

CHAPTER VIII

Electrical Conductances of Some Symmetrical Tetraalkylammonium Salts in Methanol, Acetonitrile, and Methanol + Acetonitrile Mixtures at 298.15 K

Introduction

Extensive studies on electrical conductivities in various mixed organic solvents have been performed in recent years¹⁻⁷ to examine the nature and magnitude of ion-ion and ion-solvent interactions. Such solvent properties as the viscosity and the relative permittivity have also been taken into consideration, which help determine the extent of ion association and the solute-solvent interactions.

The present study deals with mixtures of methanol-a dipolar protic solvent, and acetonitrile-a dipolar aprotic solvent. Methanol is known to be extensively self-associated through hydrogen-bonding in the pure state⁸. In the case of acetonitrile, on the other hand, there is a lack of strong specific intermolecular forces, while dipole-dipole forces predominate⁹. Recently, we have shown¹⁰ that, in the mixture containing methanol and acetonitrile, there is a breakdown of hydrogen bonds in methanol and formation of specific complexes between the unlike molecules through hydrogen bonds. In view of the complex nature of methanol-acetonitrile mixtures, it is of interest to investigate the influence of the solvent composition on the ionic association and the solvation behaviour of some tetraalkylammonium bromides using conductance measurements.

In this chapter we have reported the results of conductance measurements on six symmetrical tetraalkylammonium bromides, viz., tetraethylammonium bromide (Et_4NBr), tetrapropylammonium bromide (Pr_4NBr), tetrabutylammonium bromide (Bu_4NBr), tetrapentylammonium bromide (Pen_4NBr), tetrahexylammonium bromide (Hex_4NBr) tetraheptylammonium bromide (Hep_4NBr) along with the salt tetrabutylammonium tetraphenyl borate ($\text{Bu}_4\text{NPh}_4\text{B}$) in methanol, acetonitrile, and methanol + acetonitrile mixtures ranging in composition from 0.20 to 0.80 mole fraction of acetonitrile at 298.15 K. The salt tetrabutylammonium tetraphenylborate has been used as a "reference electrolyte" to estimate the single-ion conductivities.

Experimental

Methanol (E. Merck, India, uvasol grade, 99.5% pure) was dried over 3Å 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^{9,11}.

Acetonitrile (E. Merck, India, 99% pure) was distilled with P₂O₅ and then redistilled over CaH₂. The purified solvent had a density of 0.77686 g.cm⁻³ and a coefficient of viscosity of 0.345 m Pa.s at 298.15 K ; These values are also found to be in good agreement with literature³ values.

The purities as checked by gas chromatography were found to be better than 99.8% for methanol and 99.5% for acetonitrile.

Tetraalkylammonium bromides were of purum or puriss grade (Fluka) and were purified as described earlier by us^{12,13}. Tetrabutylammonium tetraphenylborate was prepared and purified as reported in the literature².

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 (ρ) were measured with an Ostwald Sprengal type pycnometer having a bulb volume of 25 cm³ and an internal diameter of the capillary of about 0.1cm. The pycnometer was calibrated at 298.15, 308.15, and 318.15 K with doubly distilled water and benzene. Details have been described earlier^{10,14,15}.

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell (cell constant = 0.751cm⁻¹) with an accuracy of 0.01%. The cell was calibrated by the method of Lind and co-workers¹⁵ using aqueous potassium chloride solutions. Measurements were made in an oil bath maintained at 298.15 ± 0.005 K, as described earlier¹⁶. Several independent solutions were prepared, and conductance measurements were performed with each of these to ensure the reproducibility of the results. Corrections were made for the specific conductances of the solvent.

The experimental values of densities (ρ), viscosities (η), and relative permittivities (ϵ) of methanol + acetonitrile at 298.15 K are not available at the relevant compositions in which conductance measurements have been carried out. The available values^{10,12} of ρ and η and those of ϵ are, therefore, plotted against the mole fraction of acetonitrile, and the values of ρ , η , and ϵ at all the desired compositions have been generated from the smooth master curves and are given in Table 1.

Results

Molar conductances (Λ) of electrolyte solutions as a function of molar concentration (c) are given in Table 2 in different solvent mixtures at 298.15 K.

The conductance data have been analysed by the 1978 Fuoss conductance-concentration equation^{19,20}. For a given set of conductivity values ($C_j, \Lambda_j, j = 1, 2, \dots, n$), three adjustable parameters, the limiting molar conductivity (Λ^0), the association constant (K_A), and the distance of closest approach of ions (R), are derived from the following set of equations :

$$\Lambda = \rho [\Lambda^0 (1 + R_x) + E_L] \quad (1)$$

$$\rho = 1 - \alpha(1 - \gamma) \quad (2)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (3)$$

$$-\ln f = \beta k / 2 (1 + k R) \quad (4)$$

$$\beta = e^2 / \epsilon k_B T \quad (5)$$

$$K_A = K_R / (1 - \alpha) = K_R (1 + K_S) \quad (6)$$

where R_x is the relaxation field effect, E_L is the electrophoretic countercurrent, k^{-1} is the radius of the ion atmosphere, ϵ is the relative permittivity of the solvent, e is the electron charge, k_B is the Boltzmann constant, γ is the fraction of solute present as unpaired ion, c is the molarity of the solution, f is the activity coefficient, T is the absolute temperature, and β is twice the

Bjerrum distance. The computations were performed on a computer using the program suggested by Fuoss. The initial Λ^0 values for the iteration procedure were obtained from Shedlovsky extrapolation of the data. Input for the program is the set $(c_j, \Lambda_j, j = 1, 2, \dots, n)$, n , ϵ , η , T , initial value of Λ^0 , and an instruction to cover a preselected range of R values.

In practice, calculations are performed by finding the values of Λ^0 and α that minimize the standard deviation σ ,

$$\sigma^2 = \sum [\Lambda_j (\text{calcd}) - \Lambda_j (\text{obsd})]^2 / (n - 2) \quad (7)$$

for a sequence of R values and then plotting σ against R ; the best-fit R corresponds to the minimum of the σ versus R curve. First, approximate runs over a fairly wide range of R values are made to locate the minimum, and then, a fine scan around the minimum is made. Finally, with this minimising value of R , the corresponding Λ^0 and K_A are calculated. The values of Λ^0 , K_A and R obtained by this procedure are reported in Table 3.

Discussion

The conductances of solutions of Pr_4NBr , and Bu_4NBr in acetonitrile and of Et_4NBr , Pr_4NBr , Bu_4NBr , and Pen_4NBr in methanol have also been reported earlier by other workers^{20,21}. The conductances of solutions of the reference electrolyte $\text{Bu}_4\text{NPh}_4\text{B}$ in acetonitrile and methanol are available in the literature²²⁻²⁸. They analysed their data with equations different from the one used in the present analysis. Conductance data of sufficient precision, with the exception of the works mentioned above, for any of the systems investigated here do not exist in the literature. Consequently, we compared the Λ^0 and K_A values for the above-mentioned systems with those from the present work (Table 3). It has been observed that the values of Λ^0 calculated from the previous conductance equation do not differ significantly from the values of Λ^0 calculated from the 1978 Fuoss conductance-concentration equation. The values of K_A obtained from our work are, however, generally higher. This discrepancy may be attributed to the different models used for analysis of the experimental data. We have reanalysed the literature experimental data with the 1978 Fuoss conductance equation, and the results are included in Table 3. In each case a better fit of the conductance data to the 1978 Fuoss equation than to the earlier conductance

equations has been observed. These Λ^0 and K_A values are in good agreement with our results. The association constants (K_A) in Table 3 indicate that the salts Hex_4NBr and Hep_4NBr are slightly associated in acetonitrile and methanol + acetonitrile mixtures. Tetrabutylammonium tetraphenylborate is, on the other hand, found to be somewhat more associated. In a given solvent mixture, the extent of association is always found to decrease in the order $\text{Et}_4\text{NBr} > \text{Pr}_4\text{NBr} > \text{Bu}_4\text{NBr} > \text{Pen}_4\text{NBr} > \text{Hex}_4\text{NBr} > \text{Hep}_4\text{NBr}$, similar to those observed earlier, due to an apparent decrease in the ion dipole interaction^{2,5}. For each salt, however, ionic association increases slowly with increasing methanol content in the solvent mixtures. This is quite expected due to the gradual decrease in relative permittivity of the medium with increasing amount of methanol in the mixtures.

The limiting ionic conductivities have been evaluated from division of the values of $\text{Bu}_4\text{NPh}_4\text{B}$ using the following relationship :

$$\lambda^0 (\text{Bu}_4\text{N}^+) = 1.07 \lambda^0 (\text{Ph}_4\text{B}^-) \quad (8)$$

as described in the literature^{28,29}. The values of the limiting ionic conductivity (λ^0) in methanol, acetonitrile, and methanol + acetonitrile mixtures calculated using the above equation are given in Table 4.

The λ^0 value of the bromide ion decreases gradually from pure acetonitrile to pure methanol, apparently because of the decrease in the relative permittivity of the medium with increasing methanol content. The λ^0 value of each of the tetraalkylammonium ions, on the other hand, goes through a maximum at a mole fraction of 0.2 of methanol in the mixture on passing from acetonitrile to methanol. This indicates simultaneous control of the viscosity of the medium on the ionic conductivities along with the relative permittivity.

It can be seen²⁹ from Table 3 that the distances of closest approach of ions (R) for the tetraalkylammonium bromide salts vary from 15.50 to 17.10 Å for the $\text{R}_4\text{N}^+\text{Br}^-$ ion pairs in different solvent mixtures. Although not too much can be deduced from the best fit R values, since the conductivity parameters are reproduced almost equally well over a wide range of arbitrarily chosen R values, some generalisations can be made about the R values obtained from the 1978 Fuoss conductance equation because this presupposes that ion pairs may be of solvent-separated or contact variety. The sums of the crystallographic radii (a) for Et_4NBr to Hep_4NBr are 5.80 to 7.68 Å. The diameters (d) of methanol + acetonitrile

were calculated as described²⁸. For the present solvent system, the values of R vary from 3.75 (methanol) to 4.37 (acetonitrile). The values of R are, thus, always higher than $a + d$, which has a maximum value of 12.05 Å for Hep_4NBr in acetonitrile, indicating that $\text{R}_4\text{N}^+\text{Br}^-$ ion pairs are solvent separated in all the solvent media investigated. Such large values of R for tetraalkylammonium salts have also been observed in different pure and mixed solvents^{2,5,30,31}.

The Stokes' radii of the tetraalkylammonium ions are found to be smaller than their corresponding crystallographic radii, this is physically unacceptable. They seem to indicate that the ionic radii on the basis of the Stokes' law do not appear to be correct. This probably arises from the fact that the electrolytic solutions are different from the model which underlies the Stokes' law. We have, therefore, estimated the actual radii of the ions in solution using the Stokes' law as modified by Gill³². The results indicate poor solvation of the large tetraalkylammonium ions and tetraphenylborate ion particularly in the methanol rich region, and strong solvation of the bromide ion in the pure as well mixed solvents. The tetraalkylammonium ions as well as the tetraphenyl borate ion, because of their large size and small charge density are not solvated in dipolar aprotic solvents¹⁻³. This is found in acetonitrile also. In dipolar protic solvents, on the other hand, have been reported to possess solvophobic solvation^{5,39-42}. In our case also the solvation of this ion in the methanol-rich region as in pure methanol may be ascribed to their solvophobic interaction with methanol molecules.

Reference

- 1 P. K. Muhuri. and D. K. Hazra, *Z. Phys. Chem.* , **190**, 111, 1995.
- 2 A. K. Srivastava and R. A. Samant , *J. Chem. Eng Data* , **39** , 358, 1994
- 3 H. Doe, H. Ohe , H. Matoba, A. Ichimma and T. Kitagawa, *Bull. Chem.Soc. Jpn.*, **63**, 2785, 1990.
- 4 S. Taniewska-Osinska, A. Pickarska, A. Bald and A. Szcjgis, *J. Chem. Soc. Faraday. Trans. 1.*, **85**, 3709, 1989.
- 5 N. Islam, S. B. A. Zaidi and A. A. Ansari , *Bull. Chem. Soc. Jpn.* . **62**, 309, 1989.
- 6 N. Papadopoulos, *Can. J. Chem.*, **67**, 1624, 1989
- 7 M. S. K. Niazi, *Bull. Chem. Soc. Jpn.*, **61**, 2165, 1988.
- 8 L. Pikkarainen, *J. Chem. Eng. Data*, **33**, 299, 1988.
- 9 G. Moumouzias, D. K. Panopoulos and D. K. Ritzoulis, *J. Chem. Eng. Data*, **36**, 20, 1999.
- 10 N. Saha, B. Das. and D. K. Hazra, *J. Chem. Eng. Data*, **40**, 1264, 1995.
- 11 J. Singh, T. Kaur, V. Ali and D. S. Gill, *J. Chem. Soc. Faraday Trans.*, **90**, 579, 1994.
- 12 D. S. Gill and M. S. Chauhan, *Z. Phys. Chem. Neue Folge*, **140**, 139, 1984.
- 13 B. Das and D. K. Hazra. *J. Chem. Eng. Data*, **36**, 409, 1991.
- 14 P. K. Muhuri, B. Das and D. K. Hazra, *Ind. J. Chem.* **35A**, 288, 1996.
- 15 J. E. Lind Jr, J. J. Zwolenik and R. M. Fuoss, *J. Am. Chem. Soc.* **81**, 1557, 1959.
- 16 B. Das and D. K. Hazra, *Bull. Chem. Soc. Jpn.*, **65** , 3470, 1992.
- 17 B. Das and D. K. Hazra, *Bull. Chem. Soc. Jpn.*, **68**, 734, 1995 a.
- 18 B. Das and D. K. Hazra, *J. Phys. Chem.*, **99**, 269, 1995 b.
- 19 R. M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.* . **75**, 16, 1978 a.
- 20 R. M. Fuoss, *J. Phys. Chem.*, **82**, 2427, 1978 b.
- 21 D. F. Evans, C. Zawoyski and R. L. Kay, *J. Phys. Chem.*, **69**, 38 78, 1965.

- 22 R. L. Kay, C. Zawoyski and D. F. Evans, *J. Phys. Chem.*, **69**, 4208, 1965.
- 23 F. Accascina and R. M. Fuoss, *J. Am. Chem Soc.*, **81**, 1301, 1958.
- 24 J. Barthel, L. Iberl, J. Rossmairer, J. H. Gores and B. Kaukal, *J. Solution Chem.*, **19** 321. 1990.
- 25 D. S. Berns and R. M. Fuoss, *J. Am. Chem Soc.*, **82** , 5585, 1960.
- 26 A. M. Brown and R. M. Fuoss, *J. Phys. Chem.*, **64**, 1341, 1960.
- 27 M. A. Coetzee and G. P. Cunningham, *J. Am. Chem. Soc.*, **87**, 2529 1965.
- 28 M. A. Coplan and R. M. Fuoss, *J. Phys. Chem.*, **68**, 1177, 1964.
- 29 B. Das and D. K. Hazra, *J. Solution. Chem.*, **27**, 1021, 1998.
- 30 B. Das and N. Saha *J. Chem. Eng. Data*, **44** ,1999
- 31 P. K. Muhuri and D. K. Hazra, *J. Chem. Soc. Faraday Trans.* **87**. 3511, 1991.
- 32 D. S. Gill and M. B. Sekhri, *J. Chem. Soc., Faraday Trans. 1*, **78**, 119, 1982.

Table 1. Densities (ρ), Viscosities (η), and Relative Permittivities (ϵ) for Methanol + Acetonitrile at 298.15 K

x^a	$\rho^b / \text{g}\cdot\text{cm}^{-3}$	$\eta^b / \text{mPa}\cdot\text{s}$	ϵ^c
0.00	0.78654	0.545	32.62
0.20	0.78680	0.435	33.58
0.40	0.78465	0.373	34.30
0.60	0.78212	0.343	34.92
0.80	0.77952	0.334	35.47
1.00	0.77686	0.346	35.95

^a x is the mole fraction of acetonitrile. ^bref.10. ^cref.12.

Table 2. Molar Conductances (Λ) and Corresponding Molarities (c) of Tetraalkylammonium Bromides in Methanol + Acetonitrile at 298.15 K

$10^4 c/\text{mol dm}^{-3}$	$\Lambda / \text{S cm}^2 \cdot \text{mol}^{-1}$	$10^4 c/\text{mol dm}^{-3}$	$\Lambda / \text{S cm}^2 \cdot \text{mol}^{-1}$
$x = 0.00$			
	Et ₄ NBr		Pr ₄ NBr
3.501	111.88	3.499	97.83
5.115	110.81	5.000	96.93
7.500	109.49	9.120	94.89
12.001	107.36	10.003	94.53
14.216	106.49	16.006	92.37
20.006	104.49	22.215	90.59
22.100	103.85	28.008	89.14
27.998	102.18	33.512	87.91
34.165	100.66	35.000	87.60
	Bu ₄ NBr		Pen ₄ NBr
4.002	90.52	3.501	87.04
7.497	88.78	5.071	86.10
10.101	87.65	10.210	83.92
16.001	85.66	12.503	83.14
21.978	84.02	14.001	82.66
25.000	83.29	19.004	81.26
29.986	82.18	24.999	79.83
33.059	81.53	30.017	78.78
35.003	81.19	32.992	78.21

Hex ₄ NBr		Hep ₄ NBr	
3.504	82.33	3.512	80.43
5.499	81.28	5.208	79.55
7.512	80.35	7.509	78.50
10.016	79.38	9.996	77.56
14.002	78.09	15.012	75.98
20.018	76.46	20.006	74.71
22.506	75.87	22.516	74.12
24.300	75.47	25.123	73.56
30.117	74.26	30.017	72.56
34.791	73.43	35.011	71.70

Bu ₄ NPh ₄ B	
4.101	70.00
7.456	68.03
10.017	66.77
16.104	64.34
18.266	63.60
20.004	63.04
25.106	61.54
29.982	60.24
34.808	59.15

$$x = 0.20$$

Et ₄ NBr		Pr ₄ NBr	
4.001	136.16	4.018	121.28
9.503	132.46	9.515	117.88
12.516	130.89	12.498	116.47
15.003	129.79	15.001	115.41
20.011	127.70	20.028	113.52
25.001	125.87	24.998	111.95
29.998	124.28	30.928	110.22
35.010	122.81	34.990	109.16
37.500	122.11	37.503	108.53
40.001	121.40	39.000	107.90
Bu ₄ NBr		Pen ₄ NBr	
4.038	112.89	4.000	108.40
9.495	109.70	9.501	105.30
12.499	108.36	12.496	103.99
15.001	107.36	14.998	103.04
20.103	105.57	19.989	101.34
25.006	104.12	25.013	99.92
29.999	102.75	30.016	98.59
34.998	101.52	35.001	97.42
37.510	100.93	37.520	96.97
40.010	100.40	39.998	96.92

Hex ₄ NBr		Hep ₄ NBr	
4.003	104.90	4.019	100.85
9.499	101.87	9.533	97.94
12.518	100.60	12.501	96.74
15.016	99.67	14.998	95.86
19.982	98.07	20.103	94.25
25.009	96.60	25.212	92.93
30.107	95.34	30.246	91.71
34.998	94.22	35.013	90.68
37.500	93.67	37.498	90.17
40.006	93.18	39.990	89.70

Bu ₄ NPh ₄ B	
4.213	87.59
9.546	84.17
12.506	82.71
15.111	81.56
20.008	79.63
24.990	77.98
30.145	76.41
34.868	75.12
37.488	74.45
40.011	73.85

$$x_i = 0.40$$

	Et ₄ NBr		Pr ₄ NBr	
4.301	155.39	4.343	139.17	
9.784	151.30	10.012	135.34	
12.006	149.99	11.956	134.27	
15.133	148.33	15.018	132.79	
20.198	146.01	20.333	130.51	
24.821	144.09	25.006	128.87	
30.002	142.21	29.998	127.18	
35.119	140.52	35.016	125.67	
39.903	139.05	40.105	124.25	
42.996	138.15	43.000	123.53	
	Bu ₄ NBr		Pen ₄ NBr	
4.306	130.52	4.333	125.51	
10.107	126.81	9.998	121.95	
12.315	125.68	12.036	120.95	
15.228	124.36	15.102	119.60	
20.112	122.38	20.006	117.72	
24.996	120.77	25.016	116.05	
30.121	119.15	30.008	114.57	
34.995	117.78	34.998	113.22	
40.303	116.37	40.101	111.96	
43.011	115.79	43.001	111.28	

Hex ₄ NBr		Hep ₄ NBr	
4.301	120.83	4.403	116.73
10.007	117.35	10.010	113.42
12.103	116.35	11.173	112.42
15.008	115.11	14.999	112.26
19.988	113.29	20.011	109.44
25.120	111.60	25.021	107.92
30.004	110.22	29.998	106.53
34.996	108.92	34.996	105.27
40.015	107.73	40.130	104.10
42.990	107.06	43.002	103.46

Bu ₄ NPh ₄ B	
4.410	101.79
9.985	97.96
11.996	96.86
14.998	95.38
20.013	93.24
25.102	91.30
30.080	89.67
34.998	88.19
40.021	86.80
42.998	86.03

$$x_1 = 0.60$$

	Et ₄ NBr		Pr ₄ NBr	
4.500	166.17		4.418	150.25
10.012	161.88		10.104	146.16
12.116	160.57		11.990	145.05
15.108	158.89		15.032	143.47
20.308	156.34		20.146	141.16
24.996	154.32		24.969	139.26
30.132	152.33		30.125	137.44
34.988	150.62		35.077	135.84
40.026	148.97		40.005	134.38
44.008	147.76		43.992	133.28
	Bu ₄ NBr		Pen ₄ NBr	
4.432	140.54		4.530	136.15
9.994	136.73		9.998	132.52
12.016	135.63		12.171	131.38
15.034	134.16		15.123	130.00
19.976	132.07		20.315	127.88
25.126	130.17		24.992	126.22
30.039	128.56		30.096	124.59
34.999	127.07		35.016	123.17
39.989	125.70		40.107	121.82
43.999	124.67		44.003	120.86

Hex ₄ NBr		Hep NBr	
4.502	130.58	4.515	126.84
10.300	126.87	10.118	123.33
12.012	126.00	11.998	122.41
14.992	124.65	15.009	121.07
20.038	122.65	20.004	119.16
20.075	120.92	24.996	117.50
30.192	119.36	30.036	116.01
34.996	118.02	35.034	114.67
40.102	116.72	39.981	113.45
43.998	115.79	44.033	112.52

Bu ₄ NPh ₄ B	
4.506	109.42
10.110	105.47
12.031	104.39
15.246	102.77
20.103	100.63
25.214	98.67
29.999	97.03
35.112	95.44
40.008	94.05
44.001	92.99

$x = 0.80$			
Et ₄ NBr		Pr ₄ NBr	
4.505	171.98	4.603	155.79
9.514	167.95	10.005	151.82
12.162	166.25	12.016	150.63
15.036	164.61	14.996	149.05
19.992	162.12	19.988	146.73
25.003	159.91	24.980	144.71
30.107	157.89	30.006	142.89
34.935	156.15	35.105	141.20
38.849	154.51	40.008	139.71
44.666	143.01	44.945	138.31
Bu ₄ NBr		Pen ₄ NBr	
4.566	147.06	4.514	141.67
9.862	143.34	9.965	139.97
11.924	142.19	12.055	136.85
14.900	140.70	15.022	135.42
20.001	138.48	19.886	133.38
25.010	136.59	25.112	131.48
29.979	134.90	29.982	129.89
34.998	133.36	35.114	128.38
40.110	131.91	40.027	127.04
45.001	130.63	44.925	125.80

Hex ₄ NBr		Hep ₄ NBr	
4.616	136.29	40536	132.46
10.103	132.72	9.885	129.03
12.109	131.68	12.212	127.86
15.118	130.29	14.996	126.61
20.302	128.21	20.108	124.61
25.218	126.50	25.103	122.92
29.815	125.06	30.000	121.45
35.216	123.53	35.014	120.07
40.028	122.28	40.123	118.79
45.002	121.07	44.982	117.66

Bu ₄ NPh ₄ B	
4.532	114.21
10.063	110.30
12.125	109.14
14.998	107.69
20.108	105.42
25.033	103.53
29.987	101.82
34.959	100.27
40.103	98.80
44.999	97.50

$$x = 1.00$$

	Et ₄ NBr		Pr ₄ NBr	
5.011	176.55	5.005	162.55	
7.499	174.50	11.110	158.30	
10.207	172.59	14.546	156.42	
14.990	169.76	20.249	153.75	
25.535	164.83	35.307	148.24	
35.412	161.14	40.010	146.80	
40.008	159.62	42.111	146.16	
45.163	158.01	46.124	145.08	
	Bu ₄ NBr		Pen ₄ NBr	
5.500	153.44	4.883	148.56	
10.100	150.40	7.712	146.58	
15.043	147.82	10.102	145.13	
19.226	145.99	15.408	142.49	
25.120	143.73	20.090	140.54	
30.234	142.00	24.996	138.75	
34.950	140.54	30.108	137.08	
40.111	139.07	35.311	135.54	
42.000	138.55	39.416	134.39	
45.461	137.67	45.919	132.78	

Hex ₄ NBr		Hep ₄ NBr	
4.625	143.83	4.700	140.31
7.510	141.82	7.523	138.40
10.245	140.21	10.315	136.82
15.004	137.92	14.988	134.63
19.989	135.92	19.966	132.70
25.133	134.07	25.105	130.91
30.206	132.50	30.008	129.45
34.946	131.15	35.001	128.07
40.213	129.75	40.117	126.75
45.882	128.41	45.994	125.42

Bu ₄ NPh ₄ B	
4.611	112.99
7.030	111.33
10.002	109.66
15.002	107.37
19.568	105.61
25.666	103.60
30.106	102.30
34.413	101.14
40.121	99.73
45.001	98.62

Table 3. Derived Conductivity Parameters for Tetaalkyammonium Bromides in Methanol + Acetonitrile Mixtures at 298.15 K

x	$\Lambda^0 / \text{S.cm}^2.\text{mol}^{-1}$	$K_{\Lambda} / \text{dm}^{-3}.\text{mol}^{-1}$	R/Å	$100\sigma / \Lambda^0$
		Et ₄ NBr		
0.00	117.04 ± 0.01 (117.01 ^a)	35.77 (26.12 ^a)	17.00	0.01
0.20	142.80 ± 0.02	34.17	16.90	0.02
0.40	163.21 ± 0.01	32.72	16.30	0.01
0.60	174.67 ± 0.01	31.77	16.20	0.01
0.80	180.61 ± 0.01	30.78	16.10	0.01
1.00	185.53 ± 0.01	29.38	15.80	0.01
		Pr ₄ NBr		
0.00	102.61 ± 0.01 (102.61 ^a)	35.51 (28.69 ^a)	17.50	0.01
0.20	127.53 ± 0.01	33.35	16.50	0.01
0.40	146.58 ± 0.02	32.07	16.30	0.02
0.60	158.22 ± 0.01	31.14	16.10	0.01
0.80	164.08 ± 0.01	30.30	16.00	0.01
1.00	171.11 ± 0.02 (170.60 ^a)	28.76 (25.89 ^a)	15.80	0.02
		Bu ₄ NBr		
0.00	95.45 ± 0.01 (95.48 ^a)	35.01 (29.34 ^a)	17.00	0.02
0.20	118.92 ± 0.01	32.56	16.40	0.01
0.40	137.63 ± 0.03	31.23	16.30	0.03
0.60	148.22 ± 0.01	27.97	16.00	0.01
0.80	155.00 ± 0.01	28.87	15.90	0.01
1.00	162.08 ± 0.02 (162.26 ^a)	27.17 (20.60 ^a)	15.60	0.02

Pen ₄ NBr					
0.00	91.50 ± 0.01 (91.47 ^a)	33.18 (30.98 ^a)	16.60	0.02	
0.20	114.26 ± 0.01	32.34	16.80	0.02	
0.40	132.48 ± 0.03	30.58	16.10	0.01	
0.60	143.77 ± 0.02	29.46	16.10	0.02	
0.80	149.41 ± 0.01	28.39	16.00	0.01	
1.00	156.54 ± 0.02	26.59	15.60	0.02	
Hex ₄ NBr					
0.00	86.75 0.01	34.43	16.70	0.02	
0.20	143.96 0.01	32.06	16.80	0.02	
0.40	138.01 0.01	30.31	16.30	0.01	
0.60	127.63 0.01	29.12	16.10	0.01	
0.80	110.66 0.01	27.70	15.90	0.01	
1.00	151.44 0.02	25.86	15.50	0.02	
Hep ₄ NBr					
0.00	84.79 0.01	34.20	17.10	0.02	
0.20	106.48 0.01	30.39	16.50	0.01	
0.40	123.49 0.02	29.65	16.20	0.01	
0.60	134.16 0.01	28.31	16.00	0.01	
0.80	139.93 0.01	26.95	15.80	0.01	
1.00	147.85 0.02	25.11	15.60	0.02	
Bu ₄ NPh ₄ B					
0.00	75.24 0.02(75.92)	72.98 (71.61)	19.80	0.02	
0.20	93.85 0.01	60.35	18.00	0.01	
0.40	108.97 0.03	53.79	18.00	0.01	
0.60	117.02 0.01	48.61	17.60	0.01	
0.80	121.90 0.01	44.65	17.20	0.01	
1.00	120.10 0.01	33.31	16.30	0.01	
	119.40 ^e , 119.26 ^d , 119.46 ^e , 119.44 ^f , 120.02	26.15 ^a , 20.19 ^b , 22.78 ^c , 21.73 ^d , 15.47 ^d			

^aref.23. ^bref.26. ^cref.25. ^dref.27. ^eref.24. ^fref.28.

Table 4. Limiting Ionic Conductances (λ_{\pm}^0) in Methanol + Acetonitrile Mixtures at 298.15 K

ion	x					
	0.00	0.20	0.40	0.60	0.80	1.00
Et ₄ N ⁺	59.62	72.39	81.91	86.94	88.62	85.53
Pr ₄ N ⁺	45.26	57.12	65.28	70.49	72.09	71.11
Bu ₄ N ⁺	38.89	48.51	56.33	60.49	63.01	62.08
Pen ₄ N ⁺	34.78	43.85	51.18	56.04	57.42	56.54
Hex ₄ N ⁺	30.77	40.25	46.33	50.28	51.96	51.44
Hep ₄ N ⁺	28.81	36.07	42.19	46.43	47.94	47.85
Ph ₄ B ⁻	36.35	45.34	52.64	56.53	58.89	58.02
Br ⁻	55.98	70.41	81.30	87.73	91.99	100.00