Partial Molar Volumes of Butyltriethylammonium Iodide in Single Nonaqueous Solvents at 298.15 K

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Densities of butyltriethylammonium iodide solutions in methanol, 2-propanone, acetonitrile, and nitrobenzene were measured at 298.15 K. Using published values for the Debye−Hückel limiting slopes A_V, apparent molar volume data were fitted to the Redlich−Rosenfeld−Meyer and the Pitzer equations, allowing the evaluation of partial molar volumes at infinite dilution $\bar{V}^0$ and deviation parameters B_V. The results show a similarity between the $\bar{V}^0$ values for the "*asymmetrical*" quaternary ammonium salt (where the cation has a slightly extended alkyl group) and those for the corresponding "*symmetrical*" salt (presenting the four alkyl groups identical to the longest of them). Parameter B_V is shown to be solvent dependent.

Introduction

Volumetric properties have been extensively studied because the results are of great help in characterizing the structure and properties of solutions. Limiting values of the apparent molar volumes of electrolytes provide valuable information about solute−solvent interactions,[1−7] being of fundamental importance for understanding reaction rates and equilibria involving dissolved electrolytes.

Concerning the ammonium quaternary salts (Menshutkin reaction products), these studies have been fundamentally based on "*symmetrical*" salts in pure solvents[5,8,9] or in solvent mixtures.[10,11]

A survey of the literature shows that few studies (only in water and hydroxylic solvents) have been made on the partial molar volumes of "*asymmetrical*" quaternary ammonium salts, namely, the butyltriethylammonium iodide ($BuN^+Et_3I^-$). Hence, the limiting apparent molar volumes of butyltriethylammonium iodide may lead to a better insight into the analysis of the solute−solvent interactions.

This paper reports the volumetric data for $BuN^+Et_3I^-$ in methanol (MeOH), 2-propanone (Me_2CO), acetonitrile (MeCN), and nitrobenzene ($PhNO_2$), at 25 °C and atmospheric pressure.

Experimental Section

Materials. Triethylamine (≥ 99.5 %) was obtained from Fluka, and its purity was confirmed by gas-phase chromatography. 1-Iodobutane (≥ 99.0 %) was supplied by Aldrich. Methanol (≥ 99.5 %), 2-propanone (≥ 99.5 %), and nitrobenzene (≥ 99.0 %) were obtained from Merck, and the water content of methanol was kept lower than 0.01 %. Acetonitrile (≥ 99.0 %) was supplied by Riedel-de Haën. Spectrophotometric analysis confirmed that solvents contained no organic impurities. Solvents were stored and handled under dry nitrogen, their purity being periodically checked by density and conductivity measurements.

Synthesis of Butyltriethylammonium Iodide. The alkyl iodide (1-iodobutane) was added to the triethylamine in excess, and the mixture kept from light was allowed to stand for a long period. The quaternary ammonium salt was precipitated as a white microcrystalline powder after filtration, successive recrystallizations, and vacuum drying. Purification and storage were carried out under dry-nitrogen conditions. The melting point of the salt (uncorrected) was determined on a Mettler FP51/FP5 photoelectric apparatus.

^1H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a Brüker Avance 400 spectrometer [(400.13 and 100.62) MHz]. Chemical shifts are reported as δ values in parts per million using the solvent residual signal as a reference. Coupling constants (J) are given in hertz.

Elemental analysis was determined on a Fisons EA 1108 microanalyzer.

Butyltriethylammonium iodide [$CH_3(CH_2)_3N(CH_3CH_2)_3I$]: white crystals; mp > 300 °C (from ethanol); ^1H NMR (400.13 MHz, DMSO) δ 3.22 (12H, q, $J = 7.1$ Hz), 1.16 (12H, dt, $J =$ 7.12; 7.12 Hz), ^{13}C NMR (100.62 MHz, DMSO) δ 51.9(CH_2), 51.88(CH_2), 51.85 (CH_2), 7.03 (CH_3). Anal. Calcd. for $C_{10}H_{24}NI$: C, 42.09; H, 8.48; N, 4.91. Found: C, 42.15; H, 8.41; N, 4.96.

Apparatus and Procedure. Densities were measured using a vibrating-tube digital densimeter (Anton Paar, model DMA60/512). The temperature was kept constant to within ± 0.005 °C and monitored with a digital thermometer (Anton Paar, model DT-100-20).

Prior to each set of measurements, the densimeter was calibrated with water and air.

Freshly prepared and degassed high-purity water ($\kappa = 0.8$ $\mu S \cdot m^{-1}$) was used taking[12] $\rho^*_{H_2O}(25\ °C) = 0.997047\ g \cdot cm^{-3}$. The density of dry air was calculated as[13] $\rho_{air}(25\ °C)/(g \cdot cm^{-3}) = 1.16914 \cdot 10^{-6} p/(hPa)$. All measurements were made at

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Table 1. Percentage Deviations in the Obtained Densities of Pure Solvents and Debye−Hückel Limiting Law Slopes for the Solvents Used in This Work at $T = 298.15$ K and $p = 1$ atm

solvent	ρ_{exp}[a] $\mathrm{g \cdot cm^{-3}}$	ρ_{lit} $\mathrm{g \cdot cm^{-3}}$	% deviation	A_{v}[e] $\mathrm{cm^3 \cdot dm^{3/2} \cdot mol^{-3/2}}$
MeOH	0.78638	0.78670[b]	−0.041	18.57
Me_2CO	0.78381	0.78437[b]	−0.071	29.08
MeCN	0.77601	0.77599[c]	0.000	13.40
$PhNO_2$	1.19891[a]	1.19835[d]	0.047	8.09

[a] This work. [b] Refs 8 and 9. [c] Ref 10. [d] Ref 14. [e] Ref 15. Debye−Hückel limiting law slopes. As the concentrations are expressed in molalities, the values of DHLL slopes taken from the literature were multiplied by $\rho_o^{1/2}$.

(25.000 ± 0.005) °C and atmospheric pressure. For each solvent, solutions were prepared by weight under dry nitrogen in a glovebox, without buoyancy correction. After allowing 30 min for thermal equilibration, each density measurement was taken as the average value of ten consecutive readings. The precision of density data is ± 10 $\mu\mathrm{g \cdot cm^{-3}}$.

Three independent densimetric runs were made at the mentioned temperature and pressure conditions, for each solvent, observing a mean deviation of approximately ± 0.00005 $\mathrm{g \cdot cm^{-3}}$.

Results

The observed densities (ρ) of the butyltriethylammonium iodide solutions, which represent the mean of three independent series of measurements for each solvent, were used to calculate the apparent molar volumes ($V_{\phi,2}/\mathrm{cm^3 \cdot mol^{-1}}$) of the electrolyte by means of the equation

$$V_{\phi,2} = \frac{1000(\rho_o - \rho)}{m\rho_o\rho} + \frac{M_2}{\rho} \tag{1}$$

where M_2 ($\mathrm{g \cdot mol^{-1}}$) is the molar mass of the solute; m ($\mathrm{mol \cdot kg^{-1}}$) is the molality; and ρ and ρ_o are the densities ($\mathrm{g \cdot cm^{-3}}$) of the solution and the solvent, respectively.

Errors in apparent molar volume (V_ϕ) resulting from uncertainties in molality and density measurements can be estimated by taking the partial derivatives of eq 1 with respect to m and ρ, respectively. In general, for a fixed uncertainty in ρ, the error in V_ϕ increases when molality tends to zero.[2] To validate the accuracy of the obtained results, experimental densities were compared with literature values for pure solvents, at 25 °C. The consistency is given in Table 1.

To describe the molality dependence of apparent molar volumes, two empirical correlations deduced from the Debye−Hückel Limiting Law (DHLL)[16] were used, the Redlich−Rosenfeld−Meyer equation[17] and the Pitzer equation[18] where A_V is related with

$$\underbrace{V_\phi - A_V\sqrt{m}}_{V_\phi'} = V_\phi^0 + B_v m \tag{2}$$

$$\underbrace{V_\phi - A_V b^{-1}\ln(1 + b\sqrt{m})}_{V_\phi''} = V_\phi^0 + B_v' m \tag{3}$$

the Debye−Hückel limiting coefficient; the slopes B_v and B_v' are empirical constants of the fit; and parameter b has a universal value of 1.2 $\mathrm{kg^{1/2} \cdot mol^{-1/2}}$.

The theoretical expression for A_v is well-known,[18,19] and Ananthaswamy and Atkinson[20] demonstrated the equivalence of these limiting slope values for eqs 2 and 3. In these equations, V_ϕ^0 is the apparent molar volume of the electrolyte at infinite dilution, which is a characteristic, in part, of solute−solvent interactions as it depends on the solvent relative permittivity, size and charge of the ions, pressure, and temperature.[5,21,22] Slopes B_v describe deviations from DHLL, which can be understood in terms of interactions between ion solvation shells, depending on temperature, solvent, and the electrolyte.[5,16,21,22] However, in solvents of low electric permittivity, experimentally determined B_v values will include contributions arising from the formation of ion pairs.[23]

The molalities (m), densities (ρ), and V_ϕ values obtained from the apparent molar volumes of the quaternary ammonium salt $BuN^+Et_3I^-$ in the four studied solvents are recorded in Table 2.

Apparent molar volumes at infinite dilution, V_ϕ^0, of butyltriethylammonium iodide ($BuN^+Et_3\ I^-$) solutions in the four mentioned solvents, were determined from data listed in Table 2, using least-squares fits to the linear plots of V_ϕ' (Redlich−Rosenfeld−Meyer equation) or V_ϕ'' (Pitzer equation) versus molality (m), as shown previously (eqs 2 and 3). To calculate V_ϕ', the values of A_v given in Table 1 were used.

The plots of V_ϕ' against molality were found to be linear for this quaternary ammonium compound in all solvents at 25 °C.

Through the least-squares procedure, apparent molar volumes at infinite dilution, V_ϕ^0, experimental slopes, B_v, and the related standard deviation estimates were obtained and are shown in Table 3. A representative plot for the referred salt in different solvents at 25 °C and 1 atm is shown in Figure 1.

Discussion

The experimental results exhibit linearity for both eqs 2 and 3 through a large range of molalities, which is consistent with previous studies of symmetrical quaternary ammonium salts in both aqueous and nonaqueous solvents.[2,8−10,21,24−26] The slopes B_v and B_v' agree for each solvent to within experimental error.

Partial molar volumes at infinite dilution of electrolytes in water at 25 °C are described through a simple additivity scheme based on the intrinsic volume approach. A similar approach may be applied here as long as there is no appreciable ion pair formation.[27] Thus, standard partial molar volumes of electrolytes are separated into the contributions of the cation and the anion, following the extrapolation method suggested by Conway and co-workers,[28] considering also solvent dependence.

Ionic limiting partial volumes can be divided into three components as follows[29]

$$\bar{V}_{\mathrm{ion}}^0 = \bar{V}_{\mathrm{intr}}^0 + \bar{V}_{\mathrm{elect}}^0 + \bar{V}_{\mathrm{struc}}^0 \tag{4}$$

where $\bar{V}_{\mathrm{intr}}^0$ is the intrinsic molar volume of the ion; $\bar{V}_{\mathrm{elect}}^0$ is the electrostriction partial molar volume; and $\bar{V}_{\mathrm{struc}}^0$ is any further effect the ion may have on the solvent surrounding molecules, particularly if the solvent is structured (e.g., by hydrogen bonding or dipole interactions).

The high values of the apparent molar volumes at infinite dilution V_ϕ^0 found for $BuN^+Et_3I^-$ in the studied solvents agree with the theoretical assumptions mentioned above. Actually, being the intrinsic volume in close relation to the ionic radii (anion and cation) through $V = (4/3)\pi r^3$, where r can be identified as the ionic radius in the crystal, the increasing values of $\bar{V}_{\mathrm{intr}}^0$ are compatible with known values of ionic radii of anion I^- ($r = 220$ pm, the highest one among the simple anions only overcome by values concerning At^-) and also with the values of ionic radii of cations Et_4N^+ ($r = 337$ pm) or n-Bu_4N^+ ($r = 413$ pm).[30] On the other hand, the component $\bar{V}_{\mathrm{elect}}^0$ due to the electrostriction resulting from the electrostatic interactions with the solvent presents itself reduced in these salts, namely, the

Table 2. Densities and Apparent Molar Volumes of Butyltriethylammonium Iodide ($BuN^+Et_3I^-$) in Different Solvents at 25 °C[a]

first run			second run			third run		
m mol·kg^{-1}	ρ g·cm^{-3}	$V\phi^a$ cm^3·mol^{-1}	m mol·kg^{-1}	ρ g·cm^{-3}	$V\phi^a$ cm^3·mol^{-1}	m mol·kg^{-1}	ρ g·cm^{-3}	$V\phi^a$ cm^3·mol^{-1}
			Methanol					
0.000000	0.78638	–	0.000000	0.78638	–	0.000000	0.78638	–
0.003540	0.78654	290.97	0.003542	0.78654	290.97	0.003541	0.78654	290.97
0.007080	0.78669	290.54	0.007081	0.78669	290.54	0.007079	0.78669	290.54
0.010620	0.78685	290.21	0.010617	0.78685	289.73	0.010631	0.78685	290.13
0.014161	0.78700	289.92	0.014168	0.78700	289.96	0.014167	0.78700	289.96
0.017601	0.78717	289.66	0.017602	0.78717	289.68	0.017601	0.78718	289.68
0.021240	0.78731	289.41	0.0212439	0.78731	289.41	0.021240	0.78731	289.41
0.028321	0.78762	288.97	0.028322	0.78763	288.40	0.028322	0.78762	288.97
			2-Propanone					
0.000000	0.78381	–	0.000000	0.78381	–	0.000000	0.78381	–
0.005360	0.78410	274.05	0.005361	0.78411	272.23	0.005360	0.78410	273.73
0.007107	0.78420	272.27	0.007106	0.78421	271.34	0.007105	0.78420	271.57
0.008910	0.78430	272.04	0.008909	0.78430	271.49	0.008910	0.78430	271.85
0.012421	0.78450	270.68	0.012422	0.78450	270.55	0.012421	0.78450	270.68
0.014204	0.78460	270.36	0.014203	0.78460	270.36	0.014204	0.78460	270.36
0.017703	0.78481	268.55	0.017710	0.78481	268.54	0.017703	0.78481	268.53
0.021149	0.78500	268.87	0.021148	0.78500	268.64	0.021142	0.78499	269.00
			Acetonitrile					
0.000000	0.77601	–	0.000000	0.77601	–	0.000000	0.77602	–
0.003540	0.77616	294.74	0.003541	0.77616	294.74	0.003540	0.77616	298.96
0.007081	0.77632	294.43	0.007082	0.77632	294.53	0.007081	0.77632	296.77
0.010621	0.77647	294.17	0.010620	0.77647	294.17	0.010641	0.77646	297.43
0.014161	0.77663	293.95	0.014162	0.77663	293.95	0.014168	0.77661	296.49
0.017601	0.77677	293.78	0.017603	0.77678	293.69	0.017604	0.77677	295.50
0.021242	0.77693	293.55	0.021241	0.77693	293.55	0.021242	0.77693	294.34
0.028323	0.77724	293.20	0.028322	0.77724	293.20	0.028323	0.77724	293.74
			Nitrobenzene					
0.000000	1.19891	–	0.000000	1.19891	–	0.000000	1.19891	–
0.003538	1.19897	224.77	0.003538	1.19897	224.77	0.003538	1.19897	224.77
0.007075	1.19904	224.52	0.007075	1.19904	224.52	0.007075	1.19904	224.51
0.010597	1.19910	224.39	0.010597	1.19910	224.39	0.010597	1.19910	224.25
0.014150	1.19917	224.15	0.014150	1.19917	224.15	0.014157	1.19917	224.16
0.017703	1.19923	223.97	0.017703	1.19923	223.97	0.017703	1.19923	223.97
0.021195	1.19929	223.94	0.021195	1.19929	223.94	0.021195	1.19929	223.94
0.024687	1.19935	223.89	0.024694	1.19936	223.61	0.024690	1.19936	223.60

[a] Estimated values using the Redlich−Rosenfeld−Meyer equation.

Table 3. Standard Partial Molar Volumes and Slopes B_v and B'_v from the Redlich−Meyer and Pitzer Equations for $BuN^+Et_3I^-$ in Different Solvents at 25 °C[a]

Redlich−Meyer equation[17]			Pitzer equation[18]		
solvent	$V_\phi^0 \pm \sigma_{V_\phi^0}/u$	$B_v \pm \sigma_{B_v}/u'$	solvent	$V_\phi^0 \pm \sigma_{V_\phi^0}/u$	$B'_v \pm \sigma_{B'_v}/u'$
MeOH	291.12 ± 0.71	−79.30 ± 4.28	MeOH	291.12 ± 0.07	−71.66 ± 4.22
Me_2CO	275.02 ± 0.60	−326.35 ± 44.2	Me_2CO	275.03 ± 0.60	−314.30 ± 44.1
MeCN	294.87 ± 0.05	−61.07 ± 2.86	MeCN	294.87 ± 0.05	−55.62 ± 2.82
$PhNO_2$	224.83 ± 0.07	−42.73 ± 4.60	$PhNO_2$	224.84 ± 0.07	−37.62 ± 4.58

[a] Units u = cm^3·mol^{-1}; u′ = cm^3·kg·mol^{-2}.

tetraalkylammoniun cations, R_4N^+ or R_3N^+R', where the alkylic shell is around the positive charge on the nitrogen atom, dramatically decreasing the ion−dipole electrostatic interactions with the solvent molecules. The last term, $\bar{V}^0_{\text{struc}}$, is often ignored in nonaqueous solvents and applied only for aqueous solutions of large ions, and no definite suggestions for its independent estimation have so far been made.[29]

Partial Molar Volumes. Apparent molar volumes, V_ϕ^0, of $BuN^+Et_3I^-$ in the studied solvents (MeOH, Me_2CO, MeCN, and $PhNO_2$) are all positive and of high magnitude, being in agreement with those theoretically expected. Results in Table 3 denote a higher value of V_ϕ^0 for the electrolyte in acetonitrile and, on the contrary, a lower value for nitrobenzene. On the other hand, experimental data are well fitted by the Redlich−Meyer and Pitzer equations, both leading (within the experimental error) to virtually coincident values in the four solvents.

Whenever possible, the referred values are comparable with those published for the structurally similar tetraalkylammonium salts. Values of V_ϕ^0 for $BuN^+Et_3I^-$ in MeOH, Me_2CO, and MeCN are always higher than values evaluated for tetraethylammonium iodide ($Et_4N^+I^-$), lower than the values for tetrapentylammonium iodide ($Pe_4N^+I^-$), but very close to values for the *symmetrical* salt $Bu_4N^+I^-$.[15]

Apparently, V_ϕ^0 values relating to the quaternary ammonium salt where the cation has a slightly extended alkyl group are very similar to the partial molar volumes of the corresponding *symmetrical* salt presenting the four alkyl groups likely with the longest of them. On the other hand, electrostriction is not very relevant in this class of salts. Hence, the differences observed in the V_ϕ^0 values are not significant (particularly in 2-propanone and acetonitrile), being explained by multiple factors, such as the relative permittivity or the compressibility

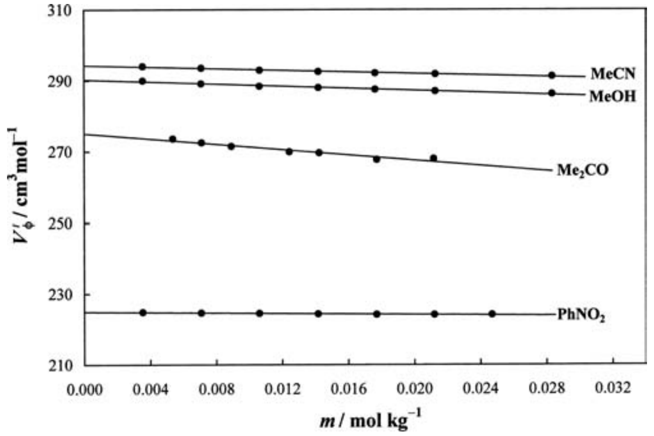

Figure 1. $BuN^+Et_3\ I^-$: typical extrapolations of $V'_{\phi} = V_{\phi} - A_v\sqrt{m}$ with respect to m for the solvents MeCN, MeOH, Me_2CO, and $PhNO_2$. Data at 25 °C from Table 2.

of the solvent. The solvent molecule shape could also account for the mentioned differences, whereas they could influence the access to positive charged centers through the space left between the alkylic chains.

Moreover, as reported before by Pinheiro and co-workers with $Et_4N^+I^-$,[5] the value of V^0_{ϕ} for $BuN^+Et_3I^-$ in MeCN (294.9 $cm^3 \cdot mol^{-1}$) is slightly higher than in MeOH (291.1 $cm^3 \cdot mol^{-1}$), which accords with the general behavior assumed for solvents having similar molecular shape, where, due to packing reasons, partial molar volumes at infinite dilution increase with the solvent molar volume. The similarity concerning the V^0_{ϕ} values in MeOH and MeCN could be related to the dependence of the solvent permittivity on the electric field in the near surrounding of the ion. On the other hand, the sequencial variation from the aliphatic solvents to the aromatic one shows a significant decrease of the apparent molar volumes ($V^0_{\phi} = 224.8$ $cm^3 \cdot mol^{-1}$ for $BuN^+Et_3I^-/PhNO_2$). This can be ascribed to the cation−π-type interactions, the occurrence of which between tetraalkylammonium cations and aromatic solvents is well confirmed.[31]

Parameter B_v. Deviations from the DHLL arising from pairwise interionic short-range interactions in the presence of the solvent are measured by the parameter B_v.

As a general rule,[32] negative values suggest the presence of attractive forces leading to a decrease in the solution volume in relation to the pure-solvent volumetric properties. Conversely, positive values point to the action of repulsive forces. Taking into account the results obtained in water, where trends in B_v values for quaternary ammonium halides are fairly well understood, negative values of B_v are believed to be determined mainly by cation−cation interactions.[33]

Nevertheless, there is much less information available for B_v parameters of organic salts in nonaqueous solvents. Therefore, a great controversy arises from the meaning of its signal (positive or negative).

As can be examined in Table 3, all values of slope B_v are negative in the four solvents. Negative slopes could be ascribed to ionic association and, additionally, to weak cation−cation interactions due to the great intrinsic volume of tetraalkylammonium cations.[1,7,23,33] However, noting the great variability of B_v values with the solvent, this parameter must be strongly dependent on the properties of the latter.

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