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Apparent Molal Volumes and Expansibilities of Tetraalkylammonium Bromides in Dilute Aqueous Solutions

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Densities of aqueous solutions of Me_4NBr, Et_4NBr, and Bu_4NBr have been measured using a magnetic float apparatus. The concentration range was from (0.005 to 0.04) $mol \cdot kg^{-1}$. The temperatures were (278.15, 288.15, 293.15, and 298.15) K. The experimental values were used to calculate apparent molal volumes, partial molal volumes at infinite dilution, and partial molal expansibilities at (278.15, 288.15, 293.15, and 298.15) K. The ionic contributions to the properties were calculated using the additivity rule. The results are interpreted in terms of solute−solvent interactions.

Introduction

Solute partial molal volume, V°_{salt}, has been useful in understanding solute−solvent interactions. The temperature dependence of V°_{salt} and some extra thermodynamic assumptions[1] can be used to calculate ionic contributions to the volumes and to get partial molal expansibilities at infinite dilution. These limiting quantities depend on ion size and ion−solvent interaction.[2]

Tetraalkylammonium salts have been extensively used in research work on water and aqueous solution structure because the salts have nonpolar groups (hydrocarbon chains) that strongly interact with water and have notorious structural influence.

In particular, hydrophobic interactions can be studied this way. Volumetric properties have been widely investigated for this purpose.[2−9] Most of the work has been done at 298.15 K; much less work has been done above 298.15 K and very little work has been done below 298.15 K.

Furthermore, complete studies of temperature dependence of volumetric properties are scarce. The work of Franks and Smith[6] deals with four salts, including three used by us, at two temperatures, (273.15 and 298.15) K. The concentration ranged from approximately (0.004 to 0.10) m. However, the experimental uncertainty in the values at concentrations below 0.04 m makes the extrapolation to zero concentration difficult. (See plots of ϕ_v vs $c^{1/2}$.) They tried to get the apparent molal expansibilities by using data for the two experimental temperatures. The uncertainty of the experimental data should be better than 0.00001 $g \cdot cm^{-3}$, a condition that is hardly filled by most literature reports. Marcus[1] has pointed out that the accuracy and the precision of the density data should be high and has said that it is desirable to have data on solutions whose concentrations decrease to at least 0.01 $mol \cdot kg^{-1}$. These conditions are hard to fill and therefore render a good deal of literature data useless for the purpose of explaining solute−solvent interactions.

Table 1. Apparent Molal Volumes of Aqueous Solutions of Tetraalkylammonium Bromides at 298.15 K

$\frac{m}{mol \cdot kg^{-1}}$	$\frac{-\,1000\Delta\rho}{g \cdot cm^{-3}}$	$\frac{V_\phi}{cm^3 \cdot mol^{-1}}$	$\frac{\sigma_v}{cm^3 \cdot mol^{-1}}$
	Bu_4NBr		
0.00512	0.1198	299.64	0.39
0.00864	0.1997	299.91	0.23
0.01498	0.3441	300.02	0.13
0.02013	0.4591	300.15	0.10
0.02646	0.6005	300.22	0.08
0.02845	0.6413	300.37	0.07
0.03628	0.8177	300.32	0.06
0.04217	0.9536	300.20	0.05
0.01148	0.2668	299.77	0.18
0.04687	1.0554	300.27	0.04
	Et_4NBr		
0.00542	0.2048	172.79	0.37
0.00732	0.2731	173.27	0.27
0.01223	0.4513	173.62	0.16
0.01483	0.5491	173.48	0.14
0.01539	0.5717	173.35	0.13
0.01941	0.7180	173.48	0.10
0.02175	0.8048	173.47	0.09
0.02387	0.8763	173.75	0.08
0.02644	0.9741	173.59	0.08
0.03050	1.1207	173.66	0.07
0.03609	1.3296	173.53	0.06
0.04225	1.5470	173.72	0.05
0.04838	1.7746	173.61	0.04
	Me_4NBr		
0.00547	0.22487	113.14	0.37
0.00696	0.28495	113.33	0.29
0.01010	0.40643	113.98	0.20
0.01541	0.61553	114.26	0.13
0.02150	0.85556	114.38	0.09
0.02769	1.09812	114.50	0.07
0.3053	1.20953	114.52	0.07
0.03727	1.47506	114.54	0.05
0.04661	1.84124	114.57	0.04
0.06023	2.36855	114.68	0.03

In this article, we report data on the densities of aqueous solutions of Me_4NBr, Et_4NBr, and Bu_4NBr from (0.005 to 0.04) $mol \cdot kg^{-1}$ and at (278.15, 288.15, 293.15, and 298.15) K.

The uncertainty of the density data was, on average, around $\pm\, 2 \cdot 10^{-6}\ g \cdot cm^{-3}$.

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Table 2. Apparent Molal Volumes of Aqueous Solutions of Tetraalkylammonium Bromides at 293.15 K

m / mol·kg^{-1}	$-1000\Delta\rho$ / g·cm^{-3}	V_ϕ / cm^3·mol^{-1}	σ_v / cm^3·mol^{-1}
	Bu_4NBr		
0.00521	0.1160	300.64	0.39
0.00768	0.1776	299.70	0.26
0.00874	0.2009	299.82	0.23
0.01127	0.2638	299.34	0.18
0.01440	0.3408	299.05	0.14
0.02106	0.4970	299.06	0.10
0.02623	0.6245	298.80	0.08
0.02999	0.7110	298.88	0.07
0.03701	0.8815	298.71	0.05
0.04096	0.9730	298.75	0.05
	Et_4NBr		
0.00692	0.2572	173.31	0.29
0.00707	0.2630	173.29	0.28
0.01025	0.3885	172.54	0.20
0.01475	0.5579	172.56	0.14
0.02076	0.7823	172.66	0.10
0.02694	1.0219	172.35	0.07
0.03023	1.1443	172.41	0.07
0.03371	1.2802	172.27	0.06
0.04326	1.6266	172.58	0.05
0.05082	1.9071	172.60	0.04
	Me_4NBr		
0.00474	0.1897	114.27	0.42
0.00682	0.2746	113.98	0.29
0.00886	0.3572	113.94	0.23
0.01393	0.5636	113.72	0.14
0.02120	0.8643	113.35	0.09
0.02737	1.1125	113.44	0.07
0.03048	1.2389	113.43	0.07
0.03834	1.5610	113.32	0.05
0.04184	1.7014	113.35	0.05
0.05604	2.2759	113.33	0.04

Experimental Section

Tetramethylammonium bromide (Me_4NBr), tetraethylammonium bromide (Et_4NBr), and tetrabutylammonium bromide (Bu_4NBr) were obtained from Aldrich. All salts were dried under vacuum for 48 h before use. The purity of salts was better than 99.8 %. The solutions were prepared by weight with degassed, doubly distilled water. A Mettler balance (AT 261) was used in all cases.

Density measurements were carried out using a magnetic float densimeter that gave an uncertainty of $\pm 2 \cdot 10^{-6}$ g·cm^{-3}. It was built following the design of a densimeter that has been described elsewhere.[10] The equilibrium current for water was checked at least one time per week. No significant variations were detected. The temperature of the thermostat was controlled to ± 0.005 K or better with a temperature control (Bayley model 123).

Results and Discussion

The densities of the solutions were measured as a function of molal concentration at (273.15, 288.15, 293.15, and 298.15) K. The apparent molal volumes of the solutes were calculated using the following equation

$$V_\phi = \frac{M_2}{\rho} - \frac{1000(\rho - \rho_o)}{m\rho\rho_o} \tag{1}$$

where ρ and ρ_o are the densities of solution and of water, respectively, and m is the molal concentration of the solute of molar mass, M_2. The density of water, ρ_o, at different temperatures was taken from Patterson and Morris.[11]

Table 3. Apparent Molal Volumes of Aqueous Solutions of Tetraalkylammonium Bromides at 288.15 K

m / mol·kg^{-1}	$-1000\Delta\rho$ / g·cm^{-3}	V_ϕ / cm^3·mol^{-1}	σ_v / cm^3·mol^{-1}
	Bu_4NBr		
0.00223	0.0597	295.77	0.90
0.00312	0.0809	296.58	0.64
0.00544	0.1410	296.56	0.37
0.00698	0.1802	296.65	0.29
0.00884	0.2281	296.64	0.23
0.01040	0.2663	296.84	0.19
0.01073	0.2726	297.04	0.19
0.01472	0.3759	296.87	0.14
0.01931	0.4901	296.99	0.10
0.02545	0.6442	297.02	0.08
0.02919	0.7406	296.93	0.07
0.03465	0.8762	296.98	0.06
0.04159	1.0505	296.96	0.05
	Et_4NBr		
0.00478	0.1885	170.98	0.42
0.00589	0.2323	170.97	0.34
0.00656	0.2553	171.49	0.31
0.01358	0.5258	171.55	0.15
0.01574	0.6093	171.54	0.13
0.02201	0.8504	171.57	0.09
0.02658	1.0261	171.57	0.08
0.03042	1.1754	171.51	0.07
0.03502	1.3478	171.63	0.06
0.03613	1.3964	171.45	0.06
0.04252	1.6436	171.40	0.05
0.04931	1.8973	171.53	0.04
	Me_4NBr		
0.00252	0.1069	111.70	0.79
0.00439	0.1844	112.11	0.46
0.00708	0.2961	112.26	0.28
0.00927	0.3874	112.29	0.22
0.01448	0.6046	112.29	0.14
0.01941	0.8086	112.38	0.10
0.02486	1.0365	112.32	0.08
0.02853	1.1853	112.44	0.07
0.03552	1.4747	112.44	0.06
0.04105	1.7007	112.51	0.05

Table 4. Apparent Molal Volumes of Aqueous Solutions of Tetraalkylammonium Bromides at 278.15 K

m / mol·kg^{-1}	$-1000\Delta\rho$ / g·cm^{-3}	V_ϕ / cm^3·mol^{-1}	σ_v / cm^3·mol^{-1}
	Bu_4NBr		
0.00662	0.1769	295.65	0.30
0.00764	0.2051	295.51	0.26
0.01144	0.3103	295.14	0.18
0.01530	0.4061	295.68	0.13
0.02816	0.7506	295.44	0.07
0.03656	0.9762	295.32	0.06
0.04369	1.1732	295.11	0.05
	Et_4NBr		
0.00831	0.3286	170.61	0.24
0.00564	0.2222	170.74	0.36
0.01279	0.4998	171.05	0.16
0.02291	0.8941	171.03	0.09
0.02885	1.1145	171.39	0.07
0.03741	1.4577	170.99	0.05
0.04611	1.7743	171.42	0.04
	Me_4NBr		
0.00455	0.1951	111.18	0.44
0.00945	0.4028	111.39	0.21
0.02336	0.9763	112.16	0.09
0.03085	1.2840	112.31	0.06
0.04684	1.9481	112.26	0.04
0.05007	2.0799	112.29	0.04

Tables 1, 2, 3, and 4 summarize the results of the difference between the density of water and the density of the solution at

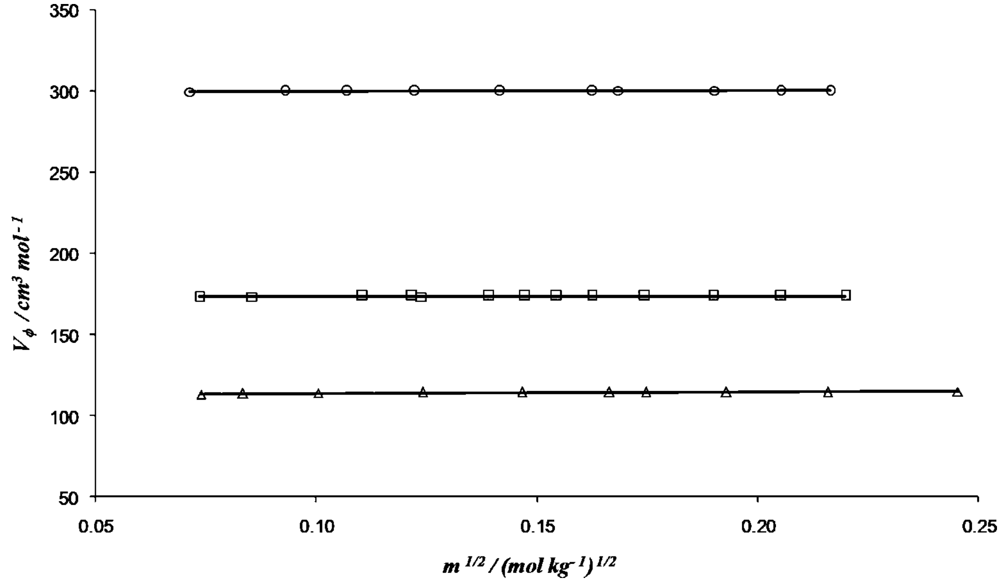

Figure 1. Apparent molal volumes of: ○, Bu_4NBr; □, Et_4NBr; and Δ, Me_4NBr in aqueous solution at 298.15 K.

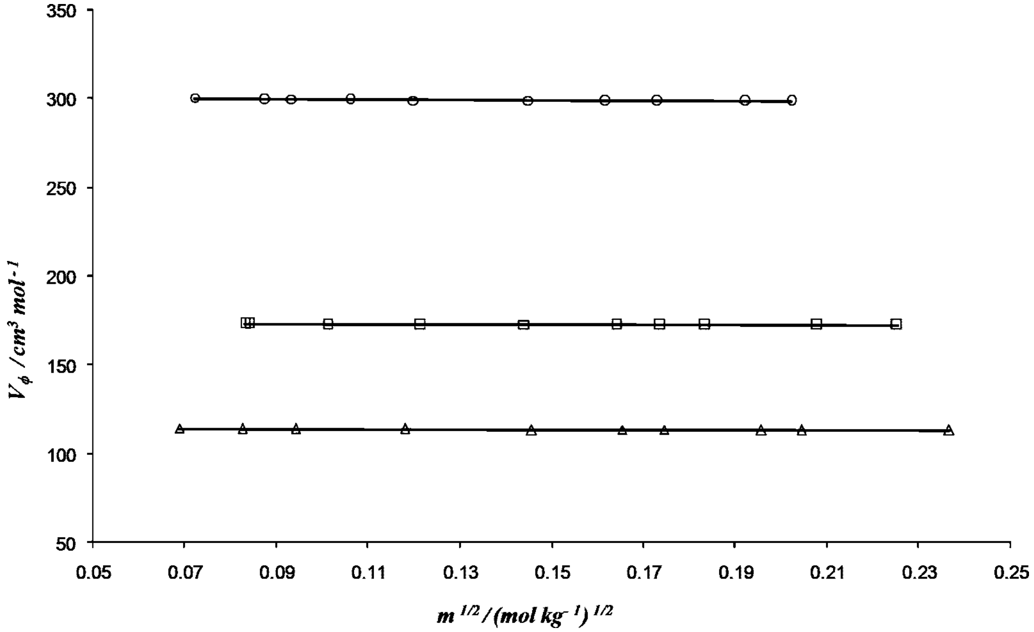

Figure 2. Apparent molal volumes of: ○, Bu_4NBr; □, Et_4NBr; and Δ, Me_4NBr in aqueous solution at 293.15 K.

several molal concentrations, the apparent molal volumes of the solutes, and their uncertainties (σ_v) at all temperatures studied. Uncertainty values were calculated according to the law of propagation of uncertainties.[12] Figures 1, 2, 3, and 4 show the dependence of V_ϕ on $m^{1/2}$ for tetraalkylammonium bromides in aqueous solution at all temperatures studied.

The molal concentration dependence of V_ϕ in a given system was determined by weighted least-squares method and was fit to the equation[13]

$$V_\phi = V^{\circ}_{\phi} + S_V m^{1/2} + B_V m \tag{2}$$

where V°_{ϕ} is the apparent molal volume at infinite dilution (which also equals the partial molal volume of the solute at infinite dilution), S_V is the Debye–Hückel limiting slope for 1:1 electrolytes at each temperature (these values were taken from ref 14), and B_V is an empirical constant. The values of V°_{ϕ} with their uncertainties are summarized in Table 5. The V°_{ϕ} values for tetraalkylammonium bromides in water reported by other authors are also shown.

The variation of V°_{ϕ} with temperature can be adjusted to the following equation

$$V^{\circ}_{\phi} = a + bT^2 \tag{3}$$

where T is the temperature in Kelvin and a and b are empirical constants. The a and b constants were determined by the method of least squares and their values, together with their uncertainties, are given in Table 6. The partial molal expansibility at infinite dilution, E°_{ϕ}, can be obtained by differentiating eq 3 with respect to temperature $E^{\circ}_{\phi} = (\partial V^{\circ}_{\phi}/\partial T)_P = 2bT$. The values of E°_{ϕ} and their uncertainties for tetraalkylammonium bromides at different temperatures are recorded in Table 5.

According to Table 5, good agreement is found with the V°_{ϕ} data reported by Frank and Smith[6] at (298.15 and 278.15) K and by Blanco and Vargas[7] at 298.15 K. The results reported by Wen and Saito[8] at 298.15 K for Bu_4NBr show differences in V°_{ϕ} when compared with this work. These differences can be attributed to the fact that Wen and Saito studied the tetraalkylammonium bromides at concentrations above 0.1 mol·kg^{-1}

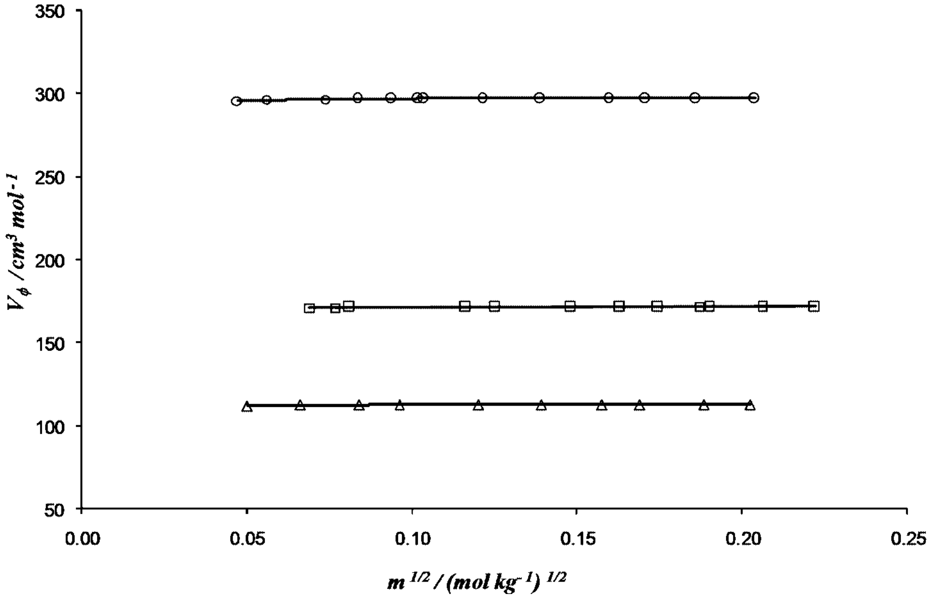

Figure 3. Apparent molal volumes of: ○, Bu_4NBr; □, Et_4NBr; and Δ, Me_4NBr in aqueous solution at 288.15 K.

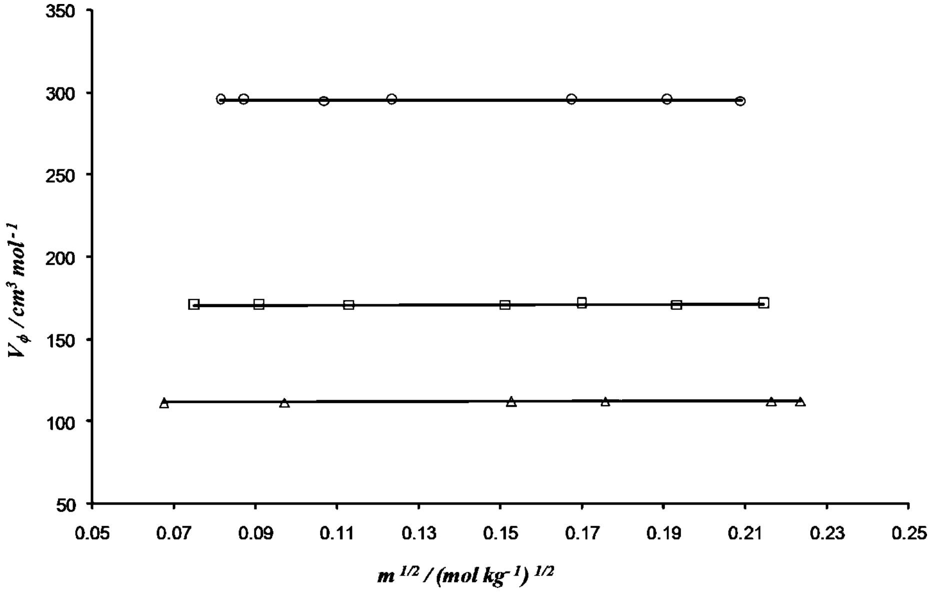

Figure 4. Apparent molal volumes of: ○, Bu_4NBr; □, Et_4NBr; and Δ, Me_4NBr in aqueous solution at 278.15 K.

where the limiting law is not followed. According to Frank and Smith,[6] the uncertainties in V°_ϕ quoted by Conway et al.[16] are not consistent with the experimental uncertainties. This could be the reason for the differences in the values of V°_ϕ reported by Conway et al.[16] and the values reported in this work.

Table 5 shows that the partial molal expansibility at infinite dilution is, within experimental uncertainty, independent of temperature. It has positive values that become more positive the longer the hydrocarbon chain.

This behavior was also observed by Leduc et al.[17] They determined partial molal expansibility of *n*-alkylamine hydrobromides in the temperature range of (288.15 to 328.15) K. De Lisi et al.[18] showed that V°_ϕ of alkyltrimethylammonium bromides are a lineal function of temperature. Torres et al.[19] also reported the same behavior for aqueous solutions of lidocaine−HCl and procaine−HCl in the range of (288.15 to 310.15) K. Millero et al.[20,21] reported E°_ϕ for tetraalkylammonium chlorides from (293.15 to 313.15) K. They found that E°_ϕ increases with the increasing of temperature.

The limiting apparent molal volume can be separated into the individual ionic contributions according to[15]

$$V^\circ_{\text{salt}} = \nu_+ V^\circ_+ + \nu_- V^\circ_- \qquad (4)$$

where ν_+ and ν_- are the stoichiometric coefficients of the ions. For tetraalkylammonium bromides, eq 4 can be expressed as

$$V^\circ_{\text{R}_4\text{NBr}} = V^\circ_{\text{R}_4\text{N}^+} + V^\circ_{\text{Br}^-} \qquad (5)$$

where $V^\circ_{\text{R}_4\text{N}^+}$ and $V^\circ_{\text{Br}^-}$ are the partial molal volumes of the tetraalkylammonium cation and bromide anion, respectively.

Hefter and Marcus[21] have criticized in detail several methods for the determination of V°_i. In this work the methods proposed by Conway el al.[16] and Jolicoeur et al.[21] are used. They found that in aqueous solution the V°_ϕ of tetra-*n*-alkylammonium salts is a lineal function of both the cation molar mass ($M_{\text{R}_4\text{N}^+}$) and the number of carbon atoms (n_c) in the alkyl chains according to the following equations

Table 5. Partial Molal Volume at Infinite Dilution ($V^{\circ}_{R_4NBr}$) and the Partial Molal Expansibility at Infinite Dilution ($E^{\circ}_{R_4NBr}$) of Tetraalkylammonium Bromides in Water from T = (278.15 to 298.15) K

T	$V^{\circ}_{R_4NBr}$	σ_v	$E^{\circ}_{R_4NBr}$	σ_E
K	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1} \cdot K^{-1}$	$cm^3 \cdot mol^{-1} \cdot K^{-1}$
		Bu_4NBr		
278.15	295.64; 295.40[a]	0.17	0.221	0.051
288.15	296.73; 300[c]	0.07	0.229	0.053
293.15	299.39	0.18	0.233	0.054
298.15	299.90; 300.35;[a] 300.38;[b] 302.9;[c] 301.0[d]	0.12	0.237	0.055
		Et_4NBr		
278.15	170.65; 171.15[a]	0.30	0.125	0.022
288.15	171.40	0.10	0.129	0.023
293.15	172.22	0.19	0.131	0.023
298.15	173.29; 173.65;[a] 172.73;[b] 175.3;[c] 174.3[d]	0.09	0.133	0.024
		Me_4NBr		
278.15	111.81; 112.20[a]	0.22	0.110	
288.15	112.05	0.05	0.114	0.034
293.15	113.44	0.11	0.116	0.035
298.15	113.98; 114.40;[a] 114.05;[b] 114.8;[c] 114.2[d]	0.11	0.118	0.035

[a] Ref 6. [b] Ref 7. [c] Ref 8. [d] Ref 16.

Table 6. Constants of Equation 3 for Tetraalkylammonium Salts in Water

salt	a	b
	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1} \cdot K^{-2}$
Bu_4NBr	264.5 (± 7.8)	0.00040 (± 0.00009)
Et_4NBr	153.1 (± 3.4)	0.00022 (± 0.00004)
Me_4NBr	96.2 (± 5.0)	0.00020 (± 0.00006)

Table 7. Partial Molal Properties of the Ions for Tetraalkylammonium Bromides in Aqueous Solutions and *w* of Equations *6* and *7* for Tetraalkylammonium Salts in Aqueous and Nonaqueous Solutions at Temperatures of (278.15 to 298.15) K

	278.15 K	288.15 K	293.15 K	298.15 K
		$V^{\circ}_{Br^-}/cm^3 \cdot mol^{-1}$		
	29.40 ± 2.9	29.47 ± 2.45	29.78 ± 3.5	30.55 ± 2.7
	30.24 ± 2.8[f]			29.2 ± 2.9[a]
				31.09 ± 2.2[b]
				30.66 ± 2.2[c]
				30.84 ± 2.6[d]
				30.68 ± 2.1[e]
				30.91 ± 2.5[f]
		$V^{\circ}_{R_4N^+}$ $/cm^3 \cdot mol^{-1}$		
Bu_4NBr	266.24	267.26	269.61	269.35
Et_4NBr	141.25	141.93	142.44	142.74
Me_4NBr	82.41	82.58	83.66	83.43
		$w/cm^3 \cdot mol^{-1}$		
aqueous solutions	1.10 ± 0.02	1.10 ± 0.02	1.11 ± 0.02	1.11 ± 0.02
	1.10 ± 0.02[f]			1.10 ± 0.02[a]
				1.11 ± 0.01[b]
				1.12 ± 0.01[c]
				1.11 ± 0.02[d]
				1.12 ± 0.01[e]
				1.11 ± 0.02[f]
			1.13 ± 0.01[g]	1.13 ± 0.01[g]
				1.11 ± 0.01[h]
nonaqueous solutions			1.19 ± 0.03[i]	1.19 ± 0.03 [i]
				1.1 ± 0.1[j]
				1.25 ± 0.01[k]
				1.25 ± 0.02[l]
				1.24 ± 0.01[m]

[a] Ref 10. [b] Ref 22. [c] Ref 16. [d] Ref 23. [e] Ref 8. [f] Ref 6. [g] From tetraalkylammonium cyclohexylsulfamates, ref 2. [h] From tetraalkylammonium hydroxides, ref 23. [i] From tetraalkylammonium perchlorates in *N,N*-dimethylformamide, ref 24. [j] From tetraalkylammonium bromides in ethanol, ref 22. [k] From tetraalkylammonium bromides in acetonitile, ref 24. [l] From tetraalkylammonium bromides in acetonitrile, ref 25. [m] From tetraalkylammonium bromides in acetonitrile, ref 23.

$$V^{\circ}_{R_4NBr} = V^{\circ}_{X^-} + wM_{R_4N^+} \tag{6}$$

$$V^{\circ}_{R_4NBr} = V^{\circ}_{X^-} + 18.04w + 14.03wn_c \tag{7}$$

where $V^{\circ}_{X^-}$ is the limiting partial molal volume of the anion and w is a constant.

In this work, linear relations, according to eqs 6 and 7, were obtained at all temperatures studied. The intercept ($V^{\circ}_{Br^-}$) and the slope (w) at all temperatures studied are given in Table 7 together with their uncertainties; values of $V^{\circ}_{R_4N^+}$ are also shown. The $V^{\circ}_{R_4NBr}$ for Pr_4NBr at (278.15 and 298.15) K reported by Franks and Smith[6] has been added to the fitting. Good agreement was found between these data and the data obtained in this work. Additionally, data of w obtained by several authors using other tetraalkylammonium salts and other solvents are shown in Table 7.

According to Marcus,[4] the molar mass of the tetraalkylammonium cation, $M_{R_4N^+}$, and the number of carbon atoms in its alkyl chain are linearly related ($M_{R_4N^+} = 18.04 + 14.03 \cdot n_C$). Therefore, eqs 6 and 7 are equivalent, and the values of w are close to 1.00 in all cases. They show the contribution of the $-CH_2-$ group to the limiting ionic volume of R_4N^+. The data summarized in Table 7 show that the values of w are independent of temperature but are dependent on the solvent used.

It is commonly said in the literature that the partial molal volume of the ion, V°_i, should depend on the properties of the ions and the solvent, according to the following empirical equation

$$V^{\circ}_i = V_{int} + V_{electr} + V_{struc} \tag{8}$$

where V_{int} is the intrinsic volume of the ion, V_{electr} is the electrostriction of the solvent surrounding the ion caused by its intensive electrical field, and V_{struc} is the structural contribution and may be described as the effect of the ion on the solvent.[1]

For aqueous solutions of tetraalkylammoniun salts, it has been established that V_{int} is proportional to the third power of the crystal radius, r_i, according to[1]

$$V_{int}/cm^3 \cdot mol^{-1} = 2522[r_{(i)}/nm]^3 \tag{9}$$

The electrostriction contribution to the ionic volume, V_{electr}, is commonly taken to be proportional to the reciprocal of the ionic radius.[1,3] In this way, Marcus and Hefter[27] have proposed an expression for the calculation of V_{electr} that can be used for aqueous and nonaqueous solutions of ions. Marcus[1] has found that for large hydrophobic ions that have alkyl or aryl groups with $r_i > 0.25$ nm, such as tetraalkylammonium ions, the electrostriction is negligible, whereas for the small cation, generally $|V_{electr}| \gg V_{int}$, the absolute value indicates that the contribution of V_{electr} is negative.[1,3]

V_{struc} of eq 8 has been ascribed to the increment caused by the structuring of water molecules around ions. Millero[28] has found that V_{struc} of monovalent ions with r_i =1.0 Å in water is positive. Marcus[1] has calculated the group increment for tetraalkyl and aryl ions in several solvents. He found that in water the increments per CH_3- group and CH_2- group are (7.5 and 5.4) $cm^3 \cdot mol^{-1} \cdot K^{-1}$, respectively. The result for group

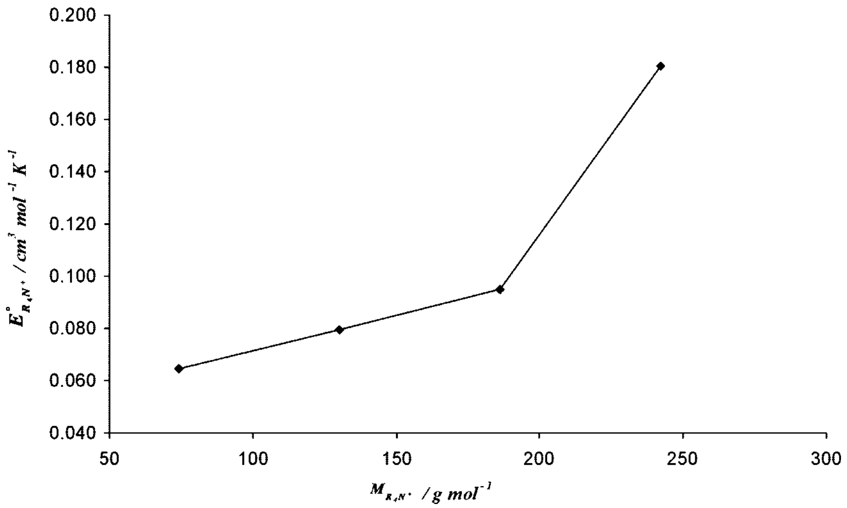

Figure 5. The limiting partial molal expansibility $E^\circ_{R_4N^+}$ against the molecular weight $M_{R_4N^+}$ of the R_4N^+ in water.

increments shows that the methylene increment is nearly independent of the solvent used but that the methyl increment appreciably depends on the solvent. The $V^\circ_{R_4}N^+$ values found in this work show an increment when the temperature increases. It can be attributed to the breakage of solvent structure, which causes an increase in the structural molal volume, V_{struc}.

In Table 5, it can be seen that the limiting partial molal expansibility at infinite dilution is independent of temperature and increases with the molecular weight of the tetraalkylammonium bromide. The limiting partial molal expansibility of the ion, E°_i, can be calculated the same way as V°_i is calculated

$$E^\circ_{R_4NBr} = E^\circ_{R_4N^+} + E^\circ_{Br^-} \qquad (10)$$

Upon differentiation of eq 8 with respect to temperature, the partial molal expansibility of an ion at infinite dilution, E°_i, is obtained

$$E^\circ_i = E_{int} + E_{electr} + E_{struc} \qquad (11)$$

where E_{int} is the intrinsic expansibility of ion, which can be assumed to be independent of temperature,[20] E_{electr} is the expansibility due to electrostriction, and E_{struc} is the expansibility due to structural changes in water. Because the R_4N^+ ion has negligible electrostriction,[1] E_{electr} can be taken as zero. $E^\circ_{R_4N^+}$ should be characterized in terms of structural hydration effects.

The $E^\circ_{Br^-}$ value has been calculated to be 0.05 $cm^3 \cdot mol^{-1} \cdot K^{-1}$ by Millero.[29] Therefore, according to eq 10, the following values were calculated for this work: $E^\circ_{Bu_4N^+}$ = 0.18 $cm^3 \cdot mol^{-1} \cdot K^{-1}$, $E^\circ_{Et_4N^+}$ = 0.08 $cm^3 \cdot mol^{-1} \cdot K^{-1}$, and $E^\circ_{Me_4N^+}$ = 0.07 $cm^3 \cdot mol^{-1} \cdot K^{-1}$. In Figure 5,$E^\circ_{R_4N^+}$ is plotted as a function of the molecular weight of the cation; data of $E^\circ_{Pr_4N^+}$ were taken from ref 29. Figure 5 shows that $E^\circ_{R_4N^+}$ increases as the molecular weight of the cation linearly increases for the first three salts; however, the value of $E^\circ_{Bu_4N^+}$ is higher than expected. Because E_{electr} is very small or zero for the tetraalkylammonium cations, the $E^\circ_{R_4N^+}$ can be attributed to E_{int} and E_{struc}.

From data of the ionic radius of the tetraalkylammonium cation,[30] it can be found that the variation of $r_{R_4N^+}$ with the molecular weight of the cation (from Me_4N^+ to Bu_{4N^+}), $M^\circ_{R_4N^+}$, obeys the relation: $r^\circ_{R_4N^+} = (7.8 \cdot 10^{-4})M_{R_4N^+} + 0.23$. Therefore, by comparison with eq 9, the deviation of the tetrabutylammonium cation can be attributed to structure formation.[5] It therefore changes the E°_{struc} term of eq 11 and shows that hydrophobic hydration plays an important role.

Literature Cited

(1) Marcus, Y. The Standard Partial Molal Volumes of Ions in Solution. Part 1. The Volumes in Single Non-Aqueous Solvents at 298.15 K. *J. Mol. Liq.* **2005**, *118*, 3–8.

(2) Klofutar, C.; Horvat, J.; Rudan-Tasic, D. Apparent Molar Volume and Apparent Molar Expansibility of Tetraethyl-, Tetra-*n*-propyl-, Tetra-*n*-butyl-, and Tetra-*n*-pentylammonum Cyclohexylsulfamates in Aqueous Solution. *Acta. Chim. Slov.* **2007**, *54*, 460–468.

(3) Millero, F. J. The Molal Volumes of Electrolytes. *Chem. Rev.* **1971**, *71*, 147–176.

(4) Marcus, Y. *Ion Solvation*; Wiley: Chichester, U.K., 1985.

(5) Wen, W. Y. Aqueous Solutions of Symmetrical Tetraalkylammonium Salts. In *Water and Aqueous Solutions: Structure, Thermodynamics, and Transport Processes*; Horne, R. A., Ed.; Wiley-Interscience: New York, 1972; pp 613−661.

(6) Franks, F.; Smith, H. T. Apparent Molal Volumes and Expansibilities of Electrolytes in Dilute Aqueous Solution. *Trans. Faraday Soc.* **1967**, *63*, 2586–2598.

(7) Blanco, L. H.; Vargas, E. F. Apparent Molar Volumes of Symetric and Asymetric Tetraalkylammonium Salts in Dilute Aqueous Solutions. *J. Solution Chem.* **2006**, *35*, 21–28.

(8) Wen, W. Y.; Saito, S. Apparent and Partial Molal Volumes of Five Symmetrical Tetraalkylammonium Bromides in Aqueous Solutions. *J. Phys. Chem.* **1964**, *68*, 2639–2644.

(9) G.Perron, G.; Desrosiers, N. Thermodynamic Properties of Tetraalkylammonium Halides: Volumes, Heat Capacities, and Expansibilities in H_2O, D_2O, and Urea-Water Mixtures from 278 to 328 K. *Can. J. Chem.* **1976**, *54*, 2163–2183.

(10) Blanco, L. H.; Vargas, E. F. An Improved Magnetic Float Densimeter. *Instrum. Sci. Technol.* **2004**, *32*, 13–20.

(11) Patterson, J. B.; Morris, E. C. Measurement of Absolute Water Density, 1 °C to 40 °C. *Metrologia* **1994**, *31*, 277–288.

(12) Taylor, B. N.; Kuyatt, C. E. *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; Adapted from NIST Technical Note 1297; National Institute of Standards and Technology: Gaithersburg, MD, 1994.

(13) Redlich, O.; Meyer, D. M. The Molal Volumes of Electrolytes. *Chem. Rev.* **1964**, *64*, 221–226.

(14) Ananthaswamy, J.; Atkinson, G. Thermodynamics of Concentrated Electrolyte Mixtures. 4. Pitzer−Debye−Huckel Limiting Slopes for Water from 0 to 100 °C and from 1 atm to 1 kbar. *J. Chem. Eng. Data* **1984**, *29*, 81–87.

(15) Marcus, Y. Ionic Volumes in Solution. *Biophys. Chem.* **2006**, *124*, 200–207.

(16) Conway, B. E.; Verall, R.E.; Desyoners, J. E. Partial Molal Volumes of Tetraalkylammonium Halides and Assignment of Individual Ionic Contributions. *Trans. Faraday Soc.* **1966**, *62*, 2738–2749.

(17) Leduc, P. A.; Fortier, J. L.; Desnoyers, J. E. Apparent Molal Volumes, Heat Capacities, and Excesss Enthalpies of *n*-Alkylamine Hydrobromides in Water as a Function of Temperature. *J. Phys. Chem.* **1974**, *78*, 1717–1225.

(18) De Lisi, R.; Milioto, S.; Verrall, R. E. Partial Molar Volumes and Compressibilities of Alkylmethylammonium Bromides. *J. Solution Chem.* **1990**, *19*, 665–692.

(19) Torres, D. R.; Blanco, L. H.; Martinez, F.; Vargas, E. F. Apparent Molal Volumes of Lidocaines-HCl and Procaine-HCl in Aqueous Solution as a Function of Temperature. *J. Chem. Eng. Data* **2007**, *52*, 1700–1703.

(20) Millero, F. J.; Drost-Hansen, W. Apparent Molal Volumes of Ammonium Chloride and Some Symmetrical Tetraalkylammonium Chlorides at Various Temperatures. *J. Phys. Chem.* **1968**, *72*, 758–763.

(21) Jolicoeur, C.; Philip, P. R.; Perron, G.; Leduc, P. A.; Desnoyers, J. E. A Comparative Study of Bu_4NBr, $NaBPh_4$, Ph_4PCl, and Ph_4AsCl in Water and Methanol at 25 °C: Partial Molal Volumes, Heat Capacities, and Viscosities. *Can. J. Chem.* **1972**, *50*, 3167–3178.

(22) Nikam, P. S.; Pawar, T. B.; Sawant, A. B.; Hasan, M. Limiting Ionic Partial Molar Volumes of R_4N^+ and Br^- in Aqueous Ethanol at 298.15 K. *J. Mol. Liq.* **2006**, *126*, 19–22.

(23) Klofutar, C. D.; Rudan-Tasic, D.; Mancic-Klofutar, V. Partial Molar Volumes of Tetraalkylammonium Hydroxides in Aqueous Solution at 25°. *J. Solution Chem.* **1977**, *26*, 1037–1047.

(24) Saha, N.; Das, B. Apparent Molar Volumes of Some Symmetrical Tetraalkylammonium Bromides in Acetonitrile at (298.15, 308.15, and 318.15) K. *J. Chem. Eng. Data* **1997**, *42*, 227–229.

(25) Bottomley, G. A.; Bremers, M. T. Electrolyte Molar Volumes at 273−373 K in Propylene Carbonate. *N*-Methylformamide, Formamide, and Methanol: Their Relation to Solvent Compressibility. Ion Association Constants in Acetonitrile at 298 K. *Aust. J. Chem.* **1986**, *39*, 1959–1981.

(26) Marcus, Y.; Hefter, G.; Pang, T.-S. Ionic Partial Molar Volumes in Non-Aqueous Solvents. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1899–1903.

(27) Marcus, Y.; Hefter, G. On the Pressure and Electric Field Dependencies of the Relative Permittivity of Liquids. *J. Solution Chem.* **1999**, *28*, 575–592.

(28) Millero, F. J. The Partial Molal Volumes of Electrolytes in Aqueous Solutions. In *Water and Aqueous Solutions: Structure, Thermodynamics, and Transport Processes*; Horne, R. A., Ed.; Wiley-Interscience: New York, 1972; p 560.

(29) Millero, F. J. Apparent Molal Expansibilites of Some Divalent Chlorides in Aqueous Solution at 25°. *J. Phys. Chem.* **1968**, *72*, 4589–4593.

(30) Marcus, Y. The Standard Partial Molar Volumes of Aqueous Ions at 298.15 K. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 713–718.

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