Apparent Molar Volumes of Benzyltrimethylammonium Bromide and its Homologs in Aqueous Solution at 15, 25, and 35°C

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Apparent molar volumes at infinite dilution of benzyltrimethylammonium bromide and its butyl and hexyl homologs at 15, 25, and 35°C and of dibenzyldimethylammonium bromide at 25°C in aqueous solution were estimated from density measurements. The additivity rule for the contribution of the methylene groups to the apparent molar volumes was found to be obeyed within a broad range of homologs, which covers the parent salt and the dodecyldimethylbenzylammonium bromide. The volumetric contribution of the phenylene ($-C_6H_4-$) group was estimated to be 61 cm³-mol⁻¹ at 25°C. A value of -16.9 ± 0.3 cm³-mol⁻¹ was suggested for the volumetric contribution of the N⁺ fragment to the apparent molar volume of alkylbenzyldimethylammonium salts.

KEY WORDS: Apparent molar volume; benzyltrimethylammonium bromide; homologs; dibenzyldimethylammonium bromide; group contributions; additivity.

1. INTRODUCTION

Two recent papers of Gianni and Lepori^(1,2) on the additivity scheme for group contributions to the partial molar volume of ionic organic solutes in aqueous solution have prompted us to extend our studies on aqueous solutions of long-chain alkyldimethylbenzylammonium halides to the short-chain homologs.

In previous studies, we have reported, among others, the apparent molar volumes V_{ϕ} of the chlorides (alkyl = decyl, dodecyl, tetradecyl, and hexadecyl)⁽³⁻⁶⁾ and bromides (alkyl = decyl and dodecyl),⁽⁷⁾ in the pre- and postmicellar region at various temperatures. For obvious reasons, the range of molalities available for

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density studies in the premicellar region was narrow and, hence, the precision of the apparent molar volumes at infinite dilution V_{ϕ}^{o} of the surfactants, was rather low. It is worth noting, however, that these values appeared self-consistent with respect to the generally accepted additivity rule for the volumetric contribution of the methylene group in the alkyl chain^(1,2) and to the difference in the apparent molal volumes suggested for the chloride and bromide ions.⁽⁸⁾ Furthermore, the V_{ϕ}^{o} value for the parent benzyltrimethylammonium cation estimated by extrapolation from our data for the long-chain homologs was found to agree, within the experimental error, with the values derived from the apparent molar volumes of benzyltrimethylammonium chloride reported by Yatome *et al.*⁽⁹⁾ Boyd,⁽¹⁰⁾ and Owens *et al.*⁽¹¹⁾

We decided to check whether the additivity rule for the volumetric contribution of methylene groups is valid in this broad range of homologs and to estimate the contribution of the N⁺ ionic constituent to the limiting apparent molal volume of the cation, which bears a benzyl group and two methyl groups linked directly to the nitrogen atom. We present here our results on density measurements of aqueous solutions of benzyltrimethylammonium bromide (C1BBr) and its short-chain alkyl homologs, namely the butyl (C4BBr) and hexyl (C6BBr) salts at 15, 25, and 35°C. We report also densitometric data for dibenzyldimethylammonium bromide (DiBBr) at 25°C. This salt was chosen to investigate whether the additivity rule holds also for the volumetric contribution of the phenylene groups in the case of bulky cations.

2. EXPERIMENTAL

C1BBr, C4BBr, and C6BBr were prepared by quaternization of benzyldimethylamine with an appropriate alkyl bromide in acetone. The reaction for C1BBr was carried out at around 0°C, whereas synthesis of the two higher homologs was carried out at room temperature. The products were recrystallized from acetone and acetone/ethanol mixtures. The detailed description of the synthetic and purification procedures will be given elsewhere. The air-dried salts were anhydrous by Karl–Fischer analysis. Results of potentiometric titration of the bromide ion with a standarized solution of silver nitrate indicated high purity of the salts.

DiBBr was synthesized as follows: the reagents and the solvent were cooled to about -10° C and a mixture of 58.45 g of benzyl bromide (Aldrich) and 46.21 g of *N*,*N*-dimethylbenzylamine (Aldrich) in 100 g of acetone was then prepared and placed, stoppered, overnight at -10° C, and then kept for 3 days at room temperature. The copious product was filtered, washed with cold acetone, and recrystallized several times from acetone. The purity of the salt was checked as above.

Deionized and distilled water was used for preparation of the solutions. Densities of the solutions were measured using a vibrating-tube density meter (Anton Paar DMA 60/602). Temperatures were kept constant within $\pm 0.001^{\circ}$ C. The experimental error in the density was within ± 0.001 kg-m⁻³.

3. RESULTS AND DISCUSSION

In the concentration and temperature ranges investigated, densities of aqueous solutions of the alkyldimethylbenzylammonium bromides increase with molality. The observed relations are, to a satisfactory approximation, linear. The slopes of density *vs*. molality plots, $\Delta \rho / \Delta m$, decrease with growth of the number, *n*, of carbon atoms in the alkyl chain, as illustrated in Fig. 1, where the data for decyl-(C10BBr) and dodecyldimethylbenzylammonium bromides (C12BBr)⁽⁷⁾ at 25°C are included. The $\Delta \rho / \Delta m$ against *n* dependence can be expressed by the relation:

$$\Delta \rho / \Delta m = 0.05325 - 0.00148n \tag{1}$$

with a correlation coefficient r = 0.9998.

The apparent molal volumes, V_{ϕ} at 15, 25, and 35°C for benzyltrimethylammonium bromide and its homologs and at 25°C for DiBBr, listed in Table I, together with the molalities *m* and densities ρ were calculated from the equation:



Fig. 1. Plot of $\Delta \rho / \Delta m$ against *n*, the number of carbon atoms in the alkyl chain of CnBBr salts at 25° C.

	15°C		25°C		35°C	
m (mol-kg ⁻¹)	ρ (g-cm ⁻³)	V_{ϕ} (cm ³ -mol ⁻¹)	ρ (g-cm ⁻³)	V_{ϕ} (cm ³ -mol ⁻¹)	ρ (g-cm ⁻³)	V_{ϕ} (cm ³ -mol ⁻¹)
			C1BBr			
0.02021	1.000215	174.8	0.998158	175.1	0.995100	177.7
0.02971	1.000732	174.9	0.998669	175.5	0.995592	178.0
0.04200	1.001400	175.0	0.999318	176.0	0.996226	178.2
0.06282	1.002484	175.8	1.000406	176.4	0.997295	178.3
0.08357	1.003600	175.6	1.001484	176.6	0.998360	178.3
0.10490	1.004734	175.5	1.002605	176.5	0.999449	178.3
0.12560	1.005819	175.6	1.003660	176.7	1.000502	178.2
0.15870	1.007609	175.1	1.005331	176.8	1.002141	178.4
			C4BBr			
0.021668	1.000170	222.7	0.998092	224.1	0.995075	224.0
0.031604	1.000673	222.2	0.998572	224.0	0.995546	224.1
0.042218	1.001199	222.1	_	_	0.996032	224.6
0.063367	1.002251	221.9	1.000114	223.6	0.997029	224.4
0.085766	1.003348	221.9	1.001168	223.8	0.998084	224.3
0.104831	1.004273	221.9	1.002091	223.5	0.998943	224.5
0.125527	1.005281	221.8	1.003055	223.5	0.999886	224.5
0.156825	1.006793	221.6	1.004520	223.4	1.001304	224.4
0.209300	1.009299	221.4	1.006944	223.2	1.003659	224.2
			C6BBr			
0.02285	1.000189	252.4	0.998082	255.2	0.995041	257.0
0.03224	1.000639	252.3	0.998512	255.0	0.995452	257.1
0.04190	1.001095	252.3	0.998917	255.7	0.995872	257.1
0.06268	1.002075	252.2	0.999855	255.3	0.996773	257.1
0.08668	1.003189	252.2	1.000947	254.9	0.997802	257.1
0.10452	1.004003	252.3	1.001741	254.8	0.998568	257.0
0.15665	1.006404	252.0	1.004004	254.7	1.000754	256.9
0.20889	1.008758	251.8	1.006264	254.4	1.002916	256.7
0.31480	1.013399	251.4	1.010618	254.3	1.007132	256.6
0.02285	1.000189	252.4	0.998082	255.2	0.995041	257.0
			DiBBr			
0.020975			0.998480	237.9		
0.031410			0.999203	237.5		
0.041990			0.999925	237.4		
0.064102			1.001416	237.5		
0.084860			1.002804	237.5		
0.104440			1.004103	237.5		
0.167080			1.008197	237.3		
0.250650			1.013574	236.9		
0.344800			1.019227	237.2		

Table I. Molalities, Densities, and Apparent Molar Volumes of C1BBr, C4BBr, and C6BBr at 15,
25, and 35°C and of DiBBr at 25°C

Volumes of Benzyltrimethylammonium Bromide

where ρ_0 is the density of pure water and M is the molar mass of the solute.

The apparent molar volumes of the salts at infinite dilution V_{ϕ}^{o} , were calculated by applying the relation:

$$V_{\phi} = V_{\phi}^{\rm o} + A_{\rm v} m^{1/2} + B_{\rm v} m \tag{3}$$

where A_v is the Debye–Hückel limiting law coefficient and B_v is an adjustable parameter that measures the deviations from the limiting law due to ion–ion interactions, which may vary with size of the cation and temperature. The parameter A_v is 1.696, 1.868, and 2.046 cm³-kg^{1/2}-mol^{-3/2} at 15, 25, and 35°C, respectively.⁽⁸⁾

As Millero pointed out,⁽⁸⁾ when concentrations are expressed as molarities C the densities of aqueous solutions of the electrolytes can be determined from the relation:

$$\rho = \rho_{\rm o} + \left(\frac{M - \rho_{\rm o} V_{\phi}^{\rm o}}{10^3}\right) C - \left(\frac{A_{\rm v} \rho_{\rm o}}{10^3}\right) C^{3/2} - \left(\frac{B_{\rm v} \rho_{\rm o}}{10^3}\right) C^2 \tag{4}$$

A more lengthy relation can be derived when concentrations are expressed as molalities. Since the $\Delta \rho / \Delta C$ against *n* can be expressed by a relation similar to (1), it can be immediately seen that the linearity of density *vs.* molarity plots in the low concentration range indicates that the second and third terms in Eq. (4) are negligibly small or cancel out. Growth of density with molarity indicates thus that the $M - \rho_0 V_{\phi}^0$ term in the first parameter in the Eq. (4) is positive. This term appears to be negative when the molecular weight of the counterion in surfactants is low and its apparent molar volume is comparatively high, as found in the case of chlorides⁽³⁾ and hydroxides.^(12,13)

The plots of V_{ϕ} –1.868 $m^{1/2}$ vs molality for C1BBr, C4BBr, and C6BBr at 25°C are shown in Fig. 2.

The values of V_{ϕ}^{o} and of the B_{v} parameters for C1BBr and its two homologs at 15, 25, and 35°C are shown in Table II, together with the standard deviations. The mean value for the methylene group contribution to the apparent molar volumes in the C1BBr to C6BBr for the homologs amounts to $16.0 \pm 0.2 \text{ cm}^3\text{-mol}^{-1}$.

As can be seen in Fig. 2, V_{ϕ} for C1Br decrease upon dilution, whereas those found for its two homologs increase, which is consistent with expectations that stronger ion–counterion interactions should occur in the case of the parent salt. Inspection of the B_v values presented in Table II confirms this observation, since the parameters for C1BBr are systematically higher compared with those estimated for the two homologs at 15, 25, and 35°C. The drop in the value of B_v estimated for C1BBr at 35°C is, however, unexpected unless it can be assumed that in the temperature range of 25–35°C the properties of C1BBr switch from structure breaking to structure making. The high thermal expansivity of C1BBr in this temperature range, which can be seen upon inspection of the data in Table II, is here worth mentioning. Spectroscopic absorption data in the UV range for aqueous solutions of the benzyltrimethylammonium chloride⁽¹⁴⁾ seem to provide evidence for specificity of



Fig. 2. Plots of V_{ϕ} –1.868 $m^{1/2}$ vs. molality of C1BBr, C4BBr, and C6BBr at 25°C.

this salt at room temperature, since its molar absorptivity at the absorption maximum of 262.2 nm amounted to 427 cm²-mmol⁻¹ and was substantially higher than the molar absorptivities at the corresponding maxima of the remaining benzyltrialkylammonium chlorides studied. For the benzyltriethylammonium chloride, the absorptivity decreased dramatically to 372 cm²-mmol⁻¹ (at 262.4 nm). Upon passing to higher homologs, the effect almost leveled off.

We will now discuss the V_{ϕ}^{o} values for C1BBr and its homologs at 25°C in view of the general additivity scheme for group contributions to V_{ϕ} suggested by Gianni and Leppori.^(1,2) According to these authors, ionic partial molar volumes can be estimated through the simple equation:

$$V_2 = A + \sum nB_i + C \tag{5}$$

where V_2 is the partial molar volume of the solute, A is a constant covolume term (equal to 9.20) B_i is the contribution of the *i*th group, which appears n_i times in the solute molecule, and C is a correction term for polyfunctional compounds and peculiar structures. This term will not be taken into account here. The following B_i values were taken from Ref.⁽²⁾ and applied for the estimation of the V_{ϕ}^{0} values of the organic cations: 21.44 cm³-mol⁻¹ for CH₃, 15.93 for CH₂, 7.99 for C_{ar}, and 12.91 for CH_{ar}. Two B_i values have been suggested for N^+ , namely, -14.94 cm³-mol⁻¹ in case of tetraalkylammonium cations (with R = Et to Pe) and -11.34 for cations of the RNMe₃⁺ and R₂NMe₂⁺ type. None of these two values appear to conform to the situation when the nitrogen atom is linked directly to a benzyl group. The best

Table II. Apparent Molar Volumes at Infinite Dilution and the B_v Coefficient for Benzyltrimethylammonium Bromide (C1BBr), Butyldimethylbenzylammonium Bromide (C4BBr), and Hexyldimethylbenzylammonium Bromide (C6BBr) at 15, 25, and 35°C

Salt	V_{ϕ}^{0} (cm ³ -mol ⁻¹)	$B_{\rm v}$ (10 ⁻³ g ² -cm ⁻³ -mol ⁻¹)
	15°C	
C1BBr	174.8 ± 0.2	0.27 ± 2.5
C4BBr	222.2 ± 0.1	-8.19 ± 1.0
C6BBr	252.2 ± 0.04	-5.52 ± 0.3
	25°C	
C1BBr	175.1 ± 0.2	7.68 ± 2.1
C4BBr	223.8 ± 0.1	-7.46 ± 0.9
C6BBr	255.0 ± 0.2	-6.27 ± 1.0
	35°C	
C1BBr	177.7 ± 0.1	-0.88 ± 2.1
C4BBr	224.0 ± 0.1	-2.64 ± 1.0
C6BBr	256.8 ± 0.02	-4.64 ± 0.2

fit of the experimental values of V_{ϕ} to those predicted by Eq. (5) occurs when a value of $-16.9 \pm 0.3 \text{ cm}^3 \text{-mol}^{-1}$ is assumed for N⁺ in the case of the C1B⁺ cation and its C4 to C12 homologs. This value was calculated on basis of our data and the data for benzyltrimethylammonium chloride taken from Boyd⁽¹⁰⁾ and Owens *et al.*⁽¹¹⁾ The experimental and calculated values of V_{ϕ}° for the C1B⁺ cation and its homologs were estimated by assuming that the apparent molal volume of the bromide and chloride anions amounts to 30,1 and 23.2 cm³-mol⁻¹, respectively.⁽²⁾ The relevant data are collected in Table III where, for comparison, the $V_{\phi calc}^{\circ}$ values calculated for N⁺ = $-14.94 \text{ cm}^3 \text{-mol}^{-1}$ are included. It can be seen that the value of N⁺ equal to $-16.9 \text{ cm}^3 \text{-mol}^{-1}$ yields $V_{\phi calc}^{\circ}$ values, which agree satisfactorily with the experimental data within a broad range of homologous alkyldimethylbenzylammonium halides.

The set of data for benzyltrimethylammonium bromide and its homologs enables us to estimate the contribution of the phenylene, $-C_6H_4-$, group to the apparent molal volumes of the CnB⁺ cations by taking into account relevant volumetric data for tetramethylammonium salts and their alkyltrimethylammonium homologs. For this purpose, we will use $V_{\phi}^{\circ} = 107.3 \text{ cm}^3 \text{-mol}^{-1}$, reported by Verrall and Conway⁽¹⁵⁾ for tetramethylammonium chloride and $V_{\phi}^{\circ} = 256.9 \text{ cm}^3 \text{-mol}^{-1}$ cited by Wettig and Verall⁽¹⁶⁾ for decyltrimethylammonium bromide. The difference in apparent volumes of C1B⁺ and the tetramethylammonium cation amounts to 60.9 cm³-mol⁻¹. The corresponding value estimated from the data for the decyl salts amounts to 61.0 cm³-mol⁻¹. Thus, the data for this broad range of compounds

Ion	$V_{\phi m exp}^{ m o}$	$V_{\phi \text{calc}}^{\text{o}}$ (N ⁺ = -16.9 ± 0.3)	$V_{\phi \text{calc}}^{\text{o}}(\text{N}^+ = -14.94 \pm 1.4)$
C1B ⁺	$145.0^a \ 145.9^b$ $145.7^c \ 147.8^d$	145.1	147.1
$C4B^+$	193.7 ^a	192.9	194.8
$C6B^+$	224.9^{a}	224.7	226.7
$C10B^+$	287.2 ^e	288.5	290.4
$C12B^+$	319.6 ^e	320.3	322.3

Table III. Apparent Molar Volumes at Infinite Dilution for Benzyltrimethylammonium Cation (C1B⁺) and its Monoalkyl Homologs (CnB⁺) Estimated form Experimental Data, $V_{\phi exp}^{o}$, and from the Additivity Scheme, $V_{\phi calc}^{o}$ in cm³-mol⁻¹

^aPresent results.

^bRef. (10).

^cRef. (11).

^dRef. (9).

^eRef. (7).

appears satisfactorily self-consistent. From the volumetric point of view, the phenylene group appears to be equivalent to almost four methylene groups. A similar correspondence was suggested for hydrophobicity of the two groups, which can be evaluated by comparison of surface activity or critical micelle concentration



Fig. 3. Plots of V_{ϕ} –1.868 $m^{1/2}$ *vs.* molality of DiBBr at 25°C.

of appropriate pairs of amphiphiles. Such results indicate that the hydrophobic character of a phenylene group corresponds to that of an aliphatic hydrocarbon chain composed of 4 ± 0.5 methylene groups.^(17,18)

The influence of a second benzyl group at the nitrogen atom on the apparent molal volume of the ammonium cation can be seen upon inspection of the plot of $V_{\phi} - 1.868 \text{ m}^{1/2} vs.$ molality of the solutions of DiBBr at 25°C, presented in Fig. 3. The extrapolated value of V_{ϕ}^{0} and the value of B_{v} amount to 237.2 ± 0.1 cm³-mol⁻¹ and -3.94 ± 0.1 , respectively. The values of V_{ϕ} for this salt show a concentration dependence similar to that found for alkyldimethylbenzylammonium bromides. The difference in V_{ϕ}^{0} found for DiBBr and C1BBr amounts to 62.1 cm³-mol⁻¹. This value is only slightly higher compared to the volumetric contribution of the phenylene group estimated for the set of alkyldimethylbenzylammonium salts and indicates that introduction of a second phenylene group at the nitrogen atom of the organic cation does not lead to substantial changes in the group contribution scheme.

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