

CHAPTER - IV

Apparent and Partial Molal Volumes of Some Symmetrical Tetra-alkylammonium Bromides in Tetrahydrofuran and 1,2-Dimethoxyethane at different Temperatures.

INTRODUCTION :

The volumetric behaviour of solutes has been proved to be very useful in elucidating the various interactions occurring in aqueous and non-aqueous solutions¹. Studies on the apparent and partial molal volumes of electrolytes have been used to examine solute-solute, solute-solvent and solvent-solvent interaction². The apparent and partial molal volumes of tetraalkylammonium salts have been investigated rather extensively in aqueous³⁻⁵ and non-aqueous solutions^{6,7}. Such measurements have also been reported for water-organic solvent binary systems⁸. However, no work has been reported on the apparent and partial molal volumes of tetraalkylammonium bromides, R_4NBr ($R = C_4H_9$ to C_7H_{15}) in tetrahydrofuran (THF) and 1,2 dimethoxyethane (DME) at 25,30,35,40 and 45°C. In recent years much attention has been given to these solvents of low dielectric constants ($\epsilon_{THF} = 7.58$ and $\epsilon_{DME} = 7.01$ at 25°C). Since, these have been reported to give good performance^{9,10}.

Experimental Section :

Tetrahydrofuran (THF) was kept several days over KOH, refluxed for 24 hours and distilled over $LiAlH_4$. The

boiling point (66°C), density (0.8807 g cm⁻³) and viscosity ($\eta_0 = 0.0046$ P) compared well with the literature values ¹¹ . The specific conductance of THF was ca. 0.81×10^{-6} Ohm⁻¹ cm⁻¹ at 25°C.

The purification of 1,2-dimethoxyethane (Fluka, Purum) has been described earlier ¹² . The solvent was shaken well with FeSO₄ , (A.R.,BDH) for 1-2 hours, decanted and distilled. The distillate was refluxed for 12 hours and distilled over metallic sodium (b.p. = 83.5°C, density = 0.8626 g/cc, viscosity = 0.0042 p)

Tetraalkylammonium bromides were of Fluka purum or puriss grades; these were purified as described in the literature ¹³ and also described earlier by us ¹⁴ . The salts were purified by recrystallization and the higher homologues were recrystallized twice to ensure highest purity. The recrystallized salts were dried under vacuum at elevated temperatures for 12 hours. The salts were stored in a vacuum desiccator and dried for 3-4 hours at 100°C prior to use.

A stock solution for each salt was prepared by weight and working solutions in the concentration range $0.01 < M < 0.10$ were obtained by weight dilution. The conversion of the molality into molarity was done by using the density values. The densities were measured with an Ostwald Sprengal type pycnometer having a bulb volume of about 25 cm³ and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 25°C with doubly distilled water. Measurements were made in an oil bath maintained

at $25 \pm 0.05^\circ\text{C}$ by means of a mercury-in-glass thermoregulator and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge. The precision of the density measurement was greater than $\pm 3 \times 10^{-5} \text{ g cm}^{-3}$.

Results and Discussion :

The apparent molal volumes, ϕ_v , of the solutes were calculated from the densities of the solutions by using the equation

$$\phi_v = \frac{M}{\rho_0} - 1000(\rho - \rho_0)/c\rho_0 \quad (1)$$

Where M is the molecular weight of the solute, ρ_0 and ρ are the densities of the solvent and the solution, respectively and c is the molar concentration in molarity.

The partial molal volumes, \bar{V}_2 , were computed from ϕ_v with the equation

$$\bar{V}_2 = \phi_v + \frac{1000 - c\phi_v}{2000 + c^{3/2}(\partial\phi_v/\partial\sqrt{c})} \sqrt{c} (\partial\phi_v/\partial\sqrt{c}) \quad (2)$$

The molar concentrations, densities, and apparent and partial molal volumes of the solutions of various tetraalkylammonium bromide4s in THF and DME at 25,30,35,40 and 45°C are reported in Table 1. The limiting apparent molal volumes, ϕ_v (equal to the partial molal volumes at infinite dilution, \bar{V}_2^0), were obtained

by least square fitting of ϕ_v values to the equation

$$\phi_v = \phi_v^{\circ} + S_v^* \sqrt{c} \quad (3)$$

Where S_v^* is the experimental slope. The plots of ϕ_v against \sqrt{c} were linear in all cases, and from the intercept and the slope one can obtain the values of ϕ_v° ($= \bar{V}_2^{\circ}$) and S_v^* , respectively. The values of ϕ_v° and S_v^* are given in Table 2. A representative plot is shown in Figures 1 and 2. The experimental slope S_v^* depends upon ion-ion interactions while ϕ_v° values can be used to examine the solute-solvent interactions since at infinite dilution the apparent molal volumes are, by definition, independent on ion-ion interactions.

The S_v^* values shown in Table 2 are large and positive for all the tetraalkylammonium bromides in both THF and DME at all the temperatures investigated. This is an indication of strong ion-ion interactions in both solvent media. This type of behaviour of tetraalkylammonium halides has been also observed in solvents of medium or low dielectric constants, e.g., 2-methoxyethanol, dimethylsulfoxide, methanol, N, N dimethyl formamide, etc.^{15,6,16}. The possible explanation for the positive slopes in THF and DME may be that the ionic association would become quite appreciable in this medium as the concentration of the electrolyte is increased, thereby weakening the ion-solvent interaction. As a consequence, contraction of the solvent would be gradually lowered with increasing concentration of the electrolyte, resulting in a net positive volume change per mole

of the added solute. The S_v^* values (and hence ion-ion interactions) increase as the size of the cation increases in DME at all the temperatures studied whereas these values increase with increasing size of the cation with the exception of Pent_4NBr in THF over the entire range of temperatures studied. (Table 2). Exactly the same conclusion regarding the ion-association behaviour of these electrolytes in DME and THF has been drawn from conductometric studies ¹⁷ .

The limiting apparent molal volumes, ϕ_v° shown in Table - 2 are large and positive, and the values increase regularly as the size of the tetraalkylammonium ion increases. This is in agreement with earlier findings in several non-aqueous solvents as well as in water and heavy water ¹⁸ . The large ϕ_v° values reveal that the solute-solvent interactions are strong in these solvents.

The calculations of the ionic limiting partial molal volumes have been done following the method suggested by Conway et al ³ . Vosaki et al ¹⁹ have used this method for the separation of some literature values and of their own $\bar{V}_{R_4NX}^\circ$ values into ionic contributions in organic electrolyte solutions. Krumgalz ¹⁸ applied the same method to a large number of partial molal volume data for non aqueous electrolyte solutions in a wide temperatures range.

The V_2° values for the tetraalkylammonium bromides in THF and DME at 25,30,35,40 and 45°C were plotted against the formula weight of the corresponding tetraalkylammonium ions. An excellent linear relationship was observed for all the salts examined. The $V_{i,0}^\circ$ values for tetraalkylammonium and bromide ions in DME and THF at 25,30,35,40 and 45°C are presented in Table 3. The

V_{ion}° values for all the tetraalkylammonium ions are positive and found to increase continuously from Bu_4N^+ to $Hept_4N^+$ in both solvent media. This fact indicates that the large tetraalkylammonium cations are scarcely solvated in these solvents media. The positive $V_{R_4N^+}^{\circ}$ values indicate that the solvent molecules form a less compact structure around the incorporated ion, thus giving rise to positive charge in volume. This fact provides additional support in favour of the unsolvation of these cations.

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TABLE - 1

Concentration (C), Molality (m), Densities (ρ), Apparent Molal Volumes (ϕ_v), and Partial Molal Volumes (\bar{V}_2) for Various Tetraalkylammonium Bromides in Various Solvents at Different Temperatures.

	C mol dm ⁻³	\sqrt{C} (mol dm ⁻³) ^½	m mol kg ⁻¹	ρ g cm ⁻³	ϕ_v cm ³ mol ⁻¹	\bar{V}_2 cm ³ mol ⁻¹
Solvent = Tetrahydrofuran (THF)						
At 25°C						
Salt = Bu ₄ NBr, Mol. Wt. of the salt = 322.38						
1.	0.064018	0.25300	0.0739885	0.88588	274.52	309.92
2.	0.0512144	0.22630	0.0589552	0.88521	266.49	298.32
3.	0.0384108	0.19598	0.0440472	0.88442	256.66	284.35
4.	0.0368949	0.19208	0.0422891	0.88434	254.69	281.65
5.	0.0256072	0.16002	0.0292612	0.88338	248.09	270.79
6.	0.0221369	0.14878	0.0252675	0.88309	244.50	265.63
7.	0.0184474	0.13582	0.0210364	0.88275	241.22	260.53
8.	0.0128036	0.11315	0.0145797	0.88220	234.55	250.66

Contd.....(2)

Salt = Pent₄NBr, Mol. Wt. of the salt = 378.49

1.	0.0402388	0.20059	0.0462579	0.885109	305.90	330.48
2.	0.0357678	0.18912	0.0410576	0.884699	303.44	326.66
3.	0.0312968	0.17690	0.0358755	0.884216	302.91	324.66
4.	0.0268258	0.16378	0.0307043	0.883833	297.96	318.13
5.	0.0223549	0.14951	0.0255508	0.883380	294.60	313.05
6.	0.0178839	0.13373	0.0204127	0.882882	292.43	309.09
7.	0.0134129	0.115814	0.0152884	0.882422	285.62	305.89

Salt = Hex₄NBr, Mol. Wt. of the Salt = 434.60

1.	0.1880575	0.43365	0.23265	0.89002	437.28	494.33
2.	0.1692517	0.41140	0.20743	0.88947	434.76	482.37
3.	0.1504460	0.38787	0.18262	0.88919	429.50	472.20
4.	0.1316402	0.36282	0.15827	0.88894	422.54	460.07
5.	0.1128345	0.33590	0.13439	0.88862	413.99	452.88
6.	0.0940287	0.30664	0.11097	0.88816	403.59	444.09
7.	0.075223	0.27426	0.08797	0.88732	393.85	434.38

Contd.....(3)

Salt = Hept₄NBr, Mol. Wt. of the Salt = 490.71

1.	0.0393032	0.1982	0.454411	0.88410	459.28	501.69
2.	0.0353729	0.1880	0.0408182	0.88395	453.39	493.71
3.	0.0314426	0.1773	0.0362131	0.88369	449.78	487.89
4.	0.0275123	0.1658	0.0316232	0.88350	442.30	478.01
5.	0.0235819	0.1535	0.0270425	0.88328	433.99	467.13
6.	0.0196516	0.1401	0.0225018	0.88297	426.89	457.19
7.	0.0157212	0.1253	0.0179658	0.88265	417.25	444.41

At 30°C

Salt = Bu₄NBr, Mol. Wt. of Salt = 322.38

1.	0.0636913	0.25237	Same as 25°C	0.88136	278.28	312.54
2.	0.0509551	0.22573	"	0.88073	270.00	300.77
3.	0.0382062	0.19546	"	0.87985	263.50	290.27
4.	0.0367018	0.191577	"	0.87979	261.32	286.51
5.	0.0254773	0.15961	"	0.87894	252.35	274.31
6.	0.0220218	0.148397	"	0.87864	249.31	269.74

Contd.....(4)

7.	0.0183539	0.13547	Same as 25°C	0.87832	246.72	265.39
8.	0.0127389	0.112866	"	0.87779	239.55	255.14

Salt = Pent₄NBr, Mol. Wt. of the Salt = 378.49

1.	0.040024	0.20005	"	0.88059	311.12	333.89
2.	0.0355837	0.18863	"	0.88021	308.44	329.95
3.	0.031143	0.17647	"	0.87987	303.11	323.27
4.	0.0266912	0.16337	"	0.87940	301.84	321.07
5.	0.0222423	0.14913	"	0.87893	299.94	319.87
6.	0.0177946	0.13339	"	0.87848	295.84	315.94
7.	0.0133463	0.11552	"	0.87803	289.46	310.03

Salt = Hex₄NBr, Mol. Wt. of the Salt = 434.68

1.	0.187056	0.43250	"	0.88529	441.45	495.99
2.	0.168412	0.41038	"	0.88506	436.96	485.38
3.	0.149636	0.38682	"	0.88441	434.53	475.28
4.	0.131012	0.36195	"	0.88439	423.25	465.46

Contd.....(5)

5.	0.112241	0.33502	Same as 25°C	0.88395	418.76	455.52
6.	0.093553	0.30586	"	0.88367	406.72	445.72
7.	0.074838	0.27356	"	0.88273	398.79	435.57

Salt = Hept₄NBr, Mol. Wt. of the Salt = 490.71

1.	0.0391081	0.1977	"	0.88308	469.12	511.94
2.	0.0351842	0.1857	"	0.87924	466.57	506.87
3.	0.0312765	0.1768	"	0.87900	457.61	496.07
4.	0.273713	0.1654	"	0.87897	450.76	486.83
5.	0.0234510	0.1531	"	0.87870	445.99	479.44
6.	0.0195505	0.1398	"	0.87843	438.89	469.50
7.	0.0156374	0.1250	"	0.87812	430.88	458.30

At 35°C

Salt = Bu₄NBr, Mol. Wt. of the Salt = 322.38

1.	0.0632441	0.2514838	"	0.87517	282.44	315.97
2.	0.0505966	0.2249368	"	0.87453	274.94	305.07

Contd.....(6)

3.	0.0379479	0.1948022	Same as 25°C	0.87376	266.48	295.98
4.	0.0364497	0.190918	"	0.87367	265.15	287.03
5.	0.0252993	0.1590575	"	0.87276	260.11	280.93
6.	0.0218691	0.147882	"	0.87256	253.32	273.07
7.	0.0182252	0.1350007	"	0.87224	249.92	264.39

Salt = Pent₄NBr, Mol. Wt. of the Salt = 378.49

1.	0.0397536	0.1993830	"	0.87443	316.15	338.27
2.	0.0353383	0.1879848	"	0.87407	313.08	334.04
3.	0.0309243	0.175853	"	0.87369	309.87	329.50
4.	0.0265045	0.162802	"	0.87325	308.30	325.08
5.	0.022088	0.1486203	"	0.87284	304.50	321.01
6.	0.0176711	0.1329326	"	0.87238	301.42	316.88
7.	0.0132535	0.1151238	"	0.87192	297.07	313.02

Salt = Hex₄NBr, Mol. Wt. of the Salt = 434.60

1.	0.1857833	0.4310258	"	0.87929	443.90	496.09
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Contd.....(7)

2.	0.1672041	0.4089059	Same as 25°C	0.87874	441.54	486.08
3.	0.1486275	0.3855223	"	0.87845	436.55	477.02
4.	0.1300888	0.3606782	"	0.87848	427.37	467.83
5.	0.1114504	0.3338418	"	0.87774	422.93	457.92
6.	0.0928685	0.3047433	"	0.87724	413.85	448.03
7.	0.0742646	0.2725153	"	0.87648	404.21	438.63

Salt = Hept₄NBr, Mol. Wt. of the Salt = 490.71

1.	0.0388208	0.1970299	"	0.87336	474.12	513.24
2.	0.0349438	0.1869326	"	0.87323	468.41	505.61
3.	0.031065	0.1762526	"	0.87308	461.91	497.05
4.	0.0271795	0.164862	"	0.87282	458.58	490.78
5.	0.0232885	0.1526057	"	0.87261	451.36	483.25
6.	0.0194148	0.139337	"	0.87234	444.78	475.66
7.	0.0155301	0.1246198	"	0.87205	436.52	467.89

Contd.....(8)

At 40°C

Salt = Bu₄NBr, Mol. Wt. of the Salt = 322.38

1.	0.0628935	0.25078	Same as 25°C	0.87083	283.05	316.80
2.	0.050311	0.22430	"	0.87016	276.09	305.26
3.	0.037758	0.19431	"	0.86935	268.74	293.55
4.	0.036247	0.19038	"	0.86927	267.08	291.41
5.	0.0251657	0.158637	"	0.86843	259.36	279.70
6.	0.0217529	0.147488	"	0.86815	256.30	275.24
7.	0.0181324	0.134656	"	0.86783	253.49	270.79
8.	0.0110557	0.105146	"	0.86737	245.47	259.91

Salt = Pent₄NBr, Mol. Wt. of the Salt = 378.49

1.	0.0395422	0.1988522	"	0.87464	320.67	352.90
2.	0.0351594	0.1875084	"	0.86965	316.19	341.14
3.	0.0307659	0.175400	"	0.86922	315.13	343.66
4.	0.0263706	0.162390	"	0.86884	312.02	338.47
5.	0.0219729	0.1482325	"	0.86840	309.23	333.42

Contd.....(9)

6.	0.0175818	0.1325960	Same as 25°C	0.86797	305.50	327.17
7.	0.0131868	0.1148337	"	0.86750	302.47	321.26

Salt = Hex₄NBr, Mol. Wt. of the Salt = 434.60

1.	0.18484	0.42993	"	0.87483	446.51	496.44
2.	0.16635	0.40786	"	0.87428	444.15	489.15
3.	0.14787	0.38454	"	0.87401	439.10	479.07
4.	0.12942	0.35975	"	0.87398	430.40	469.88
5.	0.11088	0.33299	"	0.87332	425.35	439.09
6.	0.09240	0.30397	"	0.87281	416.33	449.38
7.	0.07395	0.27193	"	0.87187	409.64	441.24

Salt = Hept₄NBr, Mol. Wt. of the Salt = 490.71

1.	0.038633	0.19655	"	0.86876	483.05	529.52
2.	0.0347699	0.186466	"	0.86862	478.40	522.59
3.	0.030908	0.17580	"	0.86846	473.55	513.07
4.	0.027040	0.16444	"	0.86829	467.32	504.92

Contd.....(10)

5.	0.0231670	0.15221	Same as 25°C	0.86808	461.43	495.03
6.	0.0193134	0.13897	"	0.86783	455.33	486.32
7.	0.0154514	0.12430	"	0.86755	448.22	478.00

At 45°C

Salt = Bu₄NBr, Mol. Wt. of the Salt = 322.38

1.	0.062530	0.250059	"	0.86626	284.03	318.89
2.	0.050023	0.223658	"	0.86552	278.50	306.23
3.	0.0375269	0.193718	"	0.86472	271.65	295.76
4.	0.0360459	0.189857	"	0.86465	269.33	292.97
5.	0.0250274	0.158200	"	0.86381	262.40	281.17
6.	0.0216359	0.147091	"	0.86354	259.22	277.62
7.	0.0180346	0.134293	"	0.86323	256.50	273.32
8.	0.0125224	0.111903	"	0.86273	251.11	265.15

Salt = Pent₄NBr, Mol. Wt. of the Salt = 378.49

1.	0.0393245	0.198304	"	0.86527	325.14	257.62
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Contd.....(11)

2.	0.03342169	0.18281	Same as 25°C	0.86477	322.35	352.35
3.	0.0305965	0.174918	"	0.86454	320.29	349.03
4.	0.0262253	0.161942	"	0.86417	317.02	343.67
5.	0.0218518	0.147823	"	0.86375	314.58	338.95
6.	0.0174849	0.13223	"	0.86331	312.68	334.52
7.	0.0131145	0.114518	"	0.86288	308.63	327.56

Salt = Hex₄NBr, Mol. Wt. of the Salt = 434.60

1.	0.18373	0.42864	"	0.8696	452.68	497.19
2.	0.16536	0.40664	"	0.86906	450.76	493.44
3.	0.14699	0.38340	"	0.86878	446.23	484.07
4.	0.128648	0.35867	"	0.86875	438.17	475.22
5.	0.110225	0.33200	"	0.86809	434.02	466.07
6.	0.091846	0.30306	"	0.86758	426.31	457.08
7.	0.073502	0.27111	"	0.86686	418.34	448.30

Salt = Hept₄NBr, Mol. Wt. of the Salt = 490.71

1.	0.0384032	0.19596	Same as 25°C	0.86387	495.07	540.98
2.	0.0345658	0.18591	"	0.86378	489.49	533.16
3.	0.030727	0.17530	"	0.86359	486.85	525.07
4.	0.026882	0.16390	"	0.86338	483.81	517.02
5.	0.023037	0.15180	"	0.86328	474.53	509.07
6.	0.019206	0.13860	"	0.86307	468.28	500.10
7.	0.015365	0.12395	"	0.86281	463.15	492.58

Solvent = 1,2-Dimethoxyethane (DME)

At 25°C

Salt = Bu₄NBr, Mol. Wt. of the Salt = 322.38

1.	0.0419794	0.2048887	0.049311	0.86485	276.66	300.26
2.	0.0377814	0.1943743	0.044323	0.86459	273.59	296.22
3.	0.0335835	0.183258	0.0393492	0.86430	271.08	292.22
4.	0.0293855	0.1714219	0.0343888	0.86398	268.92	288.73
5.	0.0251876	0.158706	0.0294395	0.86369	265.04	283.40

Contd.....(13)

6.	0.0209897	0.1448782	0.0245039	0.86335	262.22	279.00
7.	0.0167917	0.1295827	0.0195808	0.86297	260.26	275.30

Salt = Pent₄NBr, Mol. Wt. of the Salt = 378.49

1.	0.0463441	0.2152768	0.0546936	0.86488	350.22	383.47
2.	0.0440268	0.2098256	0.0519118	0.86477	348.48	380.92
3.	0.040551	0.2013727	0.0477541	0.86451	347.98	379.16
4.	0.0370752	0.1925492	0.0436051	0.86428	346.62	377.69
5.	0.0335994	0.1833013	0.0394672	0.86404	345.44	375.83
6.	0.0301236	0.1735615	0.0353385	0.86383	342.69	373.97
7.	0.0266478	0.1632415	0.0312223	0.86357	341.32	372.06

Salt = Hex₄NBr, Mol. Wt. of the Salt = 434.60

1.	0.1033670	0.3215073	0.1259579	0.86557	456.87	513.93
2.	0.0590668	0.2430366	0.0703947	0.86475	437.32	481.38
3.	0.0472534	0.2173784	0.0560011	0.86433	430.55	470.39
4.	0.0354401	0.1882554	0.0417719	0.86382	422.66	457.38

Contd.....(14)

5.	0.0236267	0.1537097	0.0277018	0.86316	413.95	444.80
6.	0.0118133	0.108689	0.0137808	0.86236	402.32	432.03

Salt = Hept₄NBr, Mol. Wt. of the Salt = 490.71

1.	0.0856958	0.2927384	0.1040618	0.86556	512.32	574.33
2.	0.048969	0.2212894	0.0582631	0.86451	494.05	533.60
3.	0.0391752	0.1979272	0.0463701	0.86406	488.38	530.68
4.	0.029814	0.1726673	0.0351186	0.86358	481.56	518.67
5.	0.0195876	0.1399557	0.022954	0.86295	473.16	503.41
6.	0.0097938	0.0989636	0.0114223	0.86223	462.14	483.50

At 30°C

Salt = Bu₄NBr, Mol. Wt. of the Salt = 322.38

1.	0.0417363	0.2042947	Same as 25°C	0.85984	277.70	301.74
2.	0.0375611	0.1938069	"	0.85955	275.74	298.58
3.	0.033273	0.1824089	"	0.85925	273.29	294.81
4.	0.0291245	0.1706592	"	0.85893	271.42	291.60

Contd.....(15)

5.	0.0250394	0.1582384	Same as 25°C	0.85861	269.20	288.23
6.	0.0208661	0.1444511	"	0.85827	266.78	285.04
7.	0.0166934	0.1292029	"	0.85792	263.84	282.07

Salt = Pent₄NBr, Mol. Wt. of the Salt = 378.49

1.	0.0460761	0.2146534	"	0.85988	351.52	385.21
2.	0.0437701	0.2092131	"	0.85973	350.75	383.67
3.	0.0403168	0.2007906	"	0.85952	349.02	381.93
4.	0.0368606	0.1919922	"	0.85928	347.90	380.07
5.	0.0334045	0.182769	"	0.85903	346.91	378.66
6.	0.0297084	0.1723615	"	0.85879	345.29	376.93
7.	0.0264925	0.1627652	"	0.85854	343.70	375.01

Salt = Hex₄NBr, Mol. Wt. of the Salt = 434.60

1.	0.1027901	0.320609	"	0.86074	457.19	514.94
2.	0.0587245	0.2423315	"	0.85974	439.32	484.09
3.	0.046976	0.2167399	"	0.85926	434.19	470.22

Contd.....(16)

4.	0.0352324	0.187703	Same as 25°C	0.85876	426.32	452.02
5.	0.0234884	0.1532592	"	0./85811	418.03	442.07
6.	0.0117442	0.1083707	"	0.85732	407.09	437.03

Hept₄NBr, Mol. Wt. of the Salt = 490.71

1.	0.0852046	0.2918984	"	0.86060	514.25	575.60
2.	0.0486837	0.2206439	"	0.85947	497.25	544.47
3.	0.038947	0.1973501	"	0.85913	491.49	534.19
4.	0.0296402	0.1721635	"	0.85855	484.79	522.25
5.	0.0914731	0.1395461	"	0.85791	477.09	510.87
6.	0.00973639	0.0986731	"	0.85718	468.70	499.37

At 35°C

Salt = Bu₄NBr, Mol. Wt. of the Salt = 322.38

1.	0.041492	0.2036959	"	0.85481	279.04	303.44
2.	0.0373408	0.1932379	"	0.85451	277.40	300.58
3.	0.033191	0.1821841	"	0.85420	275.70	297.11

Contd.....(17)

4.	0.0290422	0.1704179	Same as 25°C	0.85389	273.53	294.05
5.	0.0248924	0.1577733	"	0.85357	271.10	291.00
6.	0.0207435	0.1440263	"	0.85323	268.83	288.34
7.	0.0165953	0.1288228	"	0.85288	266.15	285.87

Salt = Pent₄NBr, Mol. Wt. of the Salt = 378.49

1.	0.0458039	0.2140184	"	0.85480	354.59	388.67
2.	0.0435109	0.2085928	"	0.85464	354.16	387.40
3.	0.0400766	0.2001915	"	0.85440	353.45	386.03
4.	0.0366422	0.1914217	"	0.85419	351.64	384.87
5.	0.0332069	0.1822278	"	0.85395	350.51	383.11
6.	0.0297699	0.1725396	"	0.85369	349.90	382.00
7.	0.0263357	0.1622829	"	0.85346	347.81	381.16

Salt = Hex₄NBr, Mol. Wt. of the Salt = 434.60

1.	0.1022049	0.3196951	"	0.85584	458.22	517.07
2.	0.0583823	0.2416244	"	0.85473	441.30	486.57

Contd.....(18)

3.	0.0467033	0.2161096	Same as 25°C	0.85427	435.57	472.80
4.	0.035026	0.1871525	"	0.85373	428.68	464.19
5.	0.0233501	0.1528076	"	0.85306	421.47	450.62
6.	0.011675	0.108051	"	0.85227	411.91	442.64

Salt = Hept₄NBr, Mol. Wt. of the Salt = 490.71

1.	0.0847126	0.2910543	"	0.85563	516.25	578.13
2.	0.0483997	0.2199993	"	0.85446	499.49	547.37
3.	0.0387185	0.1967704	"	0.85399	494.52	537.59
4.	0.0294655	0.1716554	"	0.85349	488.72	538.22
5.	0.0193582	0.139134	"	0.85285	481.77	528.93
6.	0.00967914	0.983826	"	0.85214	473.27	519.03

At 40°C

Salt = Bu₄NBr, Mol. Wt. of the Salt = 322.38

1.	0.0412357	0.2030658	"	0.84953	280.72	305.44
2.	0.0371101	0.1926399	"	0.84923	279.12	302.61

Contd.....(19)

3.	0.0329862	0.1816212	Same as 25°C	0.84893	277.13	299.89
4.	0.0288627	0.1698902	"	0.84861	275.39	296.99
5.	0.0245778	0.1567733	"	0.84828	273.54	294.03
6.	0.0206152	0.14358	"	0.84795	270.96	291.77
7.	0.0164923	0.1284226	"	0.84759	269.25	288.79

Salt = Pent₄NBr, Mol. Wt. of the Salt = 378.49

1.	0.0455172	0.2133476	"	0.84945	358.56	393.01
2.	0.0430117	0.2073928	"	0.84932	357.44	390.96
3.	0.0398276	0.1995687	"	0.84909	356.55	388.06
4.	0.0364136	0.1908236	"	0.84886	355.50	387.02
5.	0.0329997	0.1816582	"	0.84862	354.60	386.46
6.	0.02958851	0.1720032	"	0.84839	353.08	384.86
7.	0.0261719	0.1617773	"	0.84815	351.63	382.99

Salt = Hex₄NBr, Mol. Wt. of the Salt = 434.60

1.	0.1015935	0.3187374	"	0.85072	459.18	518.22
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Contd.....(20)

2.	0.0580237	0.2408811	Same as 25°C	0.84948	443.41	489.17
3.	0.0464158	0.2154433	"	0.84901	437.80	478.99
4.	0.0348094	0.1865728	"	0.84845	431.52	467.41
5.	0.0232053	0.1523331	"	0.84777	425.06	454.53
6.	0.0116024	0.1077146	"	0.84697	417.93	448.88

Salt = Hept₄NBr, Mol. Wt. of the Salt = 490.71

1.	0.0841987	0.2901702	"	0.85044	518.10	580.52
2.	0.0481012	0.2193198	"	0.84919	502.36	550.65
3.	0.0384792	0.1961611	"	0.84871	497.69	541.13
4.	0.0292833	0.1711236	"	0.84821	492.02	530.36
5.	0.0192386	0.1387034	"	0.84758	484.78	512.03
6.	0.0096194	0.0980785	"	0.84688	475.57	495.09

At 45°C

Salt = Bu₄NBr, Mol. Wt. of the Salt = 322.38

1.	0.0409804	0.2024362	"	0.84427	281.56	306.54
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Contd.....(21)

2.	0.0368803	0.1920424	Same as 25°C	0.84397	279.92	303.65
3.	0.0327811	0.1810555	"	0.84365	278.58	300.79
4.	0.0286831	0.1693609	"	0.84333	276.87	297.98
5.	0.0245756	0.1567662	"	0.84298	275.88	295.02
6.	0.0204866	0.1431314	"	0.84266	273.13	292.56
7.	0.0163894	0.1280212	"	0.84230	271.67	289.96

Salt = Pent₄NBr, Mol. Wt. of the Salt = 378.49

1.	0.045230	0.2126734	"	0.84409	362.60	397.29
2.	0.0429667	0.2072842	"	0.84395	361.87	395.72
3.	0.0395767	0.1989389	"	0.84374	360.62	294.05
4.	0.0358276	0.189282	"	0.84352	358.55	292.70
5.	0.0327924	0.1810868	"	0.84329	358.40	290.97
6.	0.0293989	0.171461	"	0.84305	357.53	288.99
7.	0.0260071	0.1612672	"	0.84281	356.42	287.03

Salt = Hex₄NBr, Mol. Wt. of the Salt = 434.60

1.	0.1009773	0.3177693	Same as 25°C	0.84556	460.37	520.04
2.	0.0576651	0.2401356	"	0.84423	445.34	491.58
3.	0.0461266	0.214771	"	0.84372	440.59	482.21
4.	0.034592	0.1859892	"	0.84315	434.74	465.04
5.	0.0230605	0.1518571	"	0.84248	428.20	457.98
6.	0.0115302	0.1073789	"	0.84170	419.95	451.21

Salt = Hept₄NBr, Mol. Wt. of the Salt = 490.71

1.	0.0836849	0.2892834	"	0.84525	519.83	596.52
2.	0.0478015	0.2186357	"	0.84390	505.52	554.30
3.	0.0382398	0.19555	"	0.84343	500.60	544.38
4.	0.0291013	0.1705912	"	0.84294	494.55	525.87
5.	0.0191188	0.1382707	"	0.84230	487.84	513.33
6.	0.0095694	0.097772	"	0.84160	479.13	497.24

TABLE - 2

Limiting Apparent Molal Volumes (ϕ_v°) and Experimental Slopes (S_v^*) for various Tetraalkylammonium Bromides in various Solvents at Different Temperatures.

Electrolyte	ϕ_v° cm ³ , mol ⁻¹	$S_{L\frac{1}{2}}^*$ mol ^{-3/2}	ϕ_v° cm ³ mol ⁻¹	$S_{L\frac{1}{2}}^*$ mol ^{-3/2}
Solvent = Tetrahydrofuran (THF)				
		Temperature = 25°C	Temperature = 30°C	
Bu ₄ NBr	203.50	285.71	209.52	277.07
Pent ₄ NBr	257.05	248.48	264.40	230.76
Hex ₄ NBr	310.50	305.55	322.00	278.00
Hept ₄ NBr	346.70	573.33	360.50	540.90
		Temperature = 35°C	Temperature = 40°C	
Bu ₄ NBr	214.67	272.09	219.00	258.33

Contd.....(2)

Pent ₄ NBr	271.50	225.00	277.00	219.10
Hex ₄ NBr	333.60	261.11	345.22	240.23
Hept ₄ NBr	374.50	507.25	388.80	482.75

Temperature = 45°C

Bu ₄ NBr	222.60	251.79		
Pent ₄ NBr	281.40	215.82		
Hex ₄ NBr	356.80	228.57		
Hept ₄ NBr	402.60	478.57		

Solvent = 1,2-Dimethoxyethane (DME)

Temperature = 25°C

Bu ₄ NBr	233.07	212.76		
Pent ₄ NBr	314.50	160.00		
Hex ₄ NBr	374.92	253.80		
Hept ₄ NBr	436.60	258.24		

Temperature = 30°C

			238.33	189.18
			319.60	142.80
			380.30	237.03
			441.98	247.36

Contd.....(3)

	Temperature = 35°C		Temperature = 40°C	
Bu ₄ NBr	242.70	174.42	246.60	168.75
Pent ₄ NBr	324.22	140.35	328.79	135.73
Hex ₄ NBr	385.70	225.00	391.10	222.20
Hept ₄ NBr	447.10	236.84	452.37	225.80

	Temperature = 45°C	
Bu ₄ NBr	249.90	160.71
Pent ₄ NBr	332.20	135.13
Hex ₄ NBr	396.40	200.00
Hept ₄ NBr	457.34	211.76

TABLE - 3

Ionic limiting partial molal volume ($\bar{V}_{\text{ion}}^{\circ}$) at 25, 30, 35, 40 and 45°C in 1,2-Dimethoxyethane and Tetrahydrofuran

Ions	$\bar{V}_{\text{ion}}^{\circ} / \text{cm}^3 \text{mol}^{-1}$ (1,2 - DME)				
	25	30	35	40	45°C
Bu ₄ N ⁺	283.95	284.30	285.56	287.55	290.62
Pent ₄ N ⁺	365.38	365.57	367.08	369.74	372.92
Hex ₄ N ⁺	425.80	426.27	428.56	432.05	437.12
Hept ₄ N ⁺	487.48	487.95	489.96	493.32	498.06
Br ⁻	-50.88	-45.97	-42.86	-40.95	-40.72
	$\bar{V}_{\text{ion}}^{\circ} / \text{cm}^3 \text{mol}^{-1}$ (THF)				
Bu ₄ N ⁺	205.29	215.98	231.41	247.77	274.00
Pent ₄ N ⁺	258.84	272.86	288.24	305.77	332.80
Hex ₄ N ⁺	312.29	328.46	350.34	373.99	408.20
Hept ₄ N ⁺	348.49	366.96	391.24	417.57	460.00
Br ⁻	-1.79	-6.46	-16.74	-28.77	-51.40

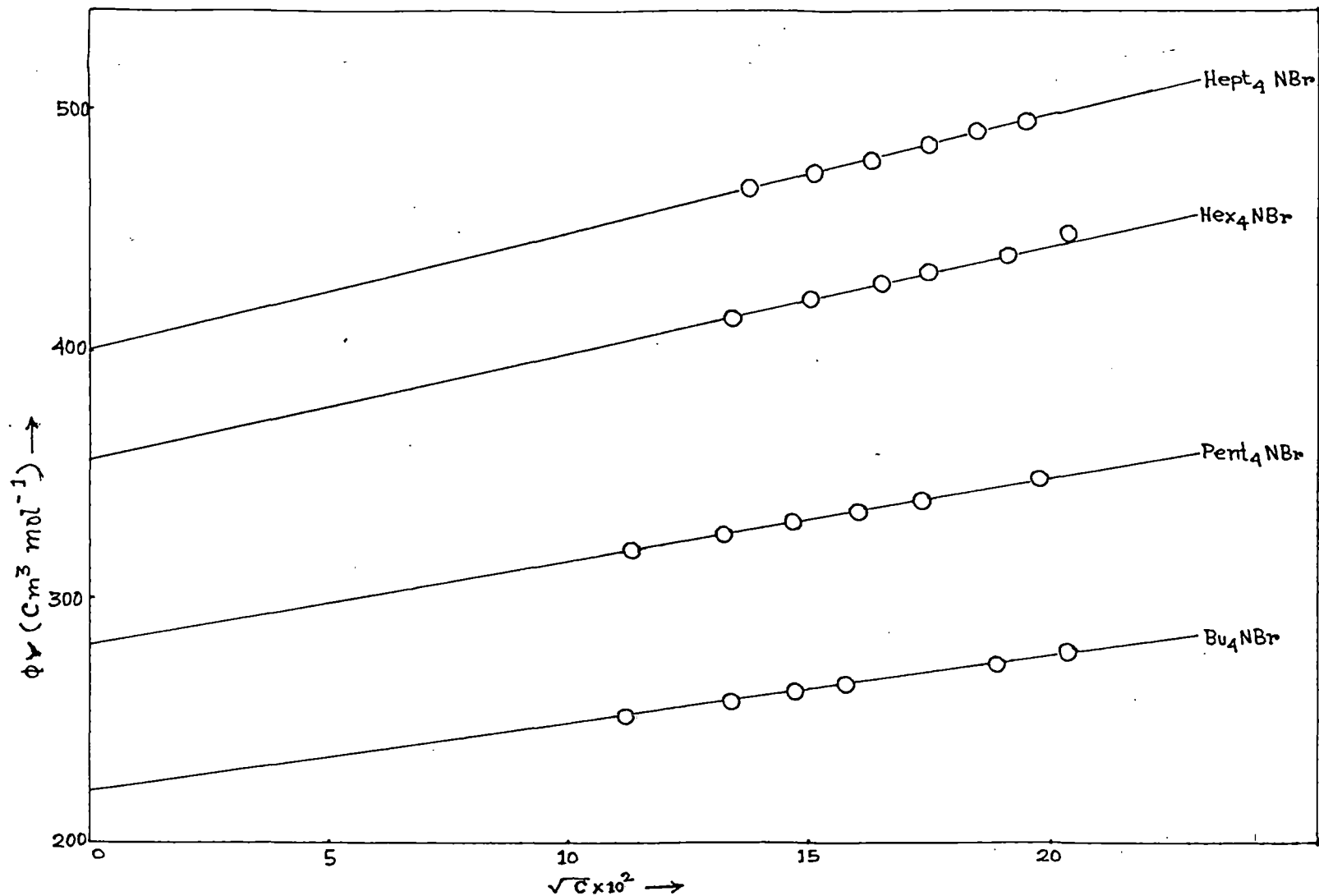


Fig-1. Representative plot of ϕ_v versus \sqrt{C} for some tetraalkylammonium bromides in tetrahydrofuran at 45°C .

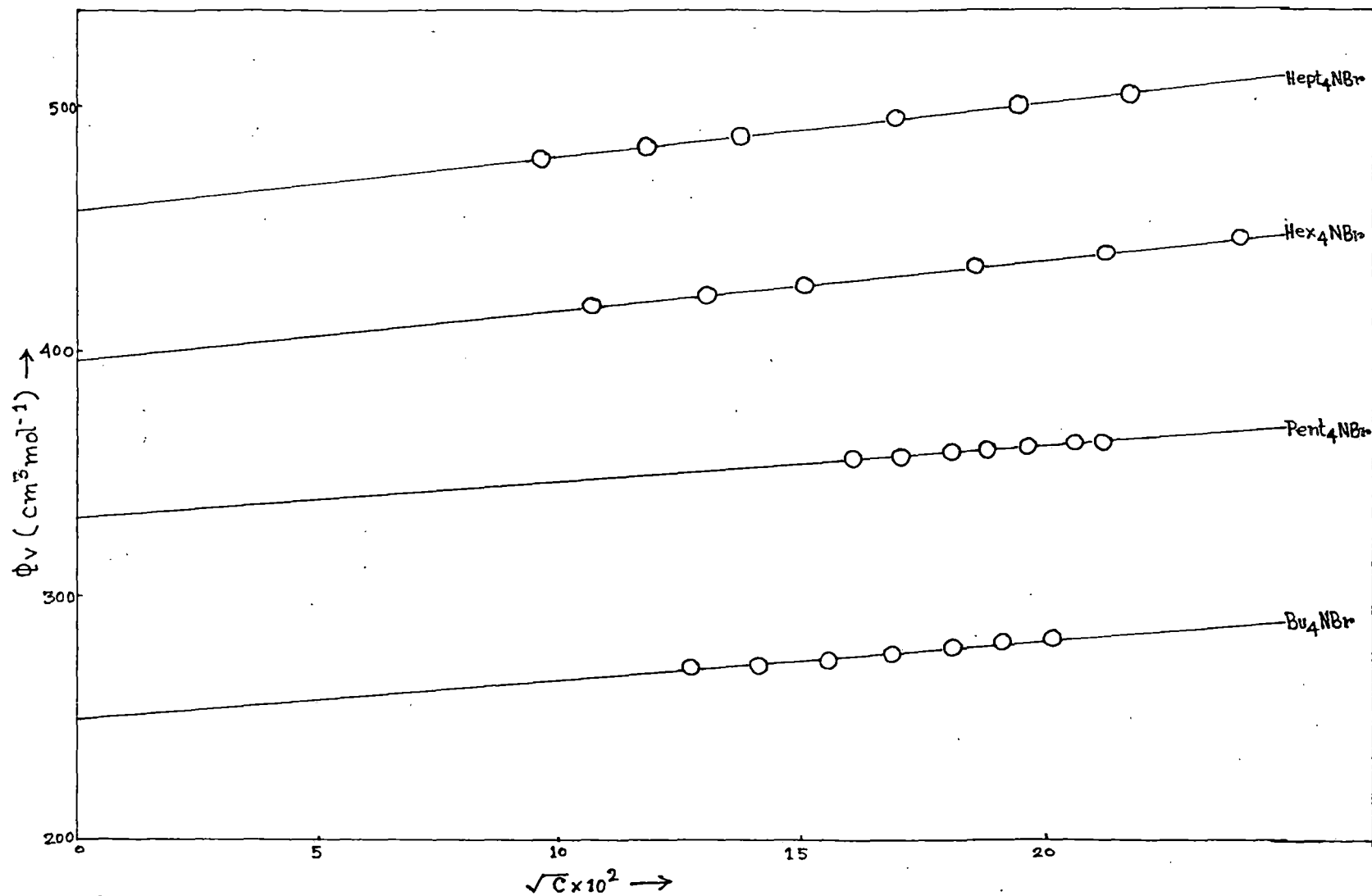


Fig-2. Representative plot of Φ_v versus \sqrt{c} for some tetraalkylammonium bromides in 1,2 dimethoxyethane at 45°C.