

Limiting Ionic Partial Molar Volumes of R_4N^+ and I^- in Aqueous Methanol at 303.15 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 and 100 mass % methanol + water at 303.15 K, limiting partial molar volumes of solutes and limiting ionic partial molar volumes of R_4N^+ and I^- have been calculated and interpreted in terms of ion-ion, ion-solvent and solvent-solvent interaction.

Keywords: 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 components¹, increase in the volume of solution due to intrinsic ionic volume and² 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 molecule 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 I^- in aqueous methanol at 303.15 K.

Experimental

The salts used in the present investigations are $(CH_3)_4NI$ (s.d.fine-chem., 99%), $(C_2H_5)_4NI$ (SISCO, 99%), $(C_3H_7)_4NI$ (Fluka, 98%), $(C_4H_9)_4NI$ (s.d.fine-chem., 99%), $NaBPh_4$ (E.Merck, 99.5%), NaI (s.d.fine chem., 99.8%). R_4NI salts were used after recrystallisation. NaI and $NaBPh_4$ 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 $KMnO_4$, 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 purification². The purity of methanol was checked by comparing its observed density $0.78665 \text{ g.cm}^{-3}$ with that of $0.78662 \text{ g.cm}^{-3}$ as reported earlier² at 303.15 K.

Methods

Methanol + water mixtures of compositions of 0,10,20,30,40,50,60,70,80,90 and 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 303.15 K with those of literature values^{2,3} 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^{4,5}. Densities were determined by using 15 cm^3 bicapillary pycnometer as described earlier⁶. Pycnometer was calibrated using conductivity water with $0.99705 \text{ g.cm}^{-3}$ as its density at 303.15 K.

Table 1. Comparison of densities of water, methanol and methanol + water mixtures at 303.15 K

Mass % methanol	$\rho \times 10^{-3} / \text{kg.m}^{-3}$ Observed	$\rho \times 10^{-3} / \text{kg.m}^{-3}$ Literature ⁷
0	0.99547	0.9957
10	0.9779	0.97806
20	0.96231	0.96207
30	0.94594	0.94589
40	0.92814	0.92812
50	0.90935	0.90795
60	0.88704	0.88613
70	0.86357	0.86255
80	0.83831	0.83764
90	0.81148	0.81051
100	0.78178	0.7818

The Pycnometer filled with air-bubble free experimental liquids, was kept in a transparent walled water bath maintained constant to $\pm 0.01 \text{ K}$ 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 $\pm 0.00002 \text{ g.cm}^{-3}$. For each solution the mean of four different density readings have been used

Results and Discussion

Apparent molar volumes $[V_\phi]$ for all electrolytes at different concentrations have been calculated at 303.15 K from the corresponding density data by using equation.

$$V_\phi = M / \rho_0 - [1000 (\rho - \rho_0) / c \rho_0] \quad (1)$$

Where ρ_0 and ρ are densities of the solvent and the solution respectively, M is the molecular weight of the electrolyte, c is molar concentration. The recommended procedure for extrapolation of V_ϕ to infinite dilution employes by Redlich – Meyer equation.

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

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 equation⁸ is used.

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

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

Table 2. Limiting partial molar volumes (V_ϕ^0), experimental slopes (S_v^*) of R_4NI , $NaBH_4$ and NaI in methanol + water at 303.15 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	126.18 (126.2) ^a (126.5) ^b	-11.15
	10	121.37	8.95
	20	123.49	2.26
	30	125.52	13.00
	40	127.56	10.8
	50	129.59	9.12
	60	131.64	7.12
	70	133.68	5.63
	80	135.71	4.00
	90	137.76	2.33
$(C_2H_5)_4NI$	100	139.79	0.79
	0	180.86 (186.3) ^b (188.7) ^a	2.97
	10	182.43	3.76
	20	184.1	4.12
	30	185.57	5.33
	40	187.20	5.83
	50	188.77	6.52
	60	190.30	7.38
	70	191.99	7.52
	80	193.45	8.57
$(C_3H_7)_4NI$	90	195.02	9.22
	100	196.60	9.76
	0	253.30(253.3) ^a (252.4) ^b	22.92
	10	252.42	5.26
	20	251.86	24.51
	30	251.29	12.34
	40	250.66	5.30
	50	250.00	0.27
	60	249.34	0.98
	70	248.69	1.59
$(C_4H_9)_4NI$	80	248.08	0.09
	90	247.37	-1.03
	100	246.72	-2.32
	0	315.90,(314.0) ^b ,(315.9) ^a	-16.69

Contd...

	10	314.58	-35.66
	20	313.29	-28.49
	30	311.98	-22.35
	40	310.71	10.44
	50	309.44	37.49
	60	308.1	-2.81
	70	306.79	-34.19
	80	305.5	-20.53
	90	304.19	-34.55
	100	302.92	-10.97
NaI	0	35.62	5.32
	10	36.42	-34.17
	20	36.43	-11.86
	30	36.44	5.02
	40	34.42	6.49
	50	33.20	4.67
	60	30.12	10.48
	70	25.03	13.13
	80	20.61	13.21
	90	16.18	13.03
	100	9.94	11.15
NaBPh ₄	0	281.67	-10.32
	10	279.72	-15.47
	20	278.64	-10.59
	30	273.82	-6.13
	40	268.04	-16.35
	50	265.43	-17.83
	60	262.13	-5.8/
	70	258.90	-9.46
	80	252.94	-10.24
	90	247.77	-5.50
	100	246.31	-6.41

^a Ref:[9], ^b Ref:[10]

V_{ϕ}^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_{ϕ}^0) of the electrolytes, are positive, suggesting strong ion –solvent interactions. V_{ϕ}^0 increases with increase in size of electrolyte. V_{ϕ}^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 Sv^* values which are the measure of ion-ion interactions. The positive Sv^* values indicate some ion –ion interactions and negative Sv^* values suggest dissociation of ion – ion interactions. Some of the V_{ϕ}^0 and Sv^* 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.*,¹. Following this procedure, the V_{ϕ}^0 values for R_4NI in water, methanol and methanol- water mixtures were plotted against a molecular weight of the corresponding R_4N^+ ions, using an equation of the form

$$V_{\phi}^0 = V_{\phi}^0(\bar{I}) + b(\text{mol wt of } R_4N^+) \quad (4)$$

Where b is a constant and $V_{\phi}^0(\bar{I})$ is the limiting ionic partial molar volume of \bar{I} 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^+ , \bar{I} 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). When an ion is introduced into solvent, the partial molar volume at infinite dilution can be expressed as^{11,12}.

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

Table 3. Ionic partial molar volumes ($V_{\phi}^{0\pm}$) $\times 10^6/\text{m}^3 \cdot \text{mol}^{-1}$ in various methanol + water mixtures at 303.15 K

Mass % methanol	\bar{I}	Na+	$(\text{CH}_3)_4\text{N}^+$	$(\text{C}_2\text{H}_5)_4\text{N}^+$	$(\text{C}_3\text{H}_7)_4\text{N}^+$	$(\text{C}_4\text{H}_9)_4\text{N}^+$	Bph_4^-
0	38.14	-2.52 -1.82	88.04 89.1 ^{a,b} 88.5 ^{a,b}	142.72	215.16	277.76	284.19
10	33.42	3.00	87.95	149.01	219.01	281.16	276.72
20	38.47	-1.05	85.02	145.63	213.39	274.82	279.69
30	42.32	-5.88	83.19	143.25	208.97	269.66	279.70
40	46.20	-11.78	81.36	140.99	204.43	264.51	279.82
50	50.04	-16.17	79.55	138.73	199.96	259.4	281.60
60	53.92	-23.81	77.72	136.37	195.42	154.18	285.94
70	57.85	-32.82	75.82	134.13	190.84	248.93	291.72
80	61.65	-41.04	74.06	131.8	186.43	243.84	293.98
90	65.53	-49.35	72.22	129.49	181.84	238.65	297.12
100	69.38	-59.43	70.41	127.22	177.34	233.54	305.74

^a Ref:[1], ^b Ref:[13],

Where $V_{\phi}^{0\text{int}}$ is the intrinsic volume of the ion and ΔV 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

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

The term $V_{\phi}^{0\text{int}}(R_4N^+)$ was calculated with the help of an equation $V_{\phi}^{0\text{int}}(R_4N^+) = 2.52$

$$r^3(R_4N^+) \quad (7)$$

Where $r[R_4N^+]$ is crystallographic radius of R_4N^+ ion. Values of ΔV for all $[R_4N^+]$ ions in methanol +water mixtures are included in Table 4. It is seen that all ΔV 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 ΔV for all $[R_4N^+]$ ions in methanol rich regions of solution suggest very weak ion-solvent interactions with methanol molecules. ΔV values for \bar{I} 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 \bar{I} ions by methanol molecules.

Table 4. $\Delta V \times 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$ values for R_4N^+ and $\bar{\text{I}}$ in methanol + water mixtures at 303.15 K

Mass % methanol	$\bar{\text{I}}$	$(\text{CH}_3)_4\text{N}^+$	$(\text{C}_2\text{H}_5)_4\text{N}^+$	$(\text{C}_3\text{H}_7)_4\text{N}^+$	$(\text{C}_4\text{H}_9)_4\text{N}^+$
0	14.05	-19.30	-22.64	-21.78	-32.14
10	10.85	-20.95	-17.57	-19.08	-30.81
20	15.15	-23.29	-19.92	-23.88	-36.95
30	19.43	-25.60	-22.33	-28.65	-43.08
40	23.71	-27.92	-24.69	-33.46	-49.19
50	27.94	-30.21	-27.11	-38.20	-55.31
60	32.22	-32.46	-29.60	-42.99	-61.43
70	36.42	-34.76	-31.95	-47.70	-67.49
80	40.68	-37.07	-34.32	-52.47	-73.62
90	44.95	-39.34	-36.76	-57.24	-79.72
100	49.25	-41.67	-39.14	62.03	-85.88

Conclusion

(R_4N^+) ions are less solvated in aqueous methanol while $\bar{\text{I}}$ ions are preferably solvated in aqueous methanol.

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