



## LIMITING IONIC PARTIAL MOLAR VOLUMES OF $R_4N^+$ AND $\Gamma^-$ IN AQUEOUS METHANOL AT 298.15 K

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### ABSTRACT

From density measurements of solutions of  $R_4NI$  ( $R = CH_3$  through  $n-C_4H_9$ ),  $NaBPh_4$  and  $NaI$  in 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mass % methanol + water at 298.15 K, limiting partial molar volumes of solutes and limiting ionic partial molar volumes of  $R_4N^+$  and  $\Gamma^-$  have been calculated and interpreted in terms of ion-ion, ion-solvent and solvent-solvent interactions.

**Key words:** Density, Partial molar volume, Ionic partial molar volume.

### INTRODUCTION

The determination of the partial molar volumes of electrolytes in different solvent mixtures is important to examine different interactions such as ion-solvent, ion-ion and solvent-solvent in various solvent systems. The partial molar volume of an ion is made of two components, (i) increase in the volume of solution due to intrinsic ionic volume and (ii) change in the volume of a solution due to modification of solvent structure arising from ion-solvent interactions. This interaction is influenced when more than one kind of solvent molecules are present, as in case of mixed solvents. The presence of other kind of molecules along with water molecules, modify the properties of ion-solvent interactions. Therefore, it becomes necessary to study the partial molar volumes of salts and their corresponding ions as a function of solvent composition. In the present investigation, we report limiting ionic partial molar volumes of  $R_4N^+$  and  $\Gamma^-$  in aqueous methanol at 298.15 K.

### EXPERIMENTAL

#### Materials

The salts used in the present investigations are,  $(CH_3)_4NI$  (s.d.fine-chem., 99%),

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(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NI (SISCO, 99%), (C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>NI (Fluka, 98%), (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NI (s.d.fine-chem., 99%), NaBPh<sub>4</sub> (E. Merck, 99.5%) and NaI (s.d.fine chem., 99.8%). R<sub>4</sub>NI salts were used after recrystallisation<sup>1</sup>. NaI and NaBPh<sub>4</sub> were used as received. All salts were stored in a vacuum desiccator and dried at 60 to 80°C in the vacuo for at least 2 days prior to use. Water was distilled in a Pyrex glass apparatus with traces of KMnO<sub>4</sub>, followed by successive distillations. The electric conductance of distilled water was  $7 \times 10^{-6} \text{ cm}^{-1}$ . Methanol (Glaxo, Excel-R, purity 99.5 %) was directly used without further purification<sup>2</sup>. The purity of methanol was checked by comparing its observed density  $0.78665 \text{ g.cm}^{-3}$  with that of  $0.78662 \text{ g.cm}^{-3}$  reported earlier<sup>2</sup> at 298.15 K.

## Methods

Methanol + water mixtures of compositions of 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mass % methanol were prepared by mixing an appropriate mass of water and methanol in glass stoppered flask. Comparison of densities of methanol + water mixtures at 298.15 K with those of literature values<sup>2,3</sup> is given in Table 1. Accurately weighed amounts of recrystallised salts were dissolved in a particular solvent to give a desired concentration. Salt concentration varied from 0.0022 to 0.0529 M. Each time freshly prepared solution was used for density measurements. The exact concentration of the salt solution was obtained from measurement of halide ion concentration using Volahrd's method or by gravimetric analysis<sup>4,5</sup>. Densities were determined by using  $15 \text{ cm}^3$  bicapillary pycnometer as described earlier<sup>6</sup>. Pycnometer was calibrated using conductivity water with  $0.99705 \text{ g.cm}^{-3}$  as its density at 298.15 K.

**Table 1: Comparison of densities of water, methanol and methanol + water mixtures at 298.15 K**

Mass % methanol	$P \times 10^{-3} / \text{Kg.m}^{-3}$ Observed	$P \times 10^{-3} / \text{Kg.m}^{-3}$ Literature
0	0.99707	0.99705 <sup>a</sup> , 0.99706 <sup>b</sup>
10	0.98035	0.97973 <sup>a</sup> , 0.97984 <sup>b</sup>
20	0.96444	0.96451 <sup>a</sup> , 0.96431 <sup>b</sup>
30	0.94878	0.94869 <sup>a</sup> , 0.94886 <sup>b</sup>
40	0.93140	0.93134 <sup>a</sup> , 0.93156 <sup>b</sup>
50	0.91213	0.91185 <sup>a</sup> , 0.91192 <sup>b</sup>
60	0.89049	0.89013 <sup>a</sup> , 0.89041 <sup>b</sup>

Cont...

Mass % methanol	$P \times 10^{-3} / \text{Kg.m}^{-3}$ Observed	$P \times 10^{-3} / \text{Kg.m}^{-3}$ Literature
70	0.86737	0.86706 <sup>a</sup> , 0.86718 <sup>b</sup>
80	0.84258	0.84217 <sup>a</sup> , 0.84244 <sup>b</sup>
90	0.81541	0.81528 <sup>a</sup> , 0.81546 <sup>b</sup>
100	0.78665	0.78662 <sup>a</sup> , 0.78662 <sup>b</sup>

<sup>a</sup>[2], <sup>b</sup>[3]

The pycnometer filled with air-bubble free experimental liquids, was kept in a transparent walled water bath maintained constant to  $\pm 0.01$  K for 10 to 15 minutes to attain thermal equilibrium. The positions of the liquid levels in the two arms were recorded with the help of a travelling microscope that could be read to 0.01 mm. The estimated accuracy of the density measurement of solvent and electrolyte solution was  $\pm 0.00002$  g.cm<sup>-3</sup>. For each solution, the mean of four different density readings have been used

## RESULTS AND DISCUSSIONS

Apparent molar volumes  $[V_{\phi}]$  for all electrolytes at different concentrations have been calculated at 298.15 K from the corresponding density data by using equation.

$$V_{\phi} = M / p_0 - [1000 (p - p_0) / c p_0] \quad \dots(1)$$

where  $p_0$  and  $p$  are densities of the solvent and the solution, respectively,  $M$  is the molecular weight of the electrolyte and  $c$  is molar concentration.

The recommended procedure for extrapolation of  $V_{\phi}$  to infinite dilution employs Redlich-Meyer equation.

$$V_{\phi} = V_{\phi}^0 + S_v \cdot c^{1/2} + q_v \cdot c \quad \dots(2)$$

where  $S_v$  is theoretical limiting slope and  $q_v$  is a constant. The calculation of numerical value for  $S_v$  requires among other things knowledge of the pressure dependences of dielectric constants, which are not available for solvents under investigation. For this reason, the Masson equation<sup>7</sup>.

$$V_{\phi} = V_{\phi}^0 + S_v^* \cdot c^{1/2} \quad \dots(3)$$

in which  $S_v^*$  is an experimental slope, has been used for extrapolating the data to infinite dilution. The corresponding extrapolated  $V_{\phi}^0$  values of different electrolytes and experimental slopes,  $S_v^*$ , are presented in Table 2.

**Table 2: Limiting partial molar volumes ( $V_{\phi}^0$ ), experimental slopes ( $S_v^*$ ) of  $R_4NI$ ,  $NaBPh_4$  and  $NaI$  in methanol + water at 298.15 K**

Electrolyte	Mass % methanol	$(V_{\phi}^0) \times 10^6 / m^3 \cdot mol^{-1}$	$S_v^* \times 10^3 / dm^3 L^{1/2} mol^{-3/2}$
$(CH_3)_4NI$	0	125.69 (125.78) <sup>a</sup> (125.27) <sup>b</sup>	-13.67
	10	121.07	5.28
	20	122.93	0.60
	30	124.80	10.05
	40	126.68	8.53
	50	128.53	8.24
	60	130.47	3.38
	70	132.28	4.51
	80	134.13	3.20
	90	136.03	1.81
	100	137.90	0.54
$(C_2H_5)_4NI$	0	178.50, (185.5) <sup>b</sup> , (185.18) <sup>c</sup>	5.54
	10	180.27	6.06
	20	182.13	6.21
	30	183.91	6.72
	40	185.75	6.87
	50	187.47	7.63
	60	189.18	8.28
	70	190.94	8.80
	80	192.73	9.05
	90	194.48	9.58
$(C_3H_7)_4NI$	0	250.75, (250.77) <sup>a</sup> , (250.9) <sup>b</sup>	0.36
	10	250.27	5.91
	20	249.79	8.01

Cont...

Electrolyte	Mass % methanol	$(V_{\theta}^0) \times 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	$S_v^* \times 10^3 / \text{dm}^3 \text{L}^{1/2} \text{mol}^{-3/2}$
$(\text{C}_4\text{H}_9)_4\text{NI}$	30	249.31	10.12
	40	248.82	5.75
	50	248.34	1.33
	60	247.86	0.28
	70	247.37	3.20
	80	246.88	2.08
	90	246.41	0.91
	100	245.92	-0.14
	0	311.96, (312.2) <sup>b</sup> , (311.97) <sup>c</sup>	-36.48
	10	310.18	-35.40
	20	308.43	-33.10
	30	306.66	-30.54
	40	304.92	29.51
	50	303.12	-33.27
	60	301.39	12.44
	70	299.61	-7.53
	80	297.83	-12.86
90	296.09	-20.34	
100	294.31	-27.22	
NaI	0	34.99, (34.98) <sup>d</sup> , (35.15) <sup>e</sup> , (35.00) <sup>f</sup>	5.56, (1.4) <sup>e</sup>
	10	35.93	3.70
	20	36.24	1.69
	30	36.32	3.74
	40	34.36	2.14
	50	33.66	1.71
	60	30.13	9.62

Cont...

Electrolyte	Mass % methanol	$(V_{\phi}^0) \times 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	$S_v^* \times 10^3 / \text{dm}^3 \text{L}^{1/2} \text{mol}^{-3/2}$
NaBPh <sub>4</sub>	70	25.41	10.91
	80	21.28	4.33
	90	17.14	8.77
	100	(11.79), (11.69) <sup>c</sup>	9.69
	0	276.38, (276.41) <sup>g</sup> , (276.12) <sup>h</sup> , (276.40) <sup>i</sup>	-10.12, (-10.38) <sup>h</sup> , (-10.03) <sup>i</sup>
	10	274.81	-11.99
	20	273.63	-10.09
	30	269.64	-4.97
	40	266.35	-16.33
	50	263.18	17.18
	60	259.65	-3.22
	70	255.88	-9.31
	80	249.68	-7.20
	90	245.38	-2.09
100	243.12, (241.00) <sup>f</sup>	-4.32, (-5.01) <sup>f</sup>	

<sup>a</sup>[1], <sup>b</sup>[10], <sup>c</sup>[11], <sup>d</sup>[12], <sup>e</sup>[13], <sup>f</sup>[14], <sup>g</sup>[15], <sup>h</sup>[6], <sup>i</sup>[16],

$V_{\phi}^0$  is considered as a criterion of measure of ion-solvent interaction. A close perusal of Table 2 shows that the limiting apparent molar volumes ( $V_{\phi}^0$ ) of the electrolytes, are positive, suggesting strong ion-solvent interactions.  $V_{\phi}^0$  increases with increase in size of electrolyte.  $V_{\phi}^0$  is also found to change with change of solvent composition. This is attributed to varying and preferential solvation of solute with size of electrolyte and with composition of solvent mixture. Table 2 also lists  $S_v^*$  values, which are the measure of ion-ion interactions. The positive  $S_v^*$  values indicate some ion-ion interactions and negative  $S_v^*$  values suggest dissociation of ion-ion interactions. Some of the  $V_{\phi}^0$  and  $S_v^*$  values are compared with available literature values (Table 2). Limiting ionic partial molar volumes ( $V_{\phi}^{0\pm}$ ) are calculated following the method suggested by Conway et al.<sup>1</sup> Following this procedure, the  $V_{\phi}^0$  values for  $R_4\text{NI}$  in water, methanol and methanol-water mixtures were plotted against a molecular weight of the corresponding  $R_4\text{N}^+$  ions, using an equation of the form.

$$V_{\phi}^0 = V_{\phi}^0(\bar{I}) + b (\text{mol wt of } R_4\text{N}^+) \quad \dots(4)$$

where  $b$  is a constant and  $V_{\phi}^0(\bar{I})$  is the limiting ionic partial molar volume of  $\Gamma^{-}$  ion. An excellent linear relationship was observed for all  $R_4NI$  salts in all solvents with correlation coefficient greater than 0.999. The limiting ionic partial molar volumes of  $R_4N^{+}$ ,  $Na^{+}$ ,  $\Gamma^{-}$  and  $BPh_4^{-}$  are included in Table 3. Some of the observed values of limiting ionic partial molar volumes agreed well with literature values (Table 3).

**Table 3: Ionic partial molar volumes ( $V_{\phi}^{0\pm}$ ) x  $10^6/m^3.mol^{-1}$  in various methanol + water mixtures at 298.15 K**

Mass % methanol	$\Gamma^{-}$	$Na^{+}$	$(CH_3)_4N^{+}$	$(C_2H_5)_4N^{+}$	$(C_3H_7)_4N^{+}$	$(C_4H_9)_4N^{+}$	$BPh_4^{-}$
0	38.78 (36.22) <sup>b</sup>	-3.79 (-4.66) <sup>d</sup>	86.91 (84.6) <sup>c</sup> (85.18) <sup>e</sup>	139.72 (143.6) <sup>a</sup> (143.23) <sup>f</sup>	211.97 (211.45) <sup>e</sup> (208.56) <sup>f</sup>	273.18 (270.2) <sup>a</sup> (272.16) <sup>e</sup>	280.17 (281.05) <sup>d</sup> (283.32) <sup>f</sup>
10	35.73	0.20	85.34	144.55	214.54	274.46	274.61
20	39.82	-3.58	83.11	142.31	209.97	268.61	277.27
30	43.89	-7.57	80.91	140.01	205.42	262.76	277.21
40	47.97	-13.61	78.71	137.77	200.84	256.94	279.96
50	52.01	-18.34	76.52	135.46	196.33	251.11	281.53
60	56.01	-25.96	74.38	133.09	191.7	245.30	285.61
70	60.09	-34.68	72.19	130.85	187.28	239.52	290.56
80	61.14	-42.86	69.99	128.59	182.74	233.69	292.54
90	68.21	-51.07	67.82	126.27	178.20	227.88	295.45
100	72.30	-60.50	65.60 (66.9) <sup>a</sup>	124.00 (125.9) <sup>a</sup>	173.63	222.01	303.62

<sup>a</sup>[17], <sup>b</sup>[18], <sup>c</sup>[19], <sup>d</sup>[20], <sup>e</sup>[21], <sup>f</sup>[6]

When an ion is introduced into solvent, the partial molar volume at infinite dilution can be expressed as<sup>8,9</sup> -

$$V_{\phi}^{0\text{ ion}} = V_{\phi}^{0\text{ int.}} + \Delta V \quad \dots(5)$$

where  $V_{\phi}^{0\text{ int.}}$  is the intrinsic volume of the ion and  $\Delta V$  is change in the volume of the system due to ion-solvent interaction. In electrolytic solutions, the anion solvation can be considered as negligible. It is argued that the solvation number at infinite dilution is really a measure of the extent to which the cation is solvated. Extending these arguments to solutions of  $R_4NI$  in

methanol + water mixtures, it can be assumed that, in the case of  $R_4NI$ , the main contribution to the solvation is due to that of the  $R_4N^+$  ions. Therefore equation (5) can be written as -

$$V_{\phi}^0 (R_4N^+) = V_{\phi}^{0 \text{ int}} (R_4N^+) + \Delta V \quad \dots(6)$$

The term  $V_{\phi}^{0 \text{ int}} (R_4N^+)$  was calculated with the help of an equation

$$V_{\phi}^{0 \text{ int}} (R_4N^+) = 2.52 r^3 (R_4N^+) \quad \dots(7)$$

where  $r [R_4N^+]$  is crystallographic radius of  $R_4N^+$  ion. Values of  $\Delta V$  for all  $[R_4N^+]$  ions in methanol + water mixtures are included in Table 4. It is seen that all  $\Delta V$  values are negative and negative values in general show a tendency to increase in magnitude with the size of  $[R_4N^+]$  ion, suggesting decrease in ion-solvent interaction with increase in the size of the  $[R_4N^+]$  ion. Higher negative values of  $\Delta V$  for all  $[R_4N^+]$  ions in methanol rich regions of solution suggest very weak ion-solvent interactions with methanol molecules.  $\Delta V$  values for  $\Gamma^-$  ions are positive and positive values in general have a tendency to increase with increase of methanol content of the solution, indicating preferable solvation of  $\Gamma^-$  ions by methanol molecules.

**Table 4:  $\Delta V \times 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$  values for  $R_4N^+$  and  $\Gamma^-$  in methanol + water mixtures at 298.15 K**

Mass % methanol	$\Gamma^-$	$(\text{CH}_3)_4\text{N}^+$	$(\text{C}_2\text{H}_5)_4\text{N}^+$	$(\text{C}_3\text{H}_7)_4\text{N}^+$	$(\text{C}_4\text{H}_9)_4\text{N}^+$
0	13.38	-18.38	-21.56	-20.74	-30.61
10	10.33	-19.95	-16.73	-18.17	-29.34
20	14.43	-22.18	-18.97	-22.74	-35.19
30	18.50	-24.38	-21.27	-27.29	-41.03
40	22.58	-26.59	-23.51	-31.87	-46.85
50	26.61	-28.77	-25.82	-36.38	-52.68
60	30.69	-30.91	-28.19	-40.94	-58.50
70	34.69	-33.10	-30.43	-45.43	-64.28
80	38.74	-35.30	-32.69	-49.97	-70.11
90	42.81	-37.47	-35.01	-54.51	-75.92
100	46.90	-39.69	-37.28	-59.08	-81.79



## CONCLUSIONS

( $R_4N^+$ ) ions are less solvated in aqueous methanol while  $I^-$  ions are preferably solvated in aqueous methanol.

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