CHAPTER VI

Apparent Molar Volumes of Some Symmetrical Tetraalkylammonium Bromides in Methanol + Acetonitrile Mixtures at 298.15, 308.15 and 318.15 K

Introduction

The volumetric behaviour of solutes has been proved to be very useful in elucidating various interactions occurring in solutions[1]. Studies on the apparent molar volumes of electrolytes have been widely used to examine the ion-ion, ion-solvent, and solvent-solvent interactions [2]. The apparent molar volumes of tetraalkylammonium salts have been investigated rather extensively in aqueous, organic, and aquo-organic solvent systems[2-14]. However, such measurements involving mixtures of organic solvents are relatively scarce. The present chapter reports the apparent molar volumes of six symmetrical tetraalkylammonium bromides. R_4NBr (R = ethyl through heptyl) in methanol + acetonitrile mixtures containing 0.00, 0.20, 0.40, 0.60 and 0.80 mole fractions of acetonitrile at 298.15, 308.15 and 318.15 K

Experimental

Methanol (E. Merck, India, uvasol grade, 99.5% pure) was dried over molecular sieves and distilled fractionally. The middle fraction was collected and redistilled. The purified solvent had a density of 0.78654 g.cm^{-3} and a viscosity of 0.545 m Pa.s at 298.15 K. These values agree well with the literature values[15].

Acetonitrile (E. Merck, India, 99% pure) was distilled with P_2O_5 and then redistilled over CaH_2. The purified solvent had a density of 0.77686 g.cm^{-3} and a viscosity of 0.345 mPa.s at 298.15 K; these values are also found to be in good agreement with literature values [16,17].

Tetraalkylammonium bromides were of purum or puriss grade (Fluka) and were purified as described in the literature[18,19]. The salts were purified by recrystallisation and the higher homologues were recrystallised twice to ensure highest purity. The recrystallised salts were dried under vacuum at 373.15 – 383.15 K for 24 h. Owing to the hygroscopic nature of the salts, these were stored in a vacuum desiccator over calcium chloride and were dried for 3-4 h at 373.15 K immediately prior to use.

A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The conversion of molality to molarity was done using the density values.

The densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15, 308.15 and 318.15 K with doubly distilled water, methanol and acetonitrile. Measurements were made in a water-bath maintained which ±0.01 K of the desired temperature by means of a mercury-in-glass thermoregulator and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.

The experimental values densities (ρ_0), viscosities (η_0) and relative permittivities (ε) of methanol + acetonitrile mixtures at 298.15,308.15 and 318.15 K as a function of mole fraction of acetonitrile (x) are given in Table 1. Relative permittivities were taken from the literature[20].

Results

The apparent molar volumes (ϕ_v) were calculated from the densities of solutions using the following equation :

$$\phi_v = M / \rho - 1000 (\rho - \rho_0) / m \rho\rho_0 \qquad (1)$$

where m is the molality of the electrolyte solution, M is the molceular mass of the solute, and ρ and ρ_0 are densities of the solution and solvent, repectively.

The apparent molar volumes of each salt in a given solvent mixture show a linear dependence on the square root of its molal concentration according to the following equation :

$$\phi_v = \phi_v^0 + S_v^* m^{1/2} \qquad (2)$$

where ϕ_v^0 is the apparent molar volume of the salt at infinite dilution, and S_v^* is the experimental slope.

The limiting apparent molar volumes ϕ_v^0 (equal to partial molar volumes at infinite dilution V_2^0), were obtained by the least-squares fitting of ϕ_v values to the above equation, and these values along with the experimental slopes S_v^* are reported in Table 2. The correlation coefficients of regression analyses are always found to be greater than or equal to 0.996. The ϕ_v^0 and S_v^* values for these salts in acetonitrile collected in this Table were taken from our earlier work[9].

Since our experimental results of apparent molar volumes can be well represented by eq. (2), we have not analysed the data on the basis of the Redlich-Mayer equation[21].

$$\phi_v = \phi_v^0 + A_v m^{1/2} + b_v m \qquad (3)$$

where A_v is the theoretial slope of the Debye-Hückel theory and b_v is a fitting constant determined empirically. Moreover, the evaluation of A_v requires the knowledge of the pressure dependence of the relative permittivity of the medium, which is not yet known for the present mixed solvents, rendering analysis of the data in terms of eq. (3) impossible. As pointed out for all salts, the plots of ϕ_v against $m^{1/2}$ give essentially straight lines. This observation suggests that the electrolytes remain nearly fully dissociated in the mixed solvents in the concentration range investigated. When, on the other hand, association occurs, ϕ_v increases sharply with $m^{1/2}$ at low concentration, and then levels off or goes through a maximum at higher concentration[22], which, obviously, is not the case here. This view is also suported by very low association constants of these electrolytes in the prersent solvent mixtures as demonstrated from our earlier conductivity studies[20,23].

In each solvent mixture, the limiting apparent molar volumes (ϕ_v^0) are large and positive (Table 3.) and the values increase regularly as the size of the tetraalkylammonium ion increases. This is found to be in agreement with earlier findings in several nonaqueous solvents as well as in water and heavy water[14].

Discussion

The calculations of ionic limiting partial molar volumes have been performed following the method suggested by Conway *et. al.*[24] Uosaki *et. al*[25] used this method for the separation of some literature values and of their own values on tetraalkylammonium halides into ionic contributions in organic electrolyte solutions. Krumgalz[14] applied the same method to a large number of partial molar volume data for nonaqueous electrolyte solutions in a wide temperature range. Earlier, we have also successfully applied this method in 2-methoxyethanol and 1,2- dimethoxyethane at different temperatures[4,6-8].

The limiting apparent molar volumes for the tetraalkylammonium bromides in methanol + acetonitrile mixtures at 298.15 , 308.15, and 318.15 K were plotted against the formula weight of the corresponding tetraalkylammonium ions. Excellent linear relationships were observed for all the salts examinaed. (Fig. 1).

The V^0_{ion} values of tetraalkylammonium ions in the mixed solvent media are presented in Table 3. Also included in this Table are the ionic limiting partial molal volumes in pure acetonitrile obtained from the division of the literature salt values in this solvent[9]. The V^0_{ion} values for tetraalkylammonium ions are positive and have been found to increase continuously from Et_4N^+ through Hep_4N^+. The positive V^0_{ion} values indicate that the solvent molecules from a less compact structure around the incorporated tetraalkylammonium ions, thus giving rise to a positive change in volume. The variation in the V^0_{ion} values of each tetraalkylammonium ion with acetonitrile content in methanol + acetonitrile mixtures, however, is small. Similar behaviour has also been exhibited by tetraalkylammonium ions in water + acetonitrile mixtures[26]. The V^0_{ion} values of tetraalkylammonium ions in methanol + acetonitrile mixtures at 298.15 K are found to be almost similar to those found in other organic solvents,[4,7,8,14]. This observation infers that the large tetraalkylammonium cations are scarcely solvated in the present solvent mixtures. The negative V^0_{ion} values for bromide ion in these mixed solvents may be ascribed to the same conclusion have also been drawn from our conductivity study on this system[20,23].

Thus, it appears that the large sizes of the tetraalkylammonium ions, their low surface charge densities and the medium relative permittivities of the mixed solvent media render these ions to be free almost unassociated and unsolvated in these solvents. Bromide ion, on the other hand, exhibits significant electrostriction around it in methanol + acetonitrile mixtures.

References

1. F. J. Millero. *Chem. Rev.*, **71**, 147, 1971.
2. F. J. Millero, "*Structure and Transport Process in Water and Aqueous Solutions*", Ed . R. A. Horne, Wiley, New York, 1972
3. O. Popovych and R. P. T. Tomkins, *Nonaqueous Solution Chemistry*", John Wiley and Sons, New York, 1981.
4. B. Das and D. K. Hazra, *J. Chem. Eng. Data*, **36**, 403 1991.
5. Y. Marcus, G. Hefter and T-S. Pang, *J. Chem. Soc., Faraday Trans*, **90**, 1899, 1994 .
6. B. Das, *Ind. J. Chem, Technol.*, **2**, 40, 1995.
7. B. Das and D. K. Hazra, *Bull. Chem. Soc. Jpn.*, **68**, 734, 1995.
8. P. K. Muhuri, B. Das and D. K. Hazra, *Ind. J. Chem.*, **35A**, 288, 1996 .
9. N. Saha and B. Das, *J. Chem. Eng. Data*, **42**, 117, 1997.
10. P. Singh, I. D. Macleod and A. J. Parker, *Aust. J. Chem.*, **36**, 1675, 1983 .
11. M. Takenaka. T. Takemura and M. Sakurai, *J. Chem. Eng. Data*, **39**, 802, 1994
12. M. M. Sanchez, B. Dominguez and R. R. Rapaso and A. Vivo, *J. Chem. Eng. Data*, **39**, 453 , 1994 .
13. B. Das and D. K. Hazra, *J. Ind. Chem. Soc.*, **74**. 108 , 1997 .
14. B. S. Krumgalz, *J. Chem. Soc., Faraday Trans. 1.*, **76**, 1887, 1980 .
15. H. Doe, T. Kitagawa and K. Sasabe, *J. Phys. Chem.*, **88**, 3341, 1984
16. G. Moumouzias. D. K. Panopoulos and G. Ritzoulis, *J. Chem. Eng. Data*, **36**, 20, 1991 .
17. J. Singh. T. Kaur. V. Ali and D. S. Gill, *J. Chem. Eng. Data*, **42**, 117 , 1997.
18. D. F. Evans. C. Zawoyski and R. L. Kay, *J. Phys. Chem.*, **69**, 387, 1965 .
19. S. Das. D. K. Hazra and S. C. Lahiri, *Z. Phys. Chem.*, **138**,185, 1986
20. B. Das and N. Saha., *J. Chem., Eng. Data*, **45**, 2, 2000 .
21. O. Redlich and D. M. Meyer. *Chem. Rev.*, **64**, 221, 1964.
22. R. Zana, G. Perron and J. E. Desnoyers, *J. Solution Chem.*, **8**, 729, 1979.
23. B. Das, N. Saha and D. K. Hazra, *J. Chem. Eng. Data*, **43**, 353, 2000.
24. B. E. Conway, R. E. Verrall and J. E. Desnoyers, *Trans. Faraday Soc.* **62**, 2738, 1966.
25. K. Uosaka., Y. Kondo and N. Tokura, *Bull. Chem. Soc. Jpn.*, **45**, 871, 1972.
26. G. Kumar. N. C. Dey, B. K. Saikia and I. Haque, *Bull. Chem. Soc. Jpn.*, **59**, 1555, 1986.

Table 1. Solvent Properties of Methanol + Acetonitrile Mixtures at 298.15, 308.15 and 318.15 K

Property	x = 0.00	x = 0.20	x = 0.40	x = 0.60	x = 0.80
			T = 298.15 K		
ρ_0 / g.cm^{-3}	0.78654	0.78680	0.78465	0.78212	0.77952
η_0 / mPa.s	0.545	0.435	0.373	0.343	0.334
			T = 308.15 K		
ρ_0 / g.cm^{-3}	0.77718	0.77750	0.77517	0.77211	0.76899
η_0 / mPa.s	0.474	0.395	0.341	0.314	0.305
			T = 318.15 K		
ρ_0 / g.cm^{-3}	0.76774	0.76811	0.76561	0.76216	0.75865
η_0 / mPa.s	0.419	0.361	0.313	0.289	0.280

Table 2. Densities of Solutions ρ and Apparent Molar Volumes ϕ_v for Tetraalkylammonium Bromides in Methanol + Acetonitrile Mixtures at 298.15, 308.15 and 318.15 K.

m/(mol.kg^{-1})	ρ /(g.cm^{-3})	ϕ_v/(cm^3.mol^{-1})	m/(mol.kg^{-1})	ρ /(g.cm^{-3})	ϕ_v/(cm^3.mol^{-1})
		T = 298.15 K			
		x = 0.00			
	Et_4NBr			Pr_4NBr	
0.00993	0.78726	149.90	0.01002	0.78727	220.70
0.02004	0.78798	150.74	0.01994	0.78798	221.48
0.02499	0.78833	151.07	0.02501	0.78834	221.81
0.02997	0.78868	151.37	0.02997	0.78869	222.09
0.03498	0.78903	151.65	0.03496	0.78904	222.35
0.04001	0.78938	151.91	0.03998	0.78939	222.60
0.04507	0.78973	152.16	0.04502	0.78974	222.83
0.05000	0.79007	152.38	0.04993	0.79008	223.05
0.06007	0.79076	152.81	0.05998	0.79077	223.45
0.06506	0.79110	153.01	0.06497	0.79111	223.36
	Bu_4NBr			Pen_4NBr	
0.01004	0.78730	287.29	0.00998	0.78728	361.11
0.01998	0.78804	287.99	0.01999	0.78801	361.78
0.02499	0.78841	288.27	0.02498	0.78837	362.04
0.03004	0.78878	288.53	0.03000	0.78873	362.29
0.03497	0.78914	288.76	0.03504	0.78909	362.51
0.03993	0.78950	288.98	0.0398	0.78944	362.72
0.04505	0.78987	289.19	0.04494	0.78979	362.91
0.05006	0.79023	289.38	0.04994	0.79014	363.10
0.06000	0.79094	289.74	0.05998	0.79.84	363.44
0.06494	0.79129	289.91	0.06505	0.79119	363.61

Hex$_4$NBr

0.01004	0.78730	429.77
0.01998	0.78804	430.37
0.02501	0.78841	430.62
0.03006	0.78878	430.84
0.03501	0.78914	431.04
0.03998	0.78950	431.23
0.04499	0.78986	431.41
0.05002	0.79022	431.58
0.06003	0.79093	431.89
0.06500	0.79128	432.04

Hep$_4$NBr

0.00994	0.78730	499.83
0.02004	0.78806	500.39
0.02502	0.78843	500.61
0.03002	0.78880	500.81
0.03506	0.78917	501.00
0.03999	0.78953	501.17
0.04495	0.78989	501.33
0.04994	0.79025	501.48
0.06000	0.79097	501.77
0.06494	0.79132	501.90

x = 0.20

Et$_4$NBr

0.00562	0.78721	149.19
0.01075	0.78758	149.75
0.02084	0.78830	150.55
0.02551	0.78863	150.88
0.03105	0.78902	151.19
0.03505	0.78930	151.41
0.03992	0.78964	151.64
0.04539	0.79002	151.89
0.05060	0.79038	152.13
0.05626	0.79077	152.35
0.06049	0.79106	152.52
0.06561	0.79141	152.71

Pr$_4$NBr

0.00463	0.78714	219.71
0.01041	0.78756	220.28
0.01472	0.78787	220.70
0.02045	0.78828	221.10
0.02508	0.78861	221.34
0.03202	0.78910	221.74
0.03472	0.78929	221.87
0.04000	0.78966	222.12
0.04501	0.79001	222.31
0.04904	0.79029	222.48
0.05410	0.79061	222.68
0.05991	0.79104	222.90

Bu_4NBr

0.00538	0.78721	286.49
0.01069	0.78761	287.05
0.01657	0.78805	287.42
0.02196	0.78845	287.76
0.02602	0.78875	287.96
0.03064	0.78909	288.17
0.03775	0.78961	288.46
0.03995	0.78977	288.56
0.04533	0.79016	288.77
0.05073	0.79055	288.95
0.05518	0.79087	289.09
0.06106	0.79129	289.30

Pen_4NBr

0.00509	0.78718	360.29
0.00915	0.78748	360.69
0.01638	0.78801	361.17
0.02161	0.78839	361.47
0.02479	0.78862	361.62
0.02966	0.78897	361.87
0.03455	0.78932	362.07
0.04116	0.78979	362.33
0.04526	0.79008	362.47
0.05010	0.79042	362.66
0.05452	0.79073	362.80
0.06055	0.79115	362.99
0.06690	0.79159	363.18

Hex_4NBr

0.00525	0.78720	429.09
0.00988	0.78755	429.34
0.01496	0.78793	429.73
0.01966	0.78828	429.95
0.02780	0.78888	430.37
0.02985	0.78903	430.47
0.03410	0.78934	430.65
0.03892	0.78969	430.83
0.04515	0.79014	431.04
0.04961	0.79046	431.19
0.05311	0.79071	431.30
0.06199	0.79134	431.57

Hep_4NBr

0.00718	0.78735	499.60
0.00981	0.78755	499.72
0.01578	0.78800	500.08
0.01979	0.78830	500.29
0.02557	0.78873	500.52
0.03004	0.78906	500.71
0.03522	0.78944	500.92
0.03988	0.78978	501.07
0.04983	0.79050	501.38
0.05457	0.79084	501.51
0.06046	0.79126	501.67
0.06568	0.79163	501.81

$x_1 = 0.40$

Et$_4$NBr

0.00588	0.78508	148.98
0.01058	0.78542	149.49
0.01545	0.78577	149.88
0.01979	0.78608	150.20
0.02966	0.78678	150.79
0.03449	0.78712	151.05
0.04020	0.78752	151.33
0.04550	0.78789	151.55
0.05141	0.78830	151.82
0.05430	0.78850	151.93
0.06068	0.78894	152.18
0.06578	0.78929	152.37

Pr$_4$NBr

0.00543	0.78505	219.60
0.01024	0.78540	220.18
0.01522	0.78576	220.59
0.01883	0.78602	220.79
0.02499	0.78646	221.20
0.03203	0.78696	221.56
0.04239	0.78769	222.01
0.04582	0.78793	222.15
0.05027	0.78824	222.34
0.05502	0.78857	222.52
0.06008	0.78892	222.70
0.06515	0.78927	222.86

Bu$_4$NBr

0.00509	0.78504	286.27
0.00984	0.78540	286.79
0.01608	0.78587	287.18
0.01942	0.78612	287.38
0.02654	0.78665	287.73
0.03114	0.78699	287.95
0.03548	0.78731	288.11
0.04149	0.78775	288.36
0.04450	0.78797	288.46
0.05056	0.78841	288.69

Pen$_4$NBr

0.00505	0.78503	359.98
0.01097	0.78547	360.58
0.01680	0.78590	360.95
0.01980	0.78612	361.11
0.02446	0.78646	361.35
0.03344	0.78711	361.75
0.03526	0.78724	361.80
0.03901	0.78751	361.97
0.04419	0.78788	362.16
0.04996	0.78829	362.35
0.05576	0.78870	362.53
0.06089	0.78906	362.69
0.06575	0.78940	362.83

Hex$_4$NBr

0.00482	0.78502	429.00
0.01073	0.78547	429.31
0.01657	0.78591	429.68
0.01964	0.78614	429.84
0.02461	0.78651	430.10
0.03055	0.78695	430.34
0.03491	0.78727	430.54
0.03969	0.78762	430.71
0.04312	0.78787	430.82
0.05003	0.78837	431.06
0.05503	0.78873	431.21
0.06090	0.78915	431.39
0.06413	0.78938	431.48

Hep$_4$NBr

0.00477	0.78502	499.17
0.01262	0.78562	499.93
0.01551	0.78584	500.02
0.02028	0.78620	500.26
0.02508	078656	500.58
0.02991	0.78692	500.67
0.03491	0.78729	500.87
0.04034	0.78769	501.05
0.04513	0.78804	501.22
0.05007	0.78840	501.35
0.05449	0.78872	501.47
0.06102	0.78919	501.64
0.06480	0.78946	501.75

x = 0.60

Et$_4$NBr

0.00584	0.78255	148.26
0.00818	0.78272	148.67
0.01605	0.78329	149.31
0.02134	0.78367	149.67
0.02596	0.78400	149.96
0.03144	0.78439	150.24
0.03469	0.78462	150.41
0.04448	0.78531	150.86
0.05048	0.78573	151.10
0.05435	0.78600	151.25
0.05982	0.78638	151.46
0.06531	0.78676	151.66

Pr$_4$NBr

0.00540	0.78252	219.24
0.01031	0.78288	219.72
0.01622	0.78331	220.17
0.01940	0.78354	220.39
0.02175	0.78371	220.49
0.02495	0.78394	220.68
0.03026	0.78432	220.97
0.03601	0.78473	221.22
0.04095	0.78508	221.44
0.04605	0.78544	221.65
0.05089	0.78578	221.84
0.05517	0.78608	221.98

Bu_4NBr

0.00545	0.78254	286.04
0.00978	0.78287	286.55
0.01439	0.78322	286.82
0.02063	0.78369	287.20
0.02503	0.78402	287.40
0.02986	0.78438	287.63
0.03539	0.78479	287.87
0.04027	0.78515	288.07
0.04651	0.78558	288.29
0.05050	0.78590	288.43
0.05585	0.78629	288.59
0.06206	0.78674	288.78

Pen_4NBr

0.00607	0.78258	359.82
0.01034	0.78290	360.26
0.01516	0.78326	360.47
0.01935	0.78357	360.76
0.02491	0.78398	361.00
0.02997	0.78435	361.26
0.03574	0.78477	361.49
0.03960	0.78505	361.62
0.04543	0.78547	362.83
0.05017	0.78581	361.98
0.05522	0.78617	362.15
0.06325	0.78674	362.38

Hex_4NBr

0.00451	0.78247	428.61
0.01050	0.78293	429.11
0.01430	0.78322	429.31
0.02064	0.78370	429.66
0.02503	0.78403	429.87
0.03051	0.78444	430.09
0.03549	0.78481	430.28
0.04063	0.78519	430.46
0.04499	0.78551	430.62
0.05032	0.78590	430.79
0.05610	0.78630	430.97
0.06024	0.78662	431.07
0.06524	0.78698	431.21

Hep_4NBr

0.00524	0.78253	499.23
0.01131	0.78300	499.65
0.01483	0.78327	499.91
0.01980	0.78365	500.11
0.02086	0.78373	500.21
0.02468	0.78402	500.34
0.02906	0.78435	500.54
0.03426	0.78474	500.72
0.03963	0.78514	500.90
0.04516	0.78555	501.05
0.04856	0.78580	501.17
0.05183	0.78604	501.26
0.05498	0.78627	501.35
0.06047	0.78667	501.49
0.06475	0.78698	501.59

x = 0.80

Et_4NBr

0.00963	0.78025	144.71
0.01564	0.78070	145.21
0.02007	0.78103	145.50
0.02587	0.78146	145.83
0.03225	0.78193	146.17
0.03552	0.78217	146.33
0.04086	0.78256	146.59
0.04456	0.78283	146.73
0.05186	0.78336	147.02
0.05421	0.78358	147.11
0.05962	0.78392	147.32

Pr_4NBr

0.00487	0.77989	216.44
0.01018	0.78029	216.89
0.01512	0.78066	217.19
0.02145	0.78113	217.61
0.02524	0.78141	217.82
0.03258	0.78195	218.16
0.03669	0.78225	218.37
0.04039	0.78252	218.51
0.04493	0.78285	218.68
0.04977	0.78320	218.87
0.05532	0.78360	219.06
0.05812	0.78380	219.19

Bu_4NBr

0.01308	0.78054	284.85
0.01594	0.78076	285.09
0.01971	0.78105	285.25
0.02508	0.78146	285.55
0.03034	0.78186	285.78
0.03549	0.78225	285.97
0.04067	0.78264	286.17
0.04534	0.78299	286.34
0.05083	0.78340	286.52
0.05473	0.78369	286.64
0.06000	0.78408	286.81
0.06542	0.78448	286.96

Pen_4NBr

0.01092	0.78038	355.54
0.01581	0.78076	355.90
0.02723	0.78164	356.45
0.03064	0.78190	356.62
0.03524	0.78225	356.80
0.04158	0.78273	357.02
0.04423	0.78293	357.10
0.04983	0.78335	357.30
0.05384	0.78365	357.41
0.05908	0.78404	357.56
0.06151	0.78422	357.64

Hex$_4$NBr

0.00513	0.77993	425.77
0.01069	0.78037	426.20
0.01450	0.78067	426.37
0.02013	0.78111	426.66
0.02490	0.78148	426.91
0.02969	0.78185	427.10
0.03660	0.78238	427.36
0.04041	0.78267	427.51
0.05284	0.78361	427.90
0.05778	0.78398	428.04
0.06355	0.78441	428.21

Hep$_4$NBr

0.01092	0.78040	496.32
0.01507	0.78073	496.59
0.02013	0.78113	496.85
0.02471	0.78149	497.04
0.03035	0.78193	497.28
0.03666	0.78242	497.47
0.04017	0.78269	497.61
0.04473	0.78304	497.75
0.04983	0.78343	497.87
0.05458	0.78379	498.03
0.05987	0.78417	498.15
0.06613	0.78466	498.31

308.15 K

$x = 0.00$

Et$_4$NBr

0.01002	0.77790	151.31
0.01998	0.77860	152.47
0.02499	0.77895	152.80
0.03003	0.77930	153.12
0.03495	0.77964	153.40
0.04004	0.77999	153.67
0.04501	0.78033	153.92
0.05000	0.78067	154.16
0.06004	0.78135	154.60
0.06494	0.78168	154.79

Pr$_4$NBr

0.01004	0.77791	222.14
0.01998	0.77862	222.99
0.02506	0.77898	223.29
0.03003	0.77933	223.57
0.03503	0.77968	223.85
0.04005	0.78003	224.09
0.04495	0.78037	224.31
0.05003	0.78072	224.56
0.05995	0.78140	224.96
0.06494	0.78174	225.15

Bu$_4$NBr			Pen$_4$NBr		
0.00996	0.77791	293.21	0.01001	0.77793	362.71
0.01994	0.77863	293.89	0.02006	0.77867	363.44
0.02498	0.77899	294.19	0.02499	0.77903	363.68
0.03004	0.77935	294.41	0.02996	0.77939	363.95
0.03500	0.77970	294.67	0.03495	0.77975	364.16
0.03998	0.78005	294.89	0.03997	0.78011	364.37
0.04498	0.78040	295.09	0.04502	0.78047	364.57
0.05002	0.78075	295.31	0.04995	0.78082	364.75
0.06000	0.78144	295.66	0.06004	0.78153	365.11
0.06496	0.78178	295.84	0.06505	0.78188	365.28

Hex$_4$NBr			Hep$_4$NBr		
0.00994	0.77793	433.84	0.00994	0.77794	504.37
0.02005	0.77868	434.48	0.02006	0.77870	505.01
0.02495	0.77904	434.71	0.02504	0.77907	505.26
0.03002	0.77941	434.94	0.03006	0.77944	505.51
0.03499	0.77977	435.17	0.03497	0.77980	505.70
0.03998	0.78013	435.36	0.04005	0.78017	505.90
0.04501	0.78049	435.57	0.04503	0.78053	506.10
0.04992	0.78084	435.74	0.05003	0.78089	506.26
0.05997	0.78155	436.08	0.06000	0.78160	506.60
0.06496	0.78190	436.23	0.06494	0.78195	506.73

$x = 0.20$

Et$_4$NBr			Pr$_4$NBr		
0.01004	0.77819	151.53	0.01002	0.77820	221.86
0.01995	0.77889	152.28	0.02006	0.77892	222.60
0.02495	0.77924	152.06	0.02498	0.77927	222.87
0.02998	0.77959	152.91	0.02993	0.77962	223.14
0.03503	0.77994	153.17	0.03505	0.77998	223.40
0.03996	0.78028	153.42	0.04006	0.78033	223.66
0.04492	0.78062	153.68	0.04494	0.78067	223.87
0.05004	0.78099	153.91	0.04999	0.78102	224.09
0.06005	0.78165	154.32	0.06001	0.78171	224.48
0.06494	0.78198	154.52	0.06498	0.78205	224.67

Bu$_4$NBr			Pen$_4$NBr		
0.00999	0.77821	291.85	0.00994	0.77821	363.42
0.02000	0.77894	292.53	0.02004	0.77895	364.05
0.2498	0.77930	292.79	0.02500	0.77931	364.30
0.02999	0.77966	293.04	0.02999	0.77967	364.53
0.03502	0.78002	293.25	0.03501	0.78003	364.75
0.03994	0.78037	293.46	0.04006	0.78039	364.97
0.04503	0.78073	293.68	0.04499	0.78074	365.14
0.05000	0.78108	293.87	0.04995	0.78109	365.33
0.06001	0.78178	294.23	0.05994	0.78179	365.66
0.06505	0.78213	294.40	0.06498	0.78214	365.83

Hex$_4$NBr			Hep$_4$NBr		
0.01006	0.77823	433.56	0.00995	0.77823	504.36
0.02002	0.77897	434.17	0.01994	0.77898	504.95
0.02505	0.77934	434.42	0.02505	0.77936	505.16
0.02998	0.77970	434.62	0.02993	0.77972	505.38
0.03507	0.78007	434.86	0.03498	0.78009	505.60
0.04006	0.78043	435.07	0.04006	0.78046	505.79
0.04507	0.78079	435.24	0.04504	0.78082	505.98
0.04998	0.78114	435.43	0.05004	0.78118	506.14
0.06001	0.78185	435.76	0.06000	0.78189	506.46
0.06499	0.78220	435.91	0.06495	0.78224	506.61

x = 0.40

Et$_4$NBr			Pr$_4$NBr		
0.01000	0.77587	151.15	0.00996	0.77588	221.43
0.02002	0.77658	151.96	0.01994	0.77660	222.18
0.02500	0.77693	152.27	0.02497	0.77696	222.46
0.03001	0.77728	152.58	0.03003	0.77732	222.73
0.03504	0.77763	152.84	0.03498	0.77767	223.00
0.03995	0.77797	153.09	0.03995	0.77802	223.23
0.04502	0.77832	153.31	0.04493	0.77837	223.42
0.04997	0.77866	153.52	0.04995	0.77872	223.64
0.05994	0.77934	153.95	0.06003	0.77942	224.00
0.06495	0.77968	154.14	0.06496	0.77976	224.18

Bu_4NBr

0.01007	0.77590	291.68
0.02002	0.77663	292.33
0.02497	0.77699	292.59
0.02994	0.77735	292.80
0.03494	0.77771	293.01
0.03997	0.77807	293.23
0.04502	0.77843	293.43
0.04996	0.77878	293.62
0.06003	0.77949	293.95
0.06503	0.77984	294.30

Pen_4NBr

0.01000	0.77590	363.21
0.02003	0.77664	363.88
0.02496	0.77700	364.16
0.03005	0.77737	364.39
0.03503	0.77773	364.59
0.04003	0.77809	364.76
0.04507	0.77845	364.97
0.04999	0.77880	365.15
0.06004	0.77951	365.40
0.06503	0.77986	365.62

Hex_4NBr

0.00998	0.77591	433.34
0.01999	0.77666	434.08
0.02498	0.77703	434.33
0.03000	0.77740	434.57
0.03505	0.777777	434.81
0.03999	0.77813	434.95
0.04496	0.77849	435.13
0.04996	0.77883	435.98
0.06003	0.77957	435.61
0.06500	0.77994	435.30

Hep_4NBr

0.00998	0.77592	504.19
0.02000	0.77668	504.48
0.02506	0.77706	505.01
0.03003	0.77743	505.26
0.03502	0.77780	505.44
0.04005	0.77817	505.64
0.04497	0.77853	505.81
0.05006	0.77890	505.98
0.06005	0.77962	506.30
0.06495	0.77997	506.44

x = 0.60

Et_4NBr			Pr_4NBr		
0.00996	0.77283	150.79	0.00992	0.77284	221.33
0.01994	0.77354	151.61	0.01999	0.77357	222.04
0.02504	0.77390	151.93	0.02500	0.77393	222.34
0.03002	0.77425	152.19	0.03004	0.77429	222.62
0.03500	0.77460	152.36	0.03496	0.77464	222.85
0.04006	0.77495	152.71	0.04004	0.77500	223.07
0.04497	0.77529	152.94	0.04500	0.77535	223.26
0.05004	0.77564	153.16	0.04998	0.77570	223.45
0.05995	0.77632	153.55	0.06000	0.77640	223.80
0.06493	0.77666	153.74	0.06506	0.77675	224.00

Bu_4NBr			Pen_4NBr		
0.00997	0.77286	291.09	0.00996	0.77287	361.95
0.01995	0.77360	291.71	0.01994	0.77362	362.57
0.02498	0.77397	291.95	0.02505	0.77400	362.86
0.03004	0.77434	292.19	0.03005	0.77437	363.09
0.03499	0.77470	292.41	0.03494	0.77473	363.29
0.03996	0.77506	292.60	0.03999	0.77510	363.48
0.04496	0.77542	292.81	0.04506	0.77547	363.64
0.04998	0.77578	292.99	0.05003	0.77583	363.83
0.05994	0.77649	293.32	0.06002	0.77655	364.12
0.06502	0.77685	293.47	0.06706	0.77691	307.95

	Hex$_4$NBr			Hep$_4$NBr	
0.01001	0.77288	433.38	0.00998	0.77289	503.98
0.02004	0.77364	433.92	0.02000	0.77366	504.63
0.02497	0.77401	434.14	0.024999	0.77404	504.78
0.02993	0.77438	434.34	0.03002	0.77442	505.01
0.03506	0.77476	434.57	0.03495	0.77479	505.22
0.03994	0.77512	434.73	0.04004	0.77517	505.40
0.04498	0.77549	434.89	0.04503	0.77554	505.58
0.05005	0.77586	435.05	0.05005	0.77591	505.75
0.06000	0.77658	435.36	0.06003	0.77664	506.04
0.06501	0.77694	435.50	0.06500	0.77700	506.20

$x = 0.80$

	Et$_4$NBr			Pr$_4$NBr	
0.00996	0.76969	149.21	0.01001	0.76971	219.46
0.01993	0.77041	149.98	0.02002	0.77045	220.09
0.02496	0.77077	150.31	0.02493	0.77081	220.36
0.03001	0.77113	150.59	0.03001	0.77118	220.65
0.03494	0.77148	150.84	0.03497	0.77154	220.88
0.04004	0.77184	151.09	0.03995	0.77190	221.09
0.04502	0.77219	151.33	0.04495	0.77226	221.28
0.05001	0.77254	151.53	0.04997	0.77262	221.47
0.06006	0.77324	151.94	0.05994	0.77333	221.83
0.06497	0.77358	152.13	0.06503	0.77369	222.01

	Bu$_4$NBr			Pen$_4$NBr	
0.00997	0.76972	290.00	0.00994	0.76973	360.94
0.01994	0.77047	290.63	0.02003	0.77050	361.56
0.02504	0.77085	290.90	0.02505	0.77088	301.79
0.03003	0.77122	291.14	0.02996	0.77125	361.97
0.03504	0.77159	219.33	0.03504	0.77163	362.19
0.03994	0.77195	219.53	0.04001	0.77200	362.38
0.04500	0.77232	291.72	0.04500	0.77237	362.55
0.04995	0.77268	291.90	0.05002	0.77274	362.73
0.06004	0.77341	292.23	0.05998	0.77347	363.02
0.00505	0.77377	292.39	0.06507	0.77384	363.18

	Hex$_4$NBr			Hep$_4$NBr	
0.01003	0.76975	431.50	0.01003	0.76976	502.79
0.01996	0.77052	432.10	0.01996	0.77054	503.29
0.02503	0.77091	432.30	0.02498	0.77093	503.54
0.03001	0.77129	432.54	0.03004	0.77132	503.79
0.03501	0.77167	432.72	0.03499	0.77170	503.97
0.04005	0.77205	432.93	0.03997	0.77208	504.14
0.04497	0.77242	433.08	0.04498	0.77246	504.31
0.05006	0.77280	433.26	0.05002	0.77284	504.47
0.06004	0.77354	433.50	0.06006	0.77359	504.79
0.06507	0.77391	433.71	0.06505	0.77396	504.92

318.15 K

$x = 0.00$

Et_4NBr			Pr_4NBr		
0.01004	0.76845	153.62	0.01000	0.76846	224.58
0.01996	0.76914	154.46	0.02003	0.76917	225.40
0.02503	0.76949	154.77	0.02503	0.76952	225.76
0.03000	0.76983	155.12	0.03005	0.76987	226.06
0.03498	0.77017	155.39	0.03496	0.77021	226.31
0.03999	0.77051	155.66	0.04002	0.77056	226.56
0.04503	0.77085	155.93	0.04497	0.77090	226.79
0.04994	0.77118	156.17	0.04995	0.77124	227.03
0.05997	0.77185	156.63	0.05997	0.77192	227.45
0.06494	0.77218	156.83	0.06501	077226	227.64

Bu_4NBr			Pen_4NBr		
0.01006	0.76848	294.84	0.01005	0.76849	366.13
0.02000	0.76920	295.52	0.02000	0.76922	366.84
0.02502	01.76956	295.82	0.02496	0.77958	367.15
0.03007	0.76992	296.10	0.02994	0.76994	367.38
0.03500	0.77027	296.32	0.03496	0.77030	367.64
0.03996	0.77062	296.55	0.04000	0.77066	367.85
0.04495	0.77097	296.77	0.04493	0.77101	368.05
0.04995	0.77132	296.95	0.05003	0.77137	368.26
0.06004	0.77202	297.33	0.06002	0.77207	368.62
0.06498	0.77236	297.52	0.06505	0.77242	368.79

Hex$_4$NBr			Hep$_4$NBr		
0.01001	0.76850	436.81	0.01001	0.76851	508.20
0.02006	0.76925	437.48	0.02007	0.76927	508.86
0.02494	0.76961	437.78	0.02502	0.76964	509.12
0.02998	0.76998	438.01	0.03000	0.77001	509.33
0.03506	0.77035	438.26	0.03502	0.77038	509.56
0.04003	0.77071	438.48	0.03994	0.77076	509.79
0.04503	0.77107	438.68	0.04502	0.77111	509.98
0.05005	0.77143	438.86	0.05000	0.77147	510.17
0.06005	0.77217	439.22	0.06002	0.77219	510.47
0.06502	0.77249	439.39	0.06496	0.77254	510.66

$x = 0.20$

Et$_4$NBr			Pr$_4$NBr		
0.00997	0.76879	152.79	0.00996	0.76880	224.04
0.01997	0.76949	153.65	0.01994	075951	224.81
0.02502	0.76984	154.02	0.02505	0.76987	225.14
0.02994	0.77018	154.30	0.03005	0.77022	2225.44
0.03504	0.77053	154.60	0.03507	0.77057	225.70
0.04002	0.77089	154.88	0.03998	0.77091	225.97
0.04502	0.77121	155.14	0.04505	0.77126	226.20
0.05004	0.77155	155.37	0.05001	0.77160	226.44
0.06000	0.77222	155.82	0.05998	0.77228	226.85
0.06494	0.77255	156.03	0.06500	0.77262	227.05

Bu_4NBr

0.01003	0.76882	294.40
0.01996	0.76954	295.20
0.02496	0.76990	295.45
0.03000	0.77026	295.73
0.03506	0.77062	295.97
0.04001	0.77097	296.19
0.04498	0.77132	296.40
0.04997	0.77167	296.58
0.06003	0.77237	296.95
0.06495	0.77271	297.12

Pen_4NBr

0.01000	0.76883	365.39
0.02003	0.76957	366.07
0.02496	0.76993	366.36
0.03005	0.77030	366.59
0.03504	0.77066	366.84
0.04006	0.77102	367.07
0.04496	0.77137	367.27
0.05002	0.77173	367.44
0.05995	0.77243	367.80
0.06495	0.77278	367.96

Hex_4NBr

0.00998	0.76884	436.28
0.02001	0.76959	437.03
0.02501	0.76996	437.31
0.03003	0.77033	437.51
0.03496	0.77069	437.76
0.04005	0.77106	437.98
0.04503	0.77142	438.17
0.05004	0.77178	438.35
0.06000	0.77249	438.69
0.06495	0.77284	438.85

Hep_4NBr

0.00996	0.76885	507.38
0.01998	0.76961	508.12
0.02504	0.76999	508.37
0.03000	0.77036	508.59
0.03499	0.77073	508.80
0.04002	0.77110	509.01
0.04494	0.77146	509.20
0.05003	0.77183	509.39
0.06002	0.77255	509.72
0.06505	0.77291	509.86

$x = 0.40$

Et_4NBr

0.00995	0.76631	152.62
0.02006	0.76702	153.45
0.02495	0.76736	153.80
0.03000	0.76771	154.08
0.03494	0.76805	154.38
0.04005	0.76840	154.66
0.04503	0.76874	154.90
0.05003	0.76908	155.13
0.05995	0.76975	155.56
0.06502	0.77009	155.78

Pr_4NBr

0.01001	0.76633	223.28
0.02005	0.76705	224.10
0.02497	0.76740	224.40
0.03006	0.76776	224.68
0.03503	0.76811	224.93
0.04003	0.76846	225.18
0.04505	0.76881	225.40
0.04995	0.76915	225.61
0.05995	0.76984	225.99
0.06506	0.77019	226.19

Bu_4NBr

0.00998	0.76634	294.32
0.01998	0.76707	295.02
0.02495	0.70743	295.27
0.02995	0.76779	295.51
0.03498	0.76815	295.75
0.04004	0.76851	295.99
0.04498	0.76886	296.20
0.04994	0.76921	296.38
0.06007	0.76992	296.74
0.06496	0.77026	296.91

Pen_4NBr

0.01005	0.76636	365.10
0.02000	0.76710	365.80
0.02501	0.76747	366.02
0.03005	0.76784	366.23
0.03499	0.76820	366.46
0.03996	0.76856	366.68
0.04495	0.76892	366.87
0.04997	0.76928	367.07
0.05994	0.76999	367.41
0.06503	0.77035	367.58

Hex_4NBr			Hep_4NBr		
0.01003	0.76637	436.22	0.00996	0.76638	506.88
0.01996	0.76712	436.84	0.01996	0.76715	507.49
0.02504	0.76750	437.09	0.02495	0.76753	507.75
0.03002	0.76787	437.33	0.02997	0.76791	507.97
0.03503	0.76824	437.55	0.03503	0.76829	508.20
0.03994	0.76860	437.77	0.03998	0.76866	508.39
0.04500	0.76897	437.94	0.04496	0.76903	508.57
0.04996	0.76933	438.12	0.04997	0.76940	508.74
0.05996	0.77005	438.47	0.05995	0.77013	509.07
0.06500	0.77041	438.63	0.06505	0.77050	509.23

$x_2 = 0.60$

Et_4NBr			Pr_4NBr		
0.01003	0.76288	152.02	0.00994	0.76289	222.84
0.01995	0.76358	152.86	0.02004	0.76362	223.63
0.02493	0.76393	153.16	0.02506	0.76398	223.92
0.02995	0.76428	153.46	0.02997	0.76433	224.19
0.03500	0.76463	153.75	0.03504	0.76469	224.44
0.04007	0.76498	154.02	0.04000	0.76504	224.68
0.04502	0.76532	154.27	0.04498	0.76539	224.91
0.04998	0.76566	154.48	0.04998	0.76574	225.11
0.05998	0.76634	154.92	0.06004	0.76644	225.49
0.06500	0.76668	155.11	0.06496	0.76678	225.68

Bu_4NBr

0.01004	0.76291	294.12
0.01997	0.76364	294.85
0.02504	0.76401	295.03
0.03000	0.76437	295.33
0.03499	0.76473	295.57
0.04001	0.76509	295.80
0.04504	0.76545	295.98
0.04997	0.76580	296.19
0.06001	0.76651	296.53
0.06500	0.76686	296.70

Pen_4NBr

0.00997	0.76292	365.11
0.1996	0.76367	365.75
0.02494	0.76404	366.03
0.02995	0.76441	366.30
0.03498	0.76478	366.51
0.04004	0.76515	366.71
0.04499	0.76551	366.91
0.04996	0.76587	367.08
0.05998	0.76659	367.42
0.06503	0.776695	367.59

Hex_4NBr

0.01001	0.76294	435.61
0.02006	0.76371	436.29
0.02506	0.76409	436.51
0.02993	0.76446	436.59
0.03504	0.76484	436.99
0.04000	0.76521	437.18
0.04499	0.76558	437.37
0.05000	0.76595	437.53
0.05998	0.76668	437.87
0.06494	0.76704	438.03

Hep_4NBr

0.00994	0.76295	506.55
0.02005	0.76374	507.18
0.02496	0.76412	507.41
0.03004	0.76451	507.66
0.03502	0.76489	507.87
0.04003	0.76527	508.07
0.04506	0.76565	508.23
0.05000	0.76602	508.67
0.05995	0.76676	508.73
0.06497	0.76713	508.88

x = 0.80

Et$_4$NBr			Pr$_4$NBr		
0.00995	0.75935	151.15	0.00996	0.75937	221.79
0.02006	0.76007	152.01	0.01994	0.76010	222.58
0.02502	0.76042	152.23	0.02504	0.76047	222.88
0.03000	0.76077	152.65	0.03002	0.76083	223.12
0.03500	0.76112	152.91	0.03503	0.76119	223.37
0.04002	0.76147	153.15	0.04007	0.76155	223.56
0.04507	0.76182	153.40	0.04498	0.76190	223.82
0.04999	0.76216	153.61	0.05006	0.76226	224.04
0.06004	0.76285	154.04	0.05999	0.76296	224.41
0.6502	0.76319	154.24	0.06499	0.76331	224.60

Bu$_4$NBr			Pen$_4$NBr		
0.01004	0.75939	293.15	0.00996	0.75940	364.32
0.01995	0.76013	293.75	0.02007	0.76017	364.95
0.02495	0.76050	294.02	0.02497	0.76054	365.19
0.02998	0.76087	294.28	0.03003	0.76092	365.41
0.03504	0.76124	294.54	0.03499	0.76129	365.64
0.03997	0.76160	294.71	0.03997	0.76166	365.84
0.04494	0.76196	294.93	0.04498	0.76203	366.04
0.05006	0.76233	295.11	0.05001	0.76240	366.21
0.05996	0.76304	295.46	0.06001	0.76313	366.55
0.06501	0.76340	295.63	0.06498	0.76349	366.71

	Hex$_4$NBr			Hep$_4$NBr	
0.01001	0.75942	435.26	0.01005	0.75944	506.31
0.02004	0.76020	435.82	0.02001	0.76023	506.88
0.02498	0.76058	436.09	0.02497	0.76062	507.08
0.02995	0.76096	436.33	0.02997	0.76101	507.31
0.03494	0.76134	436.52	0.03500	0.76140	507.52
0.03997	0.76172	436.74	0.04006	0.76179	507.71
0.04502	0.76210	436.92	0.04502	0.76217	507.89
0.04996	0.76247	437.08	0.05001	0.76255	508.07
0.06007	0.76322	437.43	0.05994	0.76330	508.38
0.06495	0.76358	437.57	0.06501	0.76368	508.53

Table 3. Limiting Apparent Molar Volumes (ϕ^0_v) and Experimental Slopes (S^*_v) of Tetraalkylammonium Bromides in Methanol + Acetonitrile Mixtures at 298.15 , 308.15 and 318.15 K

x	ϕ^0_v / cm^3. mol^{-1}	S^*_v/ cm^3 . L^{½}. mol$^{-3/2}$	ϕ^0_v / cm^3. mol^{-1}	S^*_v/ cm^3 . L^{½}. mol$^{-3/2}$
		298.15 K		
	Et_4NBr		Pr_4NBr	
0.00	140.64	17.13	212.77	16.30
0.20	142.97	17.80	215.19	16.30
0.40	146.97	18.25	218.00	17.01
0.60	147.54	18.83	218.36	17.76
0.80	147.75	19.45	218.48	18.11
	Bu_4NBr		Pen_4NBr	
0.00	280.92	14.76	350.99	14.14
0.20	283.15	15.09	354.07	14.44
0.40	284.97	15.37	358.71	14.62
0.60	285.37	15.46	359.02	14.89
0.80	285.37	15.92	359.20	15.40
	Hex_4NBr		Hep_4NBr	
0.00	422.45	13.23	492.21	12.29
0.20	424.77	13.61	495.00	12.92
0.40	427.67	13.86	498.29	13.02
0.60	427.92	13.99	498.42	13.08
0.80	427.97	14.45	498.45	13.11

308.15 K

	Et_4NBr		Pr_4NBr	
0.00	145.30	18.79	216.01	16.47
0.20	147.34	18.81	217.78	16.78
0.40	148.90	18.96	219.64	17.82
0.60	149.23	19.26	219.67	17.73
0.80	149.55	19.46	220.01	18.21
	Bu_4NBr		Pen_4NBr	
0.00	286.77	14.80	357.48	14.01
0.20	288.52	15.11	359.51	14.37
0.40	289.53	15.49	361.48	14.96
0.60	290.00	16.31	361.69	15.44
0.80	290.20	16.42	361.85	15.55
	Hex_4NBr		Hep_4NBr	
0.00	428.10	14.16	498.88	13.75
0.20	430.07	14.24	501.36	13.94
0.40	431.91	14.65	502.57	14.19
0.60	431.93	15.15	502.60	14.47
0.80	432.01	15.28	502.88	14.57

318.15 K

	Et_4NBr		Pr_4NBr	
0.00	148.08	19.65	219.10	17.98
0.20	149.16	19.93	220.02	17.83
0.40	150.02	19.98	221.04	18.23
0.60	150.56	20.48	221.44	18.63
0.80	150.70	20.89	222.07	19.51
	Bu_4NBr		Pen_4NBr	
0.00	290.21	15.97	361.19	15.56
0.20	291.49	16.19	362.75	15.47
0.40	292.45	16.67	363.51	16.00
0.60	292.64	16.73	363.50	15.92
0.80	292.70	17.39	363.72	16.66
	Hex_4NBr		Hep_4NBr	
0.00	432.24	15.22	503.32	14.37
0.20	433.72	15.09	5.4.83	14.45
0.40	434.02	15.69	505.05	15.04
0.60	434.63	15.62	505.36	15.16
0.80	434.68	16.42	505.84	15.83

Table 4. Ionic Limiting Partial Molar Volumes ($\bar{V}^0_{ion}$) in Methanol + Acetonitrile Mixtures at 298.15 , 308.15 and 318.15 K

	$\bar{V}^0_{ion}$ / $cm^3 . mol^{-1}$				
	x = 0.00	x = 0.20	x = 0.40	x = 0.60	x = 0.80
			T = 298.15 K		
Et_4N^+	162.27	162.62	163.32	163.24	163.17
Pr_4N^+	234.49	234.84	234.35	234.06	233.90
Bu_4N^+	302.65	302.80	301.32	300.91	300.79
Pen_4N^+	372.67	373.72	375.06	374.72	374.62
Hex_4N^+	444.00	444.42	444.02	443.62	443.39
Hep_4N^+	513.75	514.65	514.64	514.12	513.87
Br^-	-21.65	-19.65	-16.35	-15.70	-15.42
			T = 308.15 K		
Et_4N^+	164.17	164.63	164.53	164.39	164.35
Pr_4N^+	234.88	235.07	235.27	234.78	234.81
Bu_4N^+	305.64	305.81	305.16	305.11	305.00
Pen_4N^+	376.35	376.80	376.11	376.80	376.65
Hex_4N^+	446.97	447.36	447.54	447.04	446.81
Hep_4N^+	517.75	518.65	518.20	517.67	517.68
Br^-	-18.87	-17.29	-15.63	-15.11	-14.80
			T = 318.15 K		
Et_4N^+	164.97	165.31	164.72	164.82	164.71
Pr_4N^+	235.99	236.17	235.74	235.70	236.08
Bu_4N^+	307.10	307.64	307.15	306.90	306.71
Pen_4N^+	378.08	378.90	378.21	377.76	377.73
Hex_4N^+	449.13	449.87	448.72	448.89	448.69
Hep_4N^+	520.21	520.98	519.75	519.62	519.85
Br^-	-16.89	-16.15	-14.70	-14.26	-14.01

Fig-1

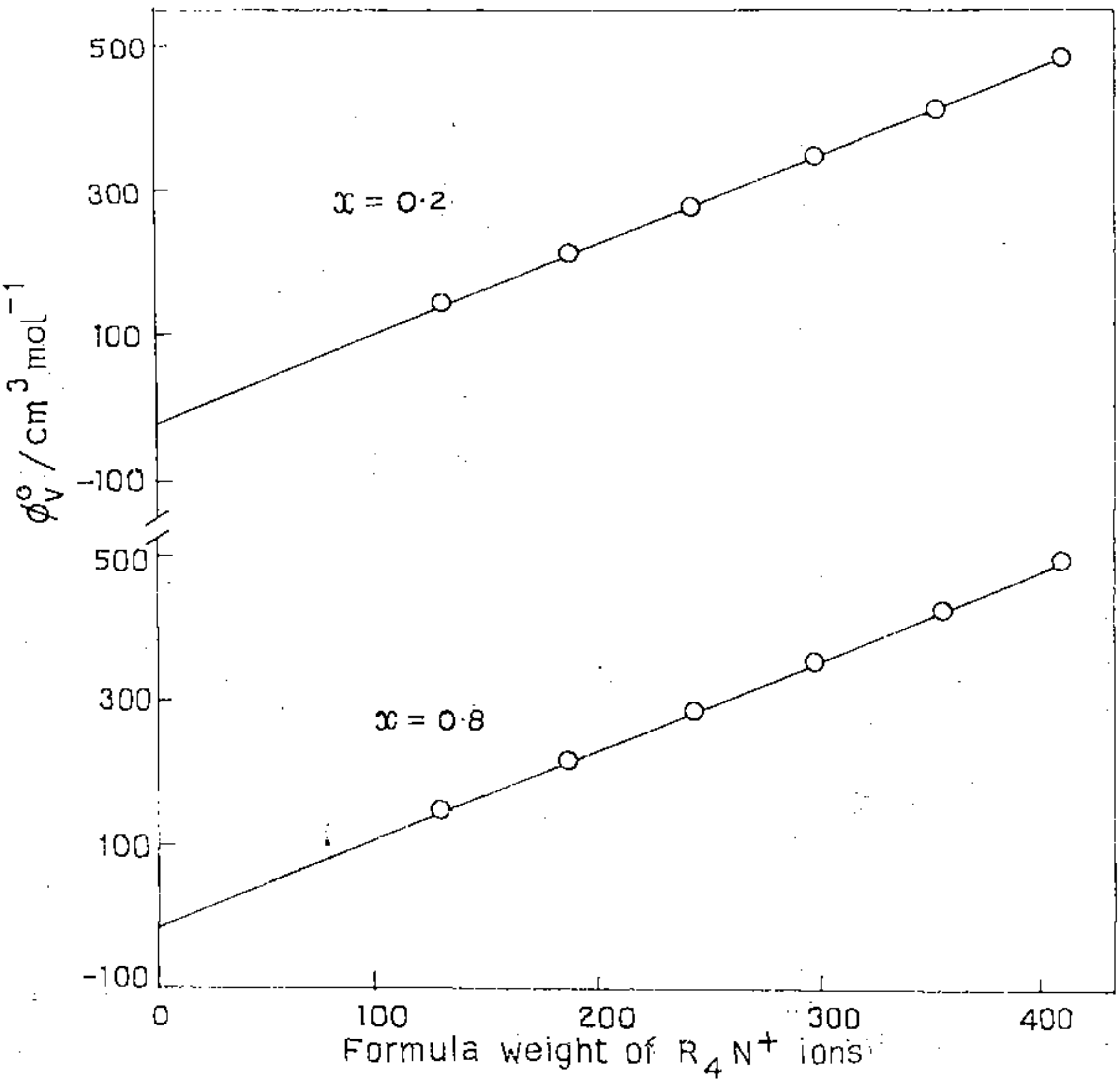

Figure - 1. Representative plot of ϕ_V^o of the R_4NBr salts vs. the formula weight of the respective R_4N^+ ions in methanol + acetonitrile mixtures at 298·15 K.