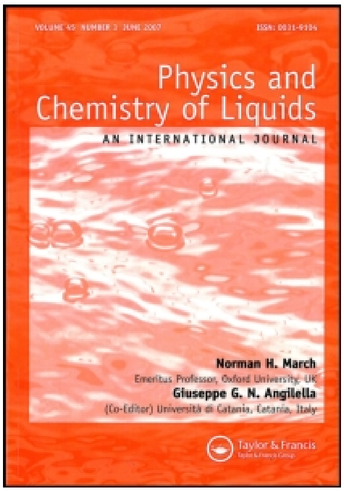

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PARTIAL MOLAL VOLUMES OF ASYMMETRIC IODIDES OF BUTYL-TRIETHYL-AMMONIUM IN AQUEOUS SOLUTIONS AT 298,15 K

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Density measurements have been made on aqueous solutions of *t*-$BuEt_3NI$, *s*-$BuEt_3NI$, *i*-$BuEt_3NI$, Bu_4NI and Et_4NI at 298,15 K from 0,01 to 0,05 m. The apparent molal volumes $\bar{V}_2^o$ calculated from the $V_{2,\varphi}$ (m) plots for the salts show a decrease value: *n*-$BuEt_3NI$ > *i*-$BuEt_3NI$ > *s*-$BuEt_3NI$ > *t*-$BuEt_3NI$. The data analysis may suggest that the cations with the butyl isomers perform two groups: *n*-$BuEt_3N^+$ and *i*-$BuEt_3N^+$ with the highest V_2^o, and *t*-$BuEt_3N^+$ and *s*-$BuEt_3N^+$ similar to Et_4N^+ one. The peculiarities of the experimental observation may be interpreted as a consequence of the structural effect over the intermolecular forces that affect the solute-water interactions deeply.

Keywords: Apparent molal volume; asymmetric tetra-alkylammonium salts

1. INTRODUCTION

The volumetric behaviour of tetra-alkylammonium Salts (TTA) in solution can provide singular information about the ion-solvent and ion-ion interaction [1]. The TAA salts with large size appear to have a promoting effect where water is encaging the alkyl chains with the result that water hydrogen-bonding network is stabilized as compared to bulk water [2].

The interaction of water and TTA salts with ions possessing asymmetrical apolar groups may provide evidence of the effect of a

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*Corresponding author.

single hydrocarbon chain of the cation over the water structure [3,4]. In a previous paper 5, the effect of the butyl isomers on the conductivity in mixtures of solvents of medium and low dielectric constant was evaluated, and the effect of branching resulted in clearly different phoreograms was found.

In this paper we report density measurements for asymmetrical branching TTA Iodides with ionic radii between those of Et_4NI and Bu_4NI. Our aim was to obtain reasonable accurate information regarding the isomers of the butyl to evaluate the structural effect volumetric property.

2. EXPERIMENTAL

Synthesis and Purification of material. Tetra-butylammonium Iodide (sigma, puriss p.a.), *i*-butyl-tri-ethylammonium iodide, *s*-butyl-tri-ethylammonium iodide, *t*-butyl-tri-ethylammonium iodide, and *n*-butyl-tri-ethylammonium iodide were recrystallized twice from suitable organic liquid mixtures and were dried under vacuum at 70–80°C for at least 48 hours. Their purity was better than 99,9%. The procedures used for the purification and analysis of these salts have been described previously [5,6]. The melting salt points found are: *i*-$BuEt_3NI$, 152,5°C; *s*-$BuEt_3NI$, 175,5°C; *t*-$BuEt_3NI$, 173,5°C; *n*-$BuEt_3NI$, 208,4°C; and Bu_4NI, 143,0°.

Preparation of solutions. All solutions were prepared on a molal basis using redistilled conductivity water $< 10^{-6}\,\text{ohm}^{-1}$ prepared as described by Friedman and Scheraga [7]. Water was taken to have a density of 0,9970474 g/cc at 298,15 K.

Measurements of Density. The magnetic-float densitometer used to make the density measurements has been described elsewhere [8,9]. The density data are precise to $\pm 0{,}000005\,\text{gcm}^{-3}$.

The density measurements were carried out in a water thermostat bath at 298,15 K and for each series of experiments, the temperature was controlled better than ±0,003 K. Density measurements for each salt were carried over a range of $1{,}0 \times 10^{-2}$ to $6{,}0 \times 10^{-2}$ m. The estimated error in the density measurement is based on uncertainty of 0,01 mg on the weight.

3. RESULTS AND DISCUSSION

The apparent volumes, listed in Table I and the corresponding plots in Figure 1, gives the complete run for the TAA studied salts showing molality, apparent volume and the change in density from that of pure water. The $V_{2,\varphi}$ were calculated from the equation:

$$V_{2,\varphi} = \frac{1}{m}\left[\left(\frac{1000 + mM}{\rho} - \frac{1000}{\rho^o}\right)\right] \quad (1)$$

where ρ^o is the density of the pure water; M, the molecular weight of the salt; ρ, the density of the solution; and m, its molality.

The infinite dilution values, $\bar{V}_2^o$, were calculated with the Redlich and Meyer equation:

$$V_{2,\varphi} = V_2^o + A_{DH}\sqrt{m} + Bm \quad (2)$$

where A_{DH} and B are empirical constants which take into account higher terms of the Debye-Hückel theory and all other solute-solute interactions [10].

Previous experimental results of $\bar{V}_2^o$ at 298,15 K are available for Et_4NI (185,0 [3], 185,5 [9]) and Bu_4NI (312,4 [9], 312,2 [11]). In each case the values agree with the present result (185,38, 312,23) $cm^3 \cdot mol^{-1}$ respectively to within their estimated experimental error. Derived results as $\bar{V}_2^o$, and A_{DH} are given in Table II.

The experimental observations described in Figures 1 and 2, show some peculiarities, as the important differences between the n-$BuEt_3N^+$ and i-$BuEt_3N^+$ behavior. They could be considered as the cations with a truly asymmetric geometry. The cations s-$BuEt_3N^+$ and t-$BuEt_3N^+$, with a very little asymmetry, as a consequence of a spatial redistribution of the butyl, have close values of $\bar{V}_2^o$ around 187 cc/mol. (see Figs. 3 and 4). An interpretation of the phenomena may be offered in terms of three effects: 1. A structural one, due to influence of the butyl isomers geometry which can not be represented by a spherical shell. 2. An electrostatic one due to permanent dipolos from an uneven spatial distribution of electronic charges about the nitrogen atom. 3. A steric effect due to repulsion forces.

A similar patron behavior was found by a conductivity study of the butyl isomers in mixtures of toluene-acetonitrile [5], where i-$BuEt_3N^+$

TABLE I Apparent molar volumes data of the TTA salts in aqueous solutions at 298,15 K

$n\text{-}BuEt_3NI$			$s\text{-}BuEt_3NI$		
$10^3 m$	$1000\Delta D$	$V_{2,\varphi}$	$10^3 m$	$1000\Delta D$	$V_{2,\varphi}$
12,34	0,92153	211,34	10,18	0,99915	188,01
16,47	1,28343	211,36	11,07	1,08576	188,00
17,61	1,32710	211,38	22,68	2,21346	188,02
21,58	1,60477	211,40	27,21	2,65153	188,01
27,58	2,04514	211,43	31,38	3,09267	188,03
30,52	2,26034	211,42	36,02	3,49770	188,03
32,37	2,39636	211,43	38,90	3,77284	188,03
38,18	2,82138	211,44	41,26	3,99879	188,02
42,35	3,12341	211,45	46,38	4,48605	188,03
45,29	3,33630	211,45	49,28	4,76042	188,04
47,35	3,48540	211,46	53,90	5,19772	188,04
52,68	3,87121	211,44	57,02	5,49285	188,03
59,02	4,32849	211,42			
$t\text{-}Et_3NI$			$i\text{-}BuEt_3NI$		
$10^3 m$	$1000\Delta D$	$V_{2,\varphi}$	$10^3 m$	$1000\Delta D$	$V_{2,\varphi}$
28,19	2,68405	190,21	20,56	1,63781	206,12
32,67	3,08729	190,77	22,59	1,78844	206,55
34,97	3,30018	190,82	25,08	1,98442	206,51
39,85	3,75362	190,83	28,15	2,22267	206,58
42,92	4,03491	190,90	30,85	2,43864	206,41
44,08	4,14405	190,86	32,04	2,51421	206,96
47,48	4,45480	190,92	35,05	2,74529	207,04
51,97	4,86878	190,91	38,47	3,00582	207,13
54,37	5,08782	190,93	41,28	3,21564	207,28
54,37	5,08782	190,93	43,67	3,39087	207,47
58,96	5,51129	190,87	46,39	3,59376	207,57
			49,34	3,82279	207,48
			52,31	4,04567	207,54
			55,24	4,27624	207,38
			56,25	4,34309	207,55
$n\text{-}Bu_4NI$			Et_4NI		
$10^3 m$	$1000\Delta D$	$V_{2,\varphi}$	$10^3 m$	$1000\Delta D$	$V_{2,\varphi}$
19,68	1,14441	312,27	16,98	1,28966	185,48
27,79	1,61091	312,27	25,49	1,96368	185,49
27,83	1,61245	312,27	32,13	2,42557	185,52
30,41	1,76001	312,28	34,49	2,60157	185,52
38,80	2,30174	312,32	42,11	3,16722	185,54
41,25	2,64442	312,31	45,53	3,41854	185,57
47,25	2,74606	312,20	47,25	3,54535	185,58
51,98	2,93685	312,19	52,61	3,94115	185,55
53,28	3,05348	312,28	57,56	4,30313	185,57
68,93	3,40873	312,30	65,77	4,90202	185,59
			68,02	5,06401	185,61

and t-$BuEt_3N^+$ presented small difference of their phoreograms especially in molar fractions 0,4–0,6 of toluene. But it was very different from the phoreogram of Bu_4N^+ which make a group with

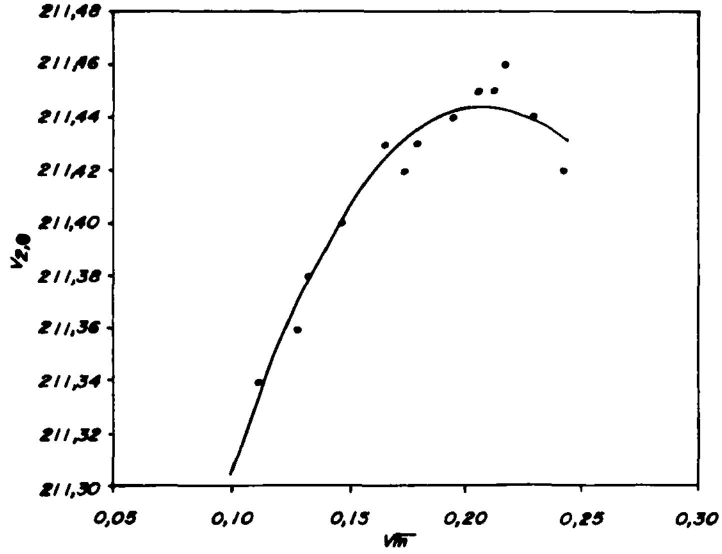

FIGURE 1 Apparent molal volumes of n-$BuEt_3NI$ *versus* $\sqrt{m}$ in water at 298,15 K.

TABLE II Molal volume at infinite dilution, $\bar{V}_2^0$ and the limiting slope of the TTA salts in aqueous solutions at 298,15 K

TAA SALT	$\bar{V}_2^0$ *cc/mol*	*A*	*B*
t-$BuEt_3NI$	187,13	33,87	− 76,02
i-$BuEt_3NI$	201,59	41,66	− 69,05
s-$BuEt_3NI$	187,98	0,10	− 0,45
n-$BuEt_3NI$	210,93	4,92	− 11,80
Bu_4NI	312,23	1,00	− 2,78
Et_4NI	185,38	− 0,58	0,96

n-$BuEt_3N^+$ and s-$BuEt_3N^+$, this data suggested that geometry had a direct effect over the conductivity. However, experimental evidence of a variety of linear, branched and cycled hydrocarbons give an approximately linear plot against the hydrocarbon surface area or the number of water molecules in contact with it, *e.g.*, in the isobutane, the insertion of the CH_2— group produces only a small increment in solvent contacts [12].

The behavior of aqueous solutions of the Bu_4NI has been interpreted by Levien [13] as a phenomenon of pair association from studies of activity and viscosity. Lindenbaum and Boyd were more emphatic and suggested the micelle formation to explain the low

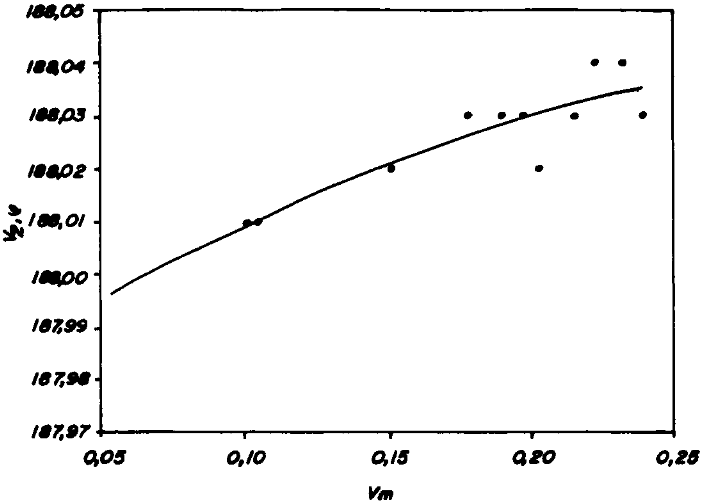

FIGURE 2 Apparent molal volumes of *s*-BuEt$_3$NI *versus* $\sqrt{m}$ in water at 298,15 K.

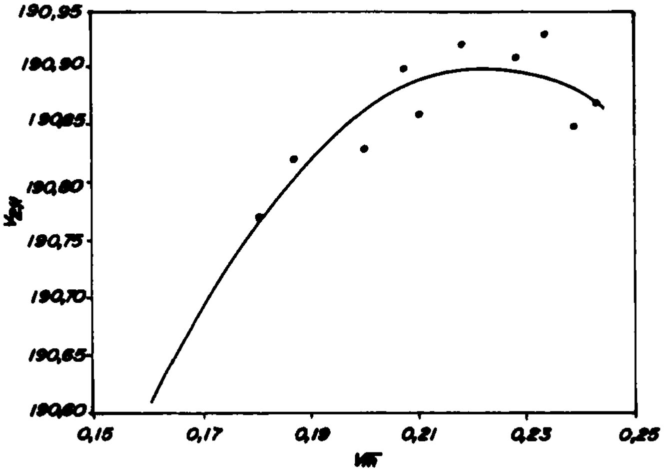

FIGURE 3 Apparent molal volumes of *t*-BuEt$_3$NI *versus* $\sqrt{m}$ in water at 298,15 K.

values of activity coefficients [14]. A more plausible explanation was proposed by Frank [15] as a structural salting-in of *n*-Bu$_4$N$^+$.

The volumetric behavior of the isomeric BuEt$_3$NI may suggest that the interactions with the solvent could be of short range, and the

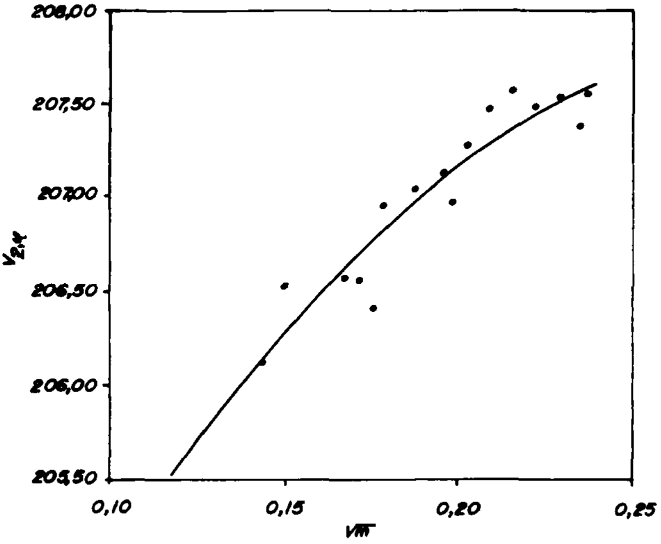

FIGURE 4 Apparent molal volumes of *i*-BuEt$_3$NI *versus* $\sqrt{m}$ in water at 298,15 K.

interaction solvent-solute may be not depend significantly on the formation of cooperative linkages of water molecules with special space requirements.

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