}. Based on the

calculated methylene increment in conjunction with the estimate for I—I $\cdots$ N$^+$Me$_3$Br$^-$, the predicted limiting partial molar volume for Me$_4$N$^+$Br$^-$(aq) is 113.9 cm^3 mol^{-1}, which is satisfactorily close to the value reported by Perron and Desnoyers[19] of 114.35 cm^3 mol^{-1}.

The consistency of these methylene group increments in partial molar volumes prompts the conclusion that the change in head group from — NMe$_3^+$ to — OSO$_3^-$ has no effect on the hydration characteristics of the alkyl chain over the range $1 < n < 8$ in (CH$_2$)$_n$ The compressibility data were analysed in an analogous fashion using the following equation, e.g. for the alkylsulphates:

$$\phi(\kappa_{Sj};\text{ aq})^{\infty} = \kappa_S[\text{I—I} \cdots \text{OSO}_3^-\text{Na}+] + n\,\kappa_S[\text{CH}_2] \qquad (7)$$

A least-squares analysis of the data in Table 1 showed that $\kappa_S[\text{I—I} \cdots \text{OSO}_3^-\text{Na}^+] = -(38.1 \pm 1.8) \times 10^{-4}$ cm^3 mol^{-1} bar^{-1} and $\kappa_S[\text{CH}_2] = -(2.6 \pm 0.4) \times 10^{-4}$ cm^3 mol^{-1} bar^{-1}. In comparison, a similar analysis showed that $\kappa_S[\text{I—I} \cdots \text{NMe}_3^+\text{Br}^-] = -(5.4 \pm 2.4) \times 10^{-4}$ cm^3 mol^{-1} bar^{-1} and, from the slope, $\kappa_S[\text{CH}_2] = -(0.54 \pm 0.52) \times 10^{-4}$ cm^3 mol^{-1} bar^{-1}. Mathieson and Conway[15] reported estimates of ionic compressibilities using $\kappa_S[\text{Cl}^-;\text{aq}] = -17 \times 10^{-4}$ cm^3 mol^{-1} bar^{-1}, i.e. $\kappa_S[\text{Na}^+;$ aq] $= -33.5 \times 10^{-4}$ cm^3 mol^{-1} bar^{-1} and $\kappa_S[\text{Br}^-;$ aq] $= -9.5 \times 10^{-4}$ cm^3 mol^{-1} bar^{-1}. In these terms, we arrive at the following estimates; $\kappa_S[\text{I—I} \cdots \text{NMe}_3^+] = +4.1 \times 10^{-4}$ cm^3 mol^{-1} bar^{-1} and $\kappa_S[\text{1—I} \cdots \text{OSO}_3^-] = -4.6 \times 10^{-4}$ cm^3 mol^{-1} bar^{-1}. The contrast between the two head groups is consistent with the fact that I—I $\cdots$ NMe$_3^+$ is hydrophobic whereas I—I $\cdots$ OSO$_3^-$ is a hydrophilic head group. For example, Mathieson and Conway[15] estimated that $\kappa_S[\text{Me}_4\text{N}^+;$ aq] $= +5.4 \times 10^{-4}$ cm^{-3} mol^{-1} bar^{-1}.

Turning to the contributions to κ_{Sj} (aq) made to each solute by a CH$_2$ group, for RMe_3N^+ Br$^-$ the impact of each CH$_2$ group over the range from R = n-propyl to n-hexyl is small, being zero within the estimated standard error. Indeed, based on the difference reported[15] between $\kappa_S(\text{Bu}_4\text{N}^+;$ aq)$^{\infty}$ and $\kappa_S(\text{Pr}_4\text{N}^+;$ aq)$^{\infty}$, the contribution per CH$_2$ group is -1.9×10^{-4} cm^3 mol^{-1} bar^{-1}. Hence there is no clear evidence either for the alkylsulphates or for the alkyltrimethylammonium ions of any striking dependence of contributions by CH$_2$ groups based on position in the alkyl chain, at least up to and including hexyl derivatives. There is, however, strong evidence that, in terms of isentropic compressibilities, the hydrophilic head group plays an important role.

There is an interesting contrast concerning conclusions drawn from volumetric data and from compressibility data about the impact of each CH$_2$ group in the alkylsulphate anion and the alkyltrimethylammonium cations. According to the pattern of the partial molar volumes the contributions are similar, but according to the pattern of partial isentropic compressibilities these contributions are head group dependent. One explanation would argue that the change in partial molar volume includes a contribution from the intrinsic volume of a

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 — OSO_3^- to — NMe_3^+ head groups has a profound influence on the hydration of linked hydrophobic alkyl groups.

Acknowledgement

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