

Ethanol-물 혼합용매에서 Tetraalkylammonium Halide 의 분몰랄 부피에 관한 연구

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(접수 72. 10. 15)

On the Partialmolal Volumes of Tetraalkylammonium-Halides in Ethanol-Water Mixtures

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요 약

Ethanol-물 혼합용매 중에서 Tetraalkylammonium Halides, Me_4NI , Et_4NI , Pr_4NI , Bu_4NI , Me_4NBr , Pr_4NBr , Me_4NCl , 및 Pr_4NCl 의 분몰랄 부피를 30°C에서 측정한 결과 Halides 이온은 모든 용매 조성에 있어서 그 크기가 커짐에 따라 V^0_X 가 증가하고, 0.3 몰 분율에서 최소치를 갖는다. 이것은 이 조성에서 electrostrictive effect가 최대임을 나타내며, 또 $V^0_{\text{R}_4\text{N}^+}$ 이 0.1 몰 분율에서 공통적으로 최소치를 나타냄은 물은 이 조성에서 가장 강화되었음을 보여준다.

Abstract

The partial molal volumes of a series of homologous tetraalkylammonium iodides, bromides and chlorides in a series of ethanol-water mixtures have been determined at 30°C. It was found that general trend in variation of anionic partial volumes $V^0_{X^-}$ with the solvent composition is the same for all the anions studied, i.e., Cl^- , Br^- and I^- , and that absolute values $V^0_{X^-}$ increase with the size of anions in all solvent compositions.

The results also indicate that at 0.1 mole fraction ethanol the maximum structuredness of water causes a minimum in the tetraalkylammonium cation partial molal volumes, while at 0.2-0.3 mole fraction the solvent structure is such that the free volume is a minimum and the electrostrictive effect of halides ion is a maximum.

Introduction

Since Debye-Hückel limiting law was proposed for aqueous electrolyte solution in 1923, the study of electrolyte solutions, especially that of the tetraalkylammonium halides has attracted special attention for many years. This is because these salts are very useful in examining the influence of certain factors, such as association and hydration, on the concentration dependence of physico-chemical properties of electrolyte solutions. Anomalous behavior of these electrolytes has been observed in such properties as activity coefficient,^{1,2,3)} enthalpy and entropy of dilution,^{4,5)} heat capacity,^{6,7,8)} partial molal volume,⁹⁻¹²⁾ partial molal expansibility,¹³⁻¹⁶⁾ partial molal compressibility,¹⁷⁻²⁰⁾ ionic conductance,²¹⁻²⁴⁾ viscosity,²⁵⁻²⁸⁾ infra-red absorption of water,²⁹⁻³²⁾ X-ray diffraction,³³⁾ ultrasonic relaxation³⁴⁾ and solubility.³⁵⁾

Frank and Evans³⁶⁾ proposed that symmetrical tetraalkylammonium ions should promote water structure as the hydrophobic nature of the ions increases with the size. Much of the information on hydrophobic hydration was provided by the tetraalkylammonium halide, since these salts are reasonably soluble in water and their hydrophobic character can be varied by changing the size and nature of the alkyl group,³⁷⁾ i.e., tetrapropyl and tetrabutylammonium ions are strong hydrophobic structure makers while tetramethylammonium ion is a weak structure breaker, and tetraethylammonium ion is on the border line of the two opposing effects.³⁸⁾ Although many workers have studied aqueous systems, little work has been done to investigate the behavior of these salts in binary solvent systems.³⁹⁻⁴⁶⁾

Lee and Hyne⁴³⁾ reported partial molal volumes of tetraalkylammonium chloride in ethanol-water mixtures, and interpreted these results in terms of varying size and surface charge of the ions and the structure of the binary solvent mixtures. Cho⁴⁵⁾ studied partial molal volumes of tetraalkylammonium chloride in isopropanol-water mixtures.

In this paper we report partial molal volumes of four tetraalkylammonium iodides, and four tetrame-

thyl and tetrapropyl-ammonium halides in a series of ethanol-water mixtures at 30°C. Our interest was to obtain more information about the structural changes accompanying the addition of ethanol to liquid water, using the hydrophobic and electrostrictive effects of these salts as an experimental probe.

Experimental

Merk's reagent grade tetraalkylammonium salts were purified by recrystallization and dried in vacuo as described in the literature.^{11,27,47)}

Merk's absolute ethanol was used without further purification (water content; 0.2%) throughout the course of experiment. In all measurements, water was redistilled twice and was equilibrated with atmospheric carbon dioxide. All solutions were made by weight (corrected to vacuum) and converted to molarities from the known densities.⁴⁸⁾ All measurements were made at $30.00 \pm 0.01^\circ\text{C}$.

Densities were measured in a 25 ml. capacity pycnometer calibrated with distilled water for 0.05-0.0016 M solutions of salt. For each salt solution and solvent, at least three measurements at 30°C were taken and the average value is reported. Average reproducibility of density was ± 0.00003 . All weighings were measured to fifth decimal Mettler H 20-T semi-micro balance and compensated to values in vacuum by removing buoyancy by air. Compensation of buoyancy was performed by our previous treatment.⁴⁹⁾ Computer IBM 1130, at the computing center, S. N. U. was used for carrying out all of these density calculations. The apparent molal volumes ϕ_v were calculated from the density data by the equation

$$\phi_v = \frac{1}{m} \left(\frac{1000 + m \cdot M_2}{d} - \frac{1000}{d_0} \right) \quad (1)$$

where d_0 is the density of solvent, M_2 the molecular weight of the salt, d the density of the solution, and m its molality. ϕ_v values were determined for each salt in each solvent composition over a concentration range of approximately 0.0016 to 0.1 M. ϕ_v^0 were then obtained from ϕ_v and its concentration dependence using Masson⁵¹⁾ equation.

$$\phi_V = \phi_V^0 + S_V \sqrt{m} \quad (2)$$

ϕ_V^0 is ϕ_V at infinite dilution and S_V the limiting slope. The precision of apparent molal volumes, ϕ_V was ± 0.1 ml./mole at $C = 0.04$ M using the equation of Redlich and Bigeleisen⁵²⁾

$$\delta\phi = \frac{1000 \delta d}{d_0 C} + \frac{1000(d-d_0)\delta C}{C^2 \cdot d_0} \quad (3)$$

where δd and δC are the uncertainties in density and concentration.

Results and Discussion

1. Concentration dependence of densities:

A linear relationship⁵⁰⁾ (4) between density (d) and concentration of tetraalkylammonium halides was assumed to hold (θ is an empirically determined constant). The results are summarized in Table(1)

$$d = d_0(1 + \theta \cdot C) \quad (4)$$

Table 1. Parameters for density equations in aqueous solution

$$d = d_0(1 + \theta C)$$

T °C	Me ₄ NI		Et ₄ NI		Pr ₄ NI	
	θ	RMSD	θ	RMSD	θ	RMSD
30	2.9873×10^{-2}	1.867×10^{-4}	2.0453×10^{-2}	1.253×10^{-4}	1.7959×10^{-2}	1.063×10^{-4}
35	2.9614	1.711	2.0391	1.269	1.7671	1.182
40	2.9454	1.780	2.0391	1.248	1.7591	1.077

T °C	Me ₄ NCI		Bu ₄ NI		Pr ₄ NCI	
	θ	RMSD	θ	RMSD	θ	RMSD
30	8.7095×10^{-3}	1.653×10^{-5}	1.5330×10^{-2}	5.645×10^{-5}	-7.7979×10^{-3}	6.7475×10^{-6}
35	8.4100	1.785	1.5026	5.482	-8.2304	9.5423
40	8.1703	1.785	1.5126	5.004	-8.4945	6.7475

T °C	Me ₄ NBr		KCl		Pr ₄ NBr	
	θ	RMSD	θ	RMSD	θ	RMSD
30	3.9676×10^{-2}	9.5422×10^{-6}	2.3177×10^{-2}	2.583×10^{-4}	2.8252×10^{-2}	1.6528×10^{-5}
35	3.9458	1.6528	2.2957	2.577	2.7727	1.7852
40	3.9291	3.0175	2.3005	2.641	2.7297	1.1687

2. Concentration dependence of apparent molal volumes

Illustrative examples of the plots of apparent molal volumes, ϕ_V , against the square root of the salt concentration are shown for Pr₄NI in various solvents in Fig. 1. In all cases ϕ_V was found to vary linearly with \sqrt{m} over the concentration range investigated. Values of ϕ_V^0 and S_V obtained from Eq. 2 are given in Table 2 and 3. It has been suggested^{53,54)} that the positive concentration dependence of the apparent molal volume is primarily due to the salting out effect of ionic electrostriction. The slope has maximum positive value for Pr₄NI at 0.2-0.3 mole fraction ethanol in the ethanol-water binary solvent mixture. This observation of a maximum in the solvent composition dependence of the slope S_V suggests that at least some of the contributing factors that determine the S_V value, probably electrostriction, is a maximum. In 1931, Redlich and Rosenfeld⁵²⁾ applied the interionic attraction theory of Debye and Hückel to the concentration dependence of ϕ_V . By differentiating with respect to pressure, they obtained the theoretical limiting slope, S_V , using the equation

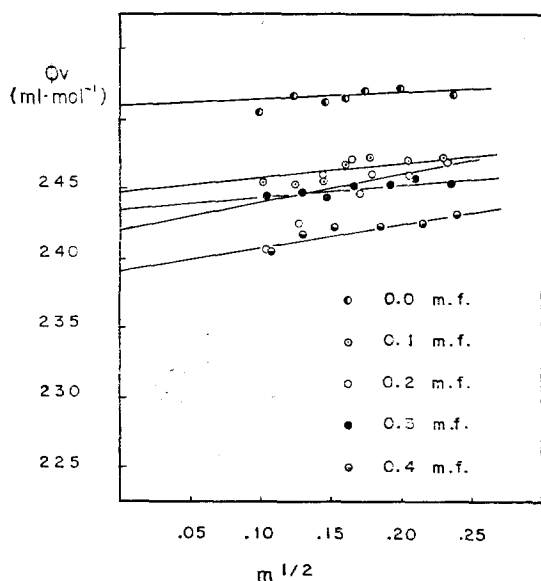
Table 2. Partial molal volumes and limiting slope of tetraalkylammonium iodides in ethanol-water mixtures at 30°C

X_{EtOH}	ϕ_V^0				S_V			
	Me_4NI	Et_4NI	Pr_4NI	Bu_4NI	Me_4NI	Et_4NI	$[\text{Pr}_4\text{NI}]$	Bu_4NI
0.0	126.2	188.7	253.3	315.9	3.5	-8.2	-7.1	-6.6
0.1	122.1	180.0	244.8	308.8	7.8	9.6	7.1	7.6
0.2	108.8	174.5	241.8	314.1	49.0	23.2	21.2	11.8
0.3	101.5	173.9	243.7	315.2	82.3	13.3	8.2	2.9
0.4	110.4	171.1	239.4	310.9	68.0	16.0	16.0	13.4
0.0*	128.0	191.3	258.4	317.3	4.0	-10.4	-20.4	-3.3

* values at 40°C

Table 3. Partial molal volumes of tetramethyl and tetrapropylammonium halides in ethanol-water mixtures at 30°C

X_{EtOH}	Me_4N^+			Pr_4N^+		
	Cl^-	Br^-	I^-	Cl^-	Br^-	I^-
0.0	107.7	115.0	126.2	231.0	240.0	253.3
0.1	104.3	110.2	122.1	218.4	230.7	244.8
0.2	101.9	106.1	108.8	223.0	228.4	241.8
0.3	100.7	102.6	101.5	223.2	229.0	243.7
0.4	99.9	104.2	110.4	220.1	228.0	239.4

Fig. 1 Apparent molal volumes of Pr_4NI in various ethanol-water mixtures at 30°C (m.f. = mole fraction ethanol) (as a typical one)

$$\begin{aligned}\phi_V &= \phi_V^0 + k \cdot W^{1.5} \cdot C^{0.5} \\ &= \phi_V^0 + S_V \cdot C^{0.5}\end{aligned}\quad (5)$$

It shows the usual linear dependence on the square root of the concentration and the influence of the valence factor W , which is given by the number δ_i of ions of species i formed by one molecule of the electrolyte and the valence Z_i according

$$W = 0.5 \sum_i \delta_i Z_i^2 \quad (6)$$

The slope K for a uni-univalent electrolyte can be expressed by means of the gas constant R , the charge θ of a univalent ion, and the compressibility β of the solvent. If the molal volumes is expressed in ml./mole the coefficient is

$$k = N^2 e^3 (8\pi/1000 D^3 RT)^{0.5} (\partial \cdot l_n D / \partial p - \beta/3) \quad (7)$$

We can take apparent molal volume ϕ_V is equal to partial molal volume \bar{V}^0 at infinite dilution, that is, $\phi_V^0 = \bar{V}^0$. The partial molal volumes of salts, \bar{V}^0 , are obtained by extrapolating the plot of ϕ_V vs. \sqrt{m} to the zero concentration. Here the slope S_V is an experimental limiting slope.

The data presented in Table 2 also show that in water the S_V value of the ϕ_V vs. \sqrt{m} for all the R_4NI (except Me_4NI) were negative at 30–40°C. The

slopes become less negative at higher temperatures for the Et_4N^+ , Pr_4N^+ iodides; however, for Me_4NI , S_V increases with increasing temperature. The value for Bu_4NI is less negative with increasing temperature. This result is similar with the work of Wen and Saito⁹⁾ for Bu_4NBr (who found $S_V = -9.0, -8.4$ and -6.3 at 15, 25 and 30°C, respectively). Thus, the S_V values in binary solvents decrease as the size of the tetraalkylammonium ion increases.

3. Ionic partial molal volumes

The additivity of the partial molal volumes of electrolytes at infinite dilution in water has adequately demonstrated by number of workers.^{18, 43, 45, 56, 57)}

The values of V^0 , for consecutive homologous in a tetraalkylammonium salt series having a common anion may be represented by the equations:

$$\bar{V}_{\text{R}_4\text{N}^+\text{I}^-}^0 = \bar{V}_{\text{R}'_4\text{N}^+\text{I}^-}^0 - b (\Delta m \cdot W)$$

$$\text{and } \bar{V}_{\text{R}_4\text{N}^+\text{I}^-}^0 = \bar{V}_{\text{R}''_4\text{N}^+\text{I}^-}^0 - b (\Delta m \cdot W) \quad (7)$$

where R'' , R' and R are homologous alkyl groups and $(\Delta m \cdot W)$ is the change of molecular weight of the salt in going up the homologous series from R to R' or from R' to R'' , i.e., by four methylene groups. The b value is almost constant for a series with a common anion since the observed relations are, to a satisfactory approximation, for all solvent systems, linear (see Fig. 2). In terms of the numerical data however, some small but significant variations of the coefficient b from a constant value arise as shown in Table 4.

Table 4. Values of b from equation (7) at 30°C

X_{EtOH}	b (ml. $\text{g}^{-1} \text{CH}_2$)			
	Me_4N^+	Et_4N^+	Pr_4N^+	Bu_4N^+
0.0	1.1144	1.1517	1.1180	
0.1	1.0321	1.1545	1.1429	
0.2	1.1723	1.1994	1.2895	
0.3	1.2893	1.2443	1.2770	
0.4	1.1224	1.1816	1.2768	

$b = 1.1844$ (mean) was found. These values are in agreement with the works of Conway et al.¹⁰⁾ for

R_4NCl , R_4NBr and R_4NI in aqueous solution (who found average $b = 1.11$) and Yoon⁵⁷⁾ for RNH_3Cl (who found $b = 1.182$).

The individual ionic partial volumes seems to differ according to the method used for its determination. The \bar{V}_{I^-} values are obtained by extrapolation of $\bar{V}_{\text{R}_4\text{NI}}^0$ versus molecular weight of the cations, R_4N^+ to zero cation weight.

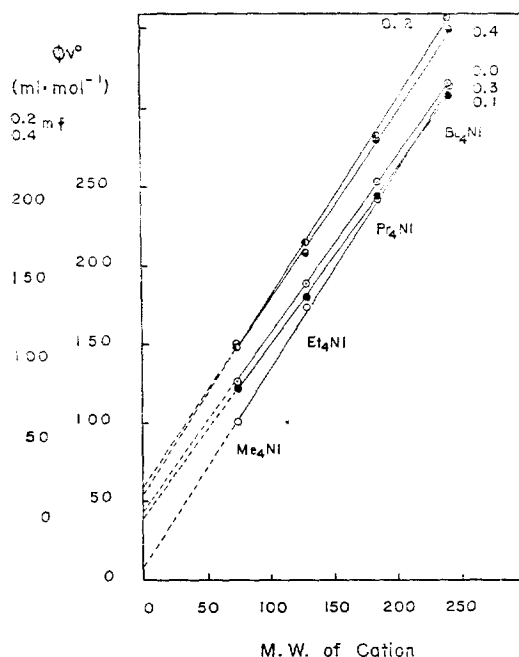


Fig. 2 Partial molal volumes of tetraalkylammonium iodides as a function of the molecular weight of Cation in Various ethanol-water mixtures at 30°C

Since the large cations are chemically very similar, and the relation in Fig. 2 is linear, it is reasonable to assume that their actual ionic volume contribution would tend to zero as their molecular weight tend to zero. Therefore, extrapolation of the straight line in Fig. 2 to zero cation molecular weight should give directly the partial molal volume of the I^- ion.¹⁰⁾

This procedure for R_4N^+ ions gives a value of 42.1 ml./mol at 30°C based on a least squares plot. The literature value is 42.3⁵⁸⁾ ml./mol at 25°C. The temperature dependence of the $\bar{V}_{\text{I}^-}^0$ value seems to be small enough so that the difference in $\bar{V}_{\text{I}^-}^0$ is well within the experimental accuracy. Fig. 3 shows a deep minimum in $\bar{V}_{\text{I}^-}^0$ at 0.3 mole fraction ethanol. Since

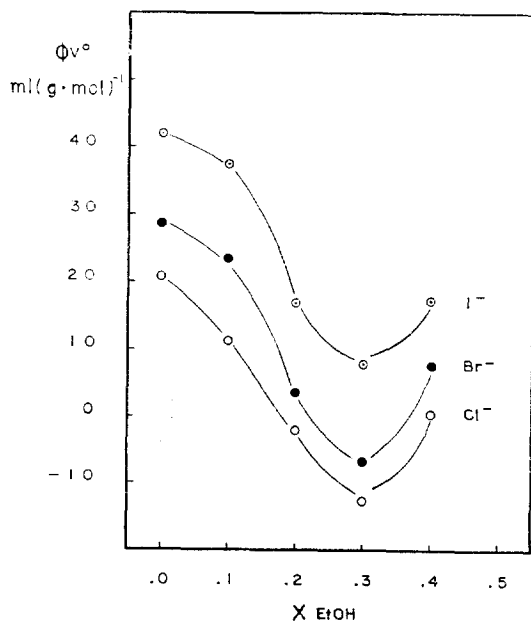


Fig. 3 Ionic Partial Molal Volume of Halide Ions as a Function of Solvent Composition (mole fraction ethanol) at 30°C

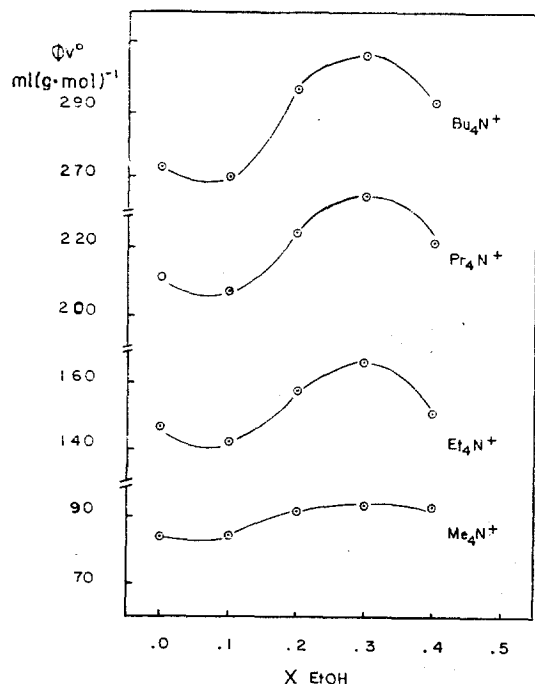


Fig. 4 Ionic Partial Molal Volume of the Tetraalkylammonium cations as a Function of Solvent Composition (mole fraction ethanol) at 30°C

iodide ion has a relatively high charge to surface ratio, the minimum at 0.3 mole fraction is probably due to the maximum in electrostriction effect, which agrees with the conclusion derived from the maximum value of the limiting slope at the same composition.

Comparison of the $\bar{V}_{X^-}^0$ values for $X^- = \text{Cl}^-$, Br^- and I^- in various solvent compositions is made in Table 5. General trends of $\bar{V}_{X^-}^0$ values versus solvent composition are seen to be the same for all the anions, i.e., they all show minima at 0.3 mole fraction ethanol. However the absolute values of $\bar{V}_{X^-}^0$ increases with the size of anions for all solvent compositions in the order,

$$\bar{V}_{\text{Cl}^-}^0 < \bar{V}_{\text{Br}^-}^0 < \bar{V}_{\text{I}^-}^0.$$

It is noteworthy that for iodide no negative ionic partial molal volumes are to be found, whereas for chloride and bromide there are negative values of $\bar{V}_{X^-}^0$.

Table 5. Comparison of $\bar{V}_{X^-}^0$ values for $X^- = \text{Cl}^-$, Br^- and I^- at 30°C.

X_{EtOH}	$\bar{V}_{\text{Cl}^-}^0$	$\bar{V}_{\text{Br}^-}^0$	$\bar{V}_{\text{I}^-}^0$
0.0	20.8	28.8	42.1
0.1	11.2	22.5	37.6
0.6	-1.9	3.5	17.0
0.3	-12.5	-6.7	8.0
0.4	0.4	7.5	18.9

The ionic partial molal volumes of the cations can be determined by subtracting the $\bar{V}_{\text{I}^-}^0$ value from the partial molal volumes of salt $\bar{V}_{\text{R}_4\text{NI}}^0$.¹⁰⁾

$$\bar{V}_{\text{R}_4\text{N}^+}^0 = \bar{V}_{\text{R}_4\text{NI}}^0 - \bar{V}_{\text{I}^-}^0,$$

$$\bar{V}_{\text{R}_4\text{N}^+}^0 = \bar{V}_{\text{R}_4\text{NBr}}^0 - \bar{V}_{\text{Br}^-}^0, \quad (8)$$

and

$$\bar{V}_{\text{R}_4\text{N}^+}^0 = \bar{V}_{\text{R}_4\text{NCl}}^0 - \bar{V}_{\text{Cl}^-}^0$$

The individual ionic partial molal volumes of the cation obtained in this manner are plotted against solvent composition in Fig. 4. All the cations show a minimum at 0.1 mole fraction and a maximum at 0.3 mole fraction. The marked similarity between the curves in Fig. 4 for the four tetraalkylammonium ions suggests that the same effects are operating,

although to varying degrees, in all cases. The observed enhancement of the extremum effects as the alkyl function is varied from methyl to *n*-butyl supports the common effects are those of hydrophobic interaction and size. It is interesting to note that even the smallest and least hydrophobic of the cations, Me_4N^+ , shows the double extremum characteristic of predominate hydrophobic and size effects.

It is interesting to compare the cationic partial molal volumes determined by extrapolation method of Conway¹⁰⁾ using R_4NI with those using R_4NCl . If the Conway's method of determining $\bar{V}_{\text{R}_4\text{N}^+}^0$ values is generally applicable the values of $\bar{V}_{\text{R}_4\text{N}^+}^0$ independently determined with two series of halides should agree to within experimental accuracies Table 6 shows the $\bar{V}_{\text{R}_4\text{N}^+}^0$ value determined in this work using iodide series and those determined by Lee and Hyne⁴³⁾ using chloride series (see Table 6). Considering the difference in the experimental temperature, agreement of the sets is gratifying. Although there are significant divergences in some cases due mainly to the experimental errors, general agreement, especially in the mixed solvents, constitutes a strong support for the applicability of extrapolation technique in determining the anionic partial molal volumes of R_4NI .

Table 6. Ionic partial Molal volumes of the tetraalkylammonium cations and iodide ion at 30°C

X_{EtOH}	Me_4N^+	Et_4N^+	Pr_4N^+	Bu_4N^+	I^-
0.0	84.1	146.6	211.2	273.8	42.1
0.1	84.5	142.4	207.2	271.2	37.6
0.2	91.8	157.6	224.9	297.1	17.0
0.3	93.6	165.9	235.7	307.3	8.0
0.4	91.5	152.2	220.5	292.0	18.9

Calculated with Lee and Hyne's data at 50.25°C⁴³⁾

X_{EtOH}	Me_4N^+	Et_4N^+	Pr_4N^+	Bu_4N^+	Cl^-
0.0	86.3	148.2	215.4	279.2	21.8
0.1	85.7	143.6	206.6	274.4	12.4
0.2	87.8	155.8	220.4	288.5	-2.1
0.3	90.5	161.8	229.3	298.3	-9.8
0.4	82.7	146.8	208.7	271.7	6.0

When the combined effects of cation and anion are considered, however, the partial molal volume

picture change considerably. The electrostriction effect of the iodide anion, which manifests itself as a minimum at 0.3 mole fraction ethanol, is then in competition with the hydrophobic and size effect of the tetraalkylammonium cation, which is characterized by a maximum at the same solvent composition.

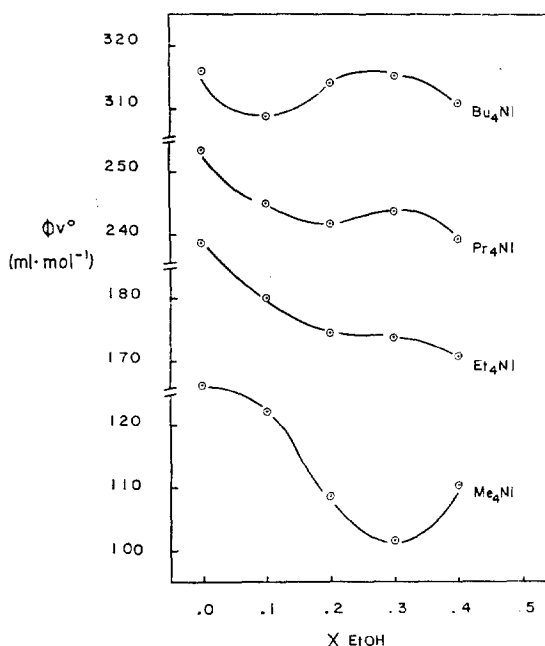


Fig. 5 Partial Molal Volumes of Tetraalkylammonium Iodide as a Function of Solvent Composition (mole fraction ethanol) at 30°C

The balance between these two competing effects is illustrated in Fig. 5, where the partial molal volumes of the salt species are plotted against solvent composition. The maximum at 0.3 mole fraction observed for the Me_4N^+ ion has now become a minimum, indicating that the electrostriction effect of the iodide ion more than compensates for the small hydrophobic and size effect of the tetramethylammonium cation. As the cation effects become larger with the size of cation, the electrostriction of iodide ion is exactly compensated in tetraethylammonium and is outweighed by the hydrophobic and size effects in tetrapropyl- and tetrabutylammonium salts. The only literature value available is for water at 25° (Table 7). Our value agrees well literature's values.

Table 7. Comparison of the partial molal volumes of tetraalkylammonium halides in H₂O at 25°C

Salts	\bar{V}^0 ml (g·mol) ⁻¹				
	Present work at 30°C	Literature values at 25°C			
Me ₄ NCl	107.7	107.4, ⁶⁴⁾	108.1 ⁴³⁾		
<i>n</i> -Pr ₄ NCl	230.9	232.9 ⁶⁴⁾	237.2 ⁴³⁾		
Me ₄ NBr	115.0	114.25 ⁶⁵⁾	114.8 ⁹⁾	114.40 ¹³⁾	114.26 ⁹⁾
<i>n</i> -Pr ₄ NBr	240.0	239.38 ²⁰⁾	239.15 ¹³⁾	239.6 ¹⁰⁾	240.8 ⁹⁾
Me ₄ NI	126.2	125.8 ⁶⁴⁾	125.75 ⁶⁵⁾		
Et ₄ NI	188.7	185.5 ⁶⁴⁾			
<i>n</i> -Pr ₄ NI	253.3	250.9 ⁶⁴⁾			
<i>n</i> -Bu ₄ NI	315.9	312.4 ⁶⁴⁾			

4. Structure of the binary solvent

The behavior of the partial molal volume of R₄NI's (R=Me, Et, Pr and Bu) and their component ions as function of solvent composition can be used as a probe to investigate the varying structure of binary solvent system. Three characteristic features may be identified.

Below $X_{\text{EtOH}}=0.3$, $V^0(\text{I}^-)$ was found to decrease from 42.1 to 8.0 ml./mol, while above $X_{\text{EtOH}}=0.3$, $V^0(\text{I}^-)$ was found to increase. The $V^0(\text{R}_4\text{N}^+)$ values found to go through a minimum at $X_{\text{EtOH}}=0.1$, which is considered to occur due to the maximum structuredness of water.⁴³⁾ At $X_{\text{EtOH}}=0.3$, the $V^0(\text{R}_4\text{N}^+)$ value is maximum, which is considered to be caused by the free volume of the solvent structure being at a minimum. Thus these results are in good agreement with Lee and Hyne's results on R₄NCl.⁴³⁾

A) A minimum in partial molal volume of R₄N⁺ ions (Fig. 4) and of the larger salts of the Bu₄NI (Fig. 5) at $X_{\text{EtOH}}=0.1$: It is generally accepted that structure of water is promoted by initial addition of the ethanol, probably as a result of hydrophobic interactions between the ethanol and the water and this effect is maximum at ~0.1 mole fraction. At the binary solvent composition where "ice-berg" structure promotion is a maximum, there will be a maximum of preformed "hole" into which the third component solute molecule may fit without the prerequisite of hole formation prior to dissolution. Accordingly the "locking up" of solvent molecules inside the void space formed by the large R₄N⁺ ions could also attribute to the decrease in the ϕ_V^0 s of the

R₄N⁺ halides at this solvent composition. This phenomenon is clearly demonstrated in Fig. 4 and to a lesser extent in Fig. 5 where the additional complication of the competing effect of the iodide ion tends to reduce this effect.

B) The $X_{\text{EtOH}}=0.3$ maximum: As the proportion of ethanol in the mixture increases, the simple bulk effect of the ethanol will begin to break down the characteristic water structure. At $X_{\text{EtOH}}=0.3$ the competition between pure water and pure ethanol structure results in the mixture having essentially a close-packed structure with consequent minimum free volume. $X_{\text{EtOH}}=0.3$, therefore, there are no preformed holes in the binary solvent and dissolution of the third component solute requires maximum expansion of the solvent to accommodate the solute. A maximum in ϕ_V^0 of the R₄NI should therefore be observed. The plot in Fig.4 demonstrate such behavior and in addition, show that the height of the ϕ_V^0 maximum is strictly size dependent, as would be expected.

C) The 0.3 mole fraction minimum: $\bar{V}^0(\text{I}^-)$ ion passes through a minimum 0.3 mole fraction. While it was suggested that at this composition the solvent was closest to close packed, it is clearly not strictly close packed, and under the influence of the strong charge field of the iodide ion, solvent molecules can be electrostricted to form solvation shells, previously described as "soft ice"⁶³⁾ to distinguish such structural ordering form that characteristic of hydrophobic interaction at $X_{\text{EtOH}}=0.1$. Such electrostriction contraction of the solvent leads to the minimum in $\bar{V}^0(\text{I}^-)$ at $X_{\text{EtOH}}=0.3$. It should also be noted (Fig.

3) that the partial molal volume of the iodide ion only begins to decrease rapidly beyond $X_{\text{EtOH}}=0.1$ after the hydrophobic structure making of the ethanol has passed its maximum and the electrostriction effect of the ion is essentially without competition.

Acknowledgement; The author wishes to express his deep appreciation to Professor I. Lee, PhD. for helpful discussions and encouragement for this work. The assistance of Mr. H.K. Ko in determining the density is gratefully acknowledged.

Nomenclature

b ; constant (ml./g) for a series with a common anion
 C ; concentration (mole/l.)
 D ; dielectric constant
 d, d_0 ; density of solution and solvent, respectively
 e ; charge of univalent ion
 M_2 ; molecular weight of the salt
 m ; molality
 N ; Avogadro's number
 Z_i ; charge on the i ions
 δ_i ; number of ions of species i formed by one molecule
 θ ; empirically determined constant
 β ; compressibility of the solvent
 π ; ionic radius
 ϕ_v ; apparent molal volume
 $\phi_v^0 (= \bar{V}^0)$; partial molal volume
 $\delta\phi$; uncertainties in apparent molal volume
 δC ; uncertainties in concentration
 δd ; uncertainties in density
 $\Delta m. W$; change of molecular weight of the salt
 X_{EtOH} ; mole fraction of ethanol
 mf ; mole fraction
 S_v ; experimental limiting slope

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