CHAPTER IX

Viscosities of Some Symmetrical Tetraalkylammonium Salts in Methanol and Methanol + Acetonitrile Mixtures at 298.15, 308.15 and 318.15 K

Introduction

Studies on the transport properties of eletrolytic solutions give very useful information about ion-ion and ion-solvent interactions. One method employed for these investigations is to study the solution viscosity. Viscometry is one of the important tools for the determination of ion-solvent interactions which are the controlling forces in dilute solutions where ion-ion interactions are absent[1]. The variation of solvational properties are reflected in the viscosity B-coefficients of the ions. Viscometric methods have been increasingly used by various workers[2-23] to explore the behavior of electrolytes in pure nonaqueous solvents as well as in their binary mixtures with water or other organic solvents although such studies in nonaqueous + nonaqueous solvent mixtures are, however, relatively scarce. These studies have highlighted the variations in the behavior of electrolytes in different solvent mixtures and the structural changes that are associated with the addition of one solvent to the other.

These considerations have led us to study the viscometric behavior of some tetraalkylammonium salts e.g., tetraethylammonium bromide (Et_4NBr), tetrapropylammonium bromide (Pr_4NBr), tetrabutylammonium bromide (Bu_4NBr), tetrapentylammonium bromide (Pen_4NBr), tetrahexylammonium bromide (Hex_4NBr), and tetraheptylammonium bromide (Hep_4NBr) along with a reference electrolyte tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) in methanol and methanol+acetonitrile mixtures containing 0.20, 0.40, 0.60, and 0.80 mole fractions of acetonitrile at 298.15, 308.15, and 318.15 K

The results of these investigations are presented in this chapter.

Experimental

The purifications of the solvents methanol and acetonitrile and those of the electrolytes have been described in chapter II.

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

The densities. ρ, 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 triply distilled water and benzene. The temperature of the bath was controlled to ± 0.01 K. Details have been described earlier (chapter II). The reproducibility of the density measurements was ± (3 x 10^{-5}) $g.cm^{-3}$.

The kinematic viscosities, ν, were measured by means of a suspended Ubbelohde viscometer. The time of efflux was measured with a stopwatch to ± 0.1 s. The viscometer was kept in vertical position in a water thermostat controlled to ± 0.01 K. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge. The efflux time for water at 298.15 K was about 540 s. The kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equations :

$$\nu = Ct - K/t \qquad (1)$$

$$\eta = \nu\rho \qquad (2)$$

where t is the efflux time, ρ is the density, and C and K are the characteristic constants of the viscometer. The values of the constants C and K determined by using the density and viscosity values of water and benzene were found[16] to be 1.648 x 10^{-5} $cm^2 .s^{-2}$ and –0.02331647 cm^2, respectively. The calibration constants were also checked with purified methanol and acetonitrile used in this study. The estimated error of the viscosity measurements was ± 0.1%.

In all cases the experiments were performed at least in five replicates for each composition and at each temperature. and the results were averaged.

The experimental values of densities (ρ_o), viscosities (η_o), and the relative permittivities (ε) of methanol+acetonitrile mixtures at the temperatures of investigation are not available at the relevant compositions in which conductance measurements have been carried out. The available values of ρ_o and η_o at 298.15, 308.15 K and 318.15 K (from chapter V) and those of ε at 298.15 K (from Gill and Chauhan[24]) are, therefore, plotted against the mole fraction of methanol, and the values of and (at 298.15, 308.15, 318.15 K) and those of ε (at 298.15) at all the desired compositions have been generated from the smooth master curves and are given in Table 1. The relative permittivities of the mixed solvents at 308.15 and 318.15 K were calculated in accordance with Pal and Bagchi[25], using the literature relative permittivity values for the pure solvents at those temperatures[26,27].

Results

The relative viscosity (η_r) and the density (ρ) data for the electrolyte solutions as functions of molar concetration (c) in metanol+acetonitrile mixtures at 298.15, 308.15, and 318.15 K are given in Table 2. The viscosity data of the electrolytes were analysed by the Jones-Dole equation as described in the literature[19].

$$\eta_r = 1 + A c^{1/2} + B c \qquad (3)$$

where A and B, the characteristic parameters for salt and solvent, depend on ion-ion and ion-solvent interaction respectively.

The plots of $(\eta_r - 1) / c^{1/2}$ Versus $c^{1/2}$ were found to be linear in all cases over the whole concentration range of the electrolytes studied. This indicates that ion pairing is not occurring to any great extent in these salt solutions. This is in agreement with our earlier volumetric and conductometric investigations on the behaviour of these salts in methanol+acetonitrile mixtures (chapters VI and VIII). The A values were calculated theoretically from the physical parameters of the solvent and the limiting ionic equivalent conductances using the Falkenhagen and Vernon equation

$$A_{theo} = \frac{0.2577\Lambda^0}{\eta_0 (\varepsilon T)^{0.5} \lambda^0_+ \lambda^0_-} \left[1 - 0.6863 \left(\frac{\lambda^0_+ - \lambda^0_-}{\Lambda^0} \right)^3 \right] \qquad (4)$$

as described earlier by us[16]. A_{theo} - values at 298.15 K reported in Table 3 were calculated according to eq. (3) using the ε and η_0 values from Table 1 and conductometric data from our earlier work (chapter VIII).

The viscosity B-coefficients were obtained by the method of least-squares from eq (3) using the theoretical A values. In view of weak temperature dependence of the A-coefficients in many solvents[10,28,29] and non-availability of limiting ionic conductances at different temperatures, the A values at 298.15 K have been utilised at other temperatures. The viscosity B-coefficients obtained at various temperatures are given in Table 4. The available literature data[7,30,31] for B-coefficients are also included in this table for comparison.

The viscosity data have also been analysed on the basis of the transition-state treatment of the relative viscosity of electrolyte solutions as suggested by Feakins et al.,[33]

$$B = \frac{\nabla_1^0 - \nabla_2^0}{1000} + \frac{\nabla_1^0}{1000}\left(\frac{\Delta\mu_2^{0*} - \Delta\mu_1^{0*}}{RT}\right) \qquad (5)$$

In the above equation ∇_1^0 and ∇_2^0 are the partial molar volumes of solvent and solute, respectively. $\Delta\mu_2^{0*}$, the contribution per mole of solute to the free energy of activation for viscous flow of the solution, has been determined from the above relationship and are reported in Table 5. $\Delta\mu_1^{0*}$, the free energy of activation per mole of pure solvent is given by the equation [24].

$$\Delta\mu_1^{0*} = \Delta G_1^{0*} = RT \ln (\eta_0 \nabla_1^0 / hN) \qquad (6)$$

where N is the Avogadro's number.

Discussion

The viscosity B–coefficients (Table 4) for all the electrolytes are large and positive and increase as we go from Et_4NBr through Hep_4NBr over the investigated temperature range in methanol as well as in its binary mixtures with acetonitrile. As can be seen from this table that over values for Et_4NBr, Pr_4NBr and Bu_4NBr in methanol are in excellent agreement with those reported by Kay *et. al.*,[30,31]; the B-coefficients for Et_4NBr and Pr_4NBr at 298.15 K from ref. 31 appear to be slightly higher. Only Bu_4NBr and Bu_4NBr have been studied in methanol+acetonitrile mixtures at 298.15 K[7]. Agreement is good for mixtures rich in methanol.

The ionic B values were calculated using Bu_4NBPh_4 as the "reference electrolyte" from the following equation[20] :

$$B\,(Bu_4NBPh_4) = B\,(Bu_4N^+) + B\,(Ph_4B^-) \qquad (7)$$

$$B\,(Ph_4B^-) \,/\, B\,(Bu_4N^+) = (5.35/5.00)^3 \qquad (8)$$

The ionic B values obtained from the above relationship are given in Table 6. This Table shows that the viscosity B-coefficients for cations and anions are positive and are also very high. The observed order of the ionic B values for the tetraalkylammonium ions are:

$$Hep_4N^+ > Hex_4N^+ > Pen_4N^+ > Bu_4N^+ > Pr_4N^- > Et_4N^+$$

This indicates that the obstruction of the solvent viscous flow increases with decrease in the charge density on these ions.

The variation of the ionic B values with temperature provides important insight as to the ion-solvent interactions. Table shows that the ionic B values show weak temperature dependence. For all the ions (with the exception of the tetraethylammonium ion) the B values decrease with rise of temperature in all methanol+acetonitrile binary mixtures, whereas in pure methanol an opposite trend is observed. For Et_4N^+ ion, on the other hand dB_i / dT is

found to be positive in methanol+acetonitrile mixtures rich in methanol and negative in the acetonitrile rich region. According to Kaminsky[34], the decrease in the $B_{\pm}$ values with the rise of temperature may be interpreted to mean that the $B_{\pm}$ values may include a contribution from long range structure promotion (arising mainly from the interactions of alkyl groups and solvent molecules for tetraalkylammonium ions) that inevitably diminishes at higher temperatures and results in negative $dB_{\pm}/dT$ values. The positive $dB_{\pm}/dT$ values, on the other hand, indicate structure breaking properties of the ions in the relevant solvent medium.

Analysis of the ionic B-coefficients have also been attempted on the basis of Einstein's equation as described earlier[16]

$$B_{\pm} = 2.5 \frac{4}{3} \pi \frac{R_{\pm}^{3} N}{1000} \qquad (9)$$

where $R_{\pm}$ is the radius of the ion assumed to be a rigid sphere moving in a continuum and 2.5 is the shape factor for a sphere. The values of $R_{\pm}$ are shown in Table 7.

The $R_{\pm}$ values for tetraalkylammonium and tetraphenylborate ions are found to be very much smaller compared to their crystallographic radii (Table 7), particularly in methanol and methanol+acetonitrile mixtures rich in methanol. This is physically unaccepatable. They seem to indicate that the ionic radii estimated on the basis of Einstein's equation do not appear to be correct for these solutions. This probably arises from the fact that the electrolytic solutions are different from the model which underlies the above equation.

Table 8 shows that the values of $\Delta\mu_2^{0\neq}$ for all the ions are positive whereas the ionic $\Delta H_2^{0\neq}$ and $T\Delta S_2^{0\neq}$ values are found to be negative. Positive $\Delta\mu_2^{0\neq}$ values suggest that the formation of the transition state is made less favourable by the presence of these ions and the negative values of $\Delta H_2^{0\neq}$ and $T\Delta S_2^{0\neq}$ indicate that the formation of the transition state is associated with bond making and an increase in order. It is interesting to note that $\Delta\mu_2^{0\neq}$, $\Delta H_2^{0\neq}$ and $T\Delta S_2^{0\neq}$ values for Ph_4B^- ion are higher than those for the Bu_4N^+ ion in spite of the fact that these two ions are almost isostructural and Ph_4B^- ion is unlikely to be highly solvated owing to its low surface charge density. However, analogous result to that observed in methanol+acetonitrile mixtures has been found in other pure and mixed solvents also[5,35].

The variation of the ionic B-coefficients with the solvent composition indicates that the obstruction of the viscous flow of the solvent increases upto a mole fraction of methanol in the neighborhood of 0.4 -0.2 followed by a decrease upto pure methanol. The changes in the viscosity B-Coefficients of the ions can be attributed to a number of factors :

(1) changes in solvation from acetonitrile to methanol at the maximum of $B_{\pm}$ vs. composition curve as methanol is added. This could explain the increase in ionic B-coefficients, but not the maxima.

(2) the ionic charge can affect the viscosity of the solvent in the ionic cosphere by breaking or increasing solvent structure.

(3) the ionic charge can change the solvent composition in the ionic cosphere by selectively interacting with the solvent components.

Futher measurements on these solvent systems are required before these different effects can be substantiated.

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

Property	× = 0.00	× = 0.20	× = 0.40	× = 0.60	× = 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
ε	32.62	33.58	34.30	34.92	35.47
$\Delta\mu_1^{0\neq}$ / kJmol^{-1}	9.96	9.54	9.29	9.21	9.27
			T = 308.15 K		
ρ_0 / g.cm^{-3}	0.77718	0.77747	0.77515	0.77211	0.76896
η_0 / mPa.s	0.474	0.395	0.340	0.314	0.305
ε	30.74	31.80	32.64	33.36	33.99
$\Delta\mu_1^{0\neq}$ / kJmol^{-1}	9.97	9.64	9.40	9.33	9.39
			T = 318.15 K		
ρ_0 / g.cm^{-3}	0.76774	0.76808	0.76560	0.76216	0.75863
η_0 / mPa.s	0.419	0.361	0.312	0.289	0.280
ε	28.92	30.99	31.02	31.82	32.51
$\Delta\mu_1^{0\neq}$ / kJmol^{-1}	10.00	9.75	9.51	9.45	9.50

Table 2. Concentration (c), Density (ρ) and Relative viscosity (η_r) of Tetraalkylammonium Bromides and Tetrabutylammonium Tetraphenylborate in Methanol + Acetonitrile Mixtures at 298.15, 308.15 and 318.15 K.

c / mol^{-1}. dm^{-3}	ρ / gcm^{-3}	η_r	c / mol^{-1}. dm^{-3}	ρ /gcm^{-3}	η_r
		298.15 K			
		x = 0.00			
	Et_4NBr			Pr_4NBr	
0.00780	0.78726	1.0051	0.00787	0.78727	1.0069
0.01572	0.78798	1.0095	0.01563	0.78798	1.0127
0.01960	0.78833	1.0116	0.01959	0.78834	1.0156
0.02349	0.78868	1.0137	0.02345	0.78869	1.0184
0.02740	0.78903	1.0157	0.02733	0.78904	1.0212
0.03132	0.78938	1.0178	0.03123	0.78939	1.0240
0.03526	0.78973	1.0199	0.03513	0.78974	1.0268
0.03909	0.79007	1.0218	0.03893	0.79008	1.0295
0.04691	0.79076	1.0259	0.04668	0.79077	1.0350
0.05077	0.79110	1.0279	0.05052	0.79111	1.0377
	Bu_4NBr			Pen_4NBr	
0.00788	0.78730	1.0084	0.00783	0.78728	1.0094
0.01564	0.78804	1.0156	0.01563	0.78801	1.0077
0.01954	0.78841	1.0192	0.01951	0.78837	1.0218
0.02347	0.78878	1.0228	0.02340	0.78873	1.0259
0.02729	0.78914	1.0263	0.02729	0.78909	1.0299
0.03112	0.78950	1.0297	0.031090	0.78944	1.0339
0.03507	0.78987	1.0333	0.03490	0.78979	1.0378
0.03893	0.79023	1.0367	0.03873	0.79014	1.0417
0.04655	0.79094	1.0435	0.04638	0.79084	1.0496
0.05033	0.79129	1.0469	0.05023	0.79119	1.0535

Hex_4NBr			Hep_4NBr		
0.00787	0.78730	1.0111	0.00779	0.78730	1.0124
0.01561	0.78804	1.0208	0.01564	0.78806	1.0237
0.01951	0.78841	1.0257	0.01949	0.78843	1.0292
0.02340	0.78878	1.0305	0.02333	0.78880	1.0346
0.02721	0.78914	1.0352	0.02720	0.78917	1.0400
0.03102	0.78950	1.0399	0.03097	0.78953	1.0453
0.03485	0.78986	1.0445	0.03474	0.78989	1.0506
0.03869	0.79022	1.0492	0.03852	0.79025	1.0558
0.04627	0.79093	1.0584	0.046100	0.79097	1.0663
0.05002	0.79128	1.0630	0.04980	0.79132	1.0715

Bu_4NBPh_4		
0.00786	0.78683	1.0114
0.01552	0.78712	1.0214
0.01941	0.78726	1.0263
0.02332	0.78740	1.0313
0.02706	0.78753	1.0360
0.03079	0.78766	1.0407
0.03456	0.78779	1.0454
0.03837	0.78792	1.0501
0.04609	0.78818	1.0597
0.04969	0.78830	1.0642

x = 0.20

Et_4NBr			Pr_4NBr		
0.00437	0.78721	1.0033	0.00364	0.78714	1.0036
0.00845	0.78758	1.0058	0.00818	0.78756	1.0073
0.01636	0.78830	1.0106	0.01155	0.78787	1.0099
0.02001	0.78863	1.0127	0.01603	0.78828	1.0133
0.02434	0.78902	1.0152	0.01965	0.78861	1.0161
0.02746	0.78930	1.0171	0.02505	0.78910	1.0201
0.03126	0.78964	1.0193	0.02715	0.78929	1.0217
0.03552	0.79002	1.0217	0.03125	0.78966	1.0247
0.03957	0.79038	1.0240	0.03514	0.79001	1.0276
0.04397	0.79077	1.0265	0.03826	0.79029	1.0299
0.04725	0.79106	1.0284	0.04216	0.79061	1.0328
0.05122	0.79141	1.0307	0.04665	0.79104	1.0361

Bu_4NBr			Pen_4NBr		
0.00423	0.78721	1.0050	0.00400	0.78718	1.0053
0.00839	0.78761	1.0093	0.00718	0.78748	1.0089
0.01299	0.78805	1.0138	0.01283	0.78801	1.0151
0.01719	0.78845	1.0179	0.01690	0.78839	1.0195
0.02035	0.78875	1.0210	0.01937	0.78862	1.0222
0.02394	0.78909	1.0245	0.02314	0.78897	1.0262
0.02945	0.78961	1.0297	0.03201	0.78979	1.0356
0.03115	0.78977	1.0314	0.03516	0.79008	1.0389
0.03530	0.79016	1.0353	0.03886	0.79042	1.0428
0.03946	0.79055	1.0393	0.04224	0.79073	1.0464
0.04288	0.79087	1.0425	0.04683	0.79115	1.0512
0.04738	0.79129	1.0468	0.05165	0.79159	1.0562

Hex_4NBr

0.00412	0.78720	1.0062
0.0775	0.78755	1.0971
0.01537	0.78828	1.0207
0.02167	0.78888	1.0286
0.02325	0.78903	1.0306
0.02652	0.78934	1.0346
0.03022	0.78969	1.0392
0.03499	0.79014	1.0451
0.03837	0.79026	1.0492
0.04105	0.79071	1.0526
0.04789	0.79134	1.0610

Hep_4NBr

0.00563	0.78735	1.0093
0.00769	0.78755	1.0124
0.01234	0.78800	1.0192
0.01545	0.78830	1.0237
0.01992	0.78873	1.0301
0.02336	0.78906	1.0350
0.02733	0.78944	1.0407
0.03089	0.78978	1.0457
0.03845	0.79050	1.0564
0.04203	0.79084	1.0614
0.04664	0.79126	1.0679
0.05037	0.79163	1.0731

Bu_4NBPh_4

0.00786	0.78711	1.0124
0.01549	0.78740	1.0231
0.01950	0.78755	1.0286
0.02329	0.78769	1.0338
0.02712	0.78783	1.0390
0.03099	0.78797	1.0443
0.03461	0.78810	1.0491
0.03854	0.78824	1.0544
0.04594	0.78850	1.0644
0.05043	0.78863	1.0704

x = 0.40

Et_4NBr			Pr_4NBr		
0.00461	0.78508	1.0039	0.00426	0.78505	1.0045
0.00829	0.78542	1.0069	0.00802	0.78540	1.0078
0.01210	0.78577	1.0094	0.01191	0.78576	1.0111
0.01549	0.78608	1.0117	0.01473	0.78602	1.0135
0.02319	0.78678	1.0169	0.01952	0.78646	1.0174
0.02695	0.78712	1.0194	0.02500	0.78696	1.0219
0.03139	0.78752	1.0224	0.03302	0.78769	1.0284
0.03550	0.78789	1.0251	0.03567	0.78793	1.0305
0.04009	0.78830	1.0281	0.03910	0.78824	1.0333
0.04233	0.78850	1.0296	0.04276	0.78857	1.0362
0.04727	0.78894	1.0328	0.04665	0.78892	1.0393
0.05121	0.78929	1.0354	0.05054	0.78927	1.0424

Bu_4NBr			Pen_4NBr		
0.00399	0.78504	1.0049	0.00396	0.78503	1.0053
0.00770	0.78540	1.0089	0.00858	0.78547	1.0106
0.01257	0.78587	1.0140	0.01312	0.78590	1.0157
0.01517	0.78612	1.0166	0.01545	0.78612	1.0182
0.02070	0.78665	1.0223	0.01906	0.78646	1.0222
0.02426	0.78699	1.0259	0.02599	0.78711	1.0298
0.02762	0.78731	1.0292	0.02739	0.78724	1.0313
0.03455	0.78775	1.0362	0.03027	0.78751	1.0344
0.03911	0.78841	1.0407	0.03424	0.78788	1.0387
			0.03865	0.78829	1.0434
			0.04307	0.78870	1.0482
			0.04696	0.78906	1.0523
			0.5064	0.78940	1.0563

Hex_4NBr			Hep_4NBr		
0.00378	0.78502	1.0059	0.00366	0.78502	1.0065
0.00839	0.78547	1.0121	0.00985	0.78562	1.0159
0.01293	0.78591	1.0180	0.01209	0.78584	1.0192
0.01531	0.78614	1.0211	0.01579	0.78620	1.0246
0.01915	0.78651	1.0260	0.01949	0.78656	1.0300
0.02380	0.78695	1.0319	0.02320	0.78692	1.0354
0.02707	0.78727	1.0361	0.02702	0.78729	1.0410
0.03073	0.78762	1.0407	0.03116	0.78769	1.0469
0.03335	0.78787	1.0440	0.03479	0.78804	1.0521
0.03860	0.78837	1.0506	0.03853	0.78840	1.0575
0.04239	0.78873	1.0554	0.04186	0.78872	1.0622
0.04682	0.78915	1.0609	0.04676	0.78919	1.0692
0.04925	0.78938	1.0639	0.04958	0.78946	1.0733

Bu_4NBPh_4		
0.00775	0.78499	1.0126
0.01553	0.78532	1.0239
0.01936	0.78548	1.0295
0.02324	0.78564	1.0350
0.03083	0.78595	1.0406
0.03455	0.78610	1.0511
0.03829	0.78625	1.0563
0.04586	0.78655	1.0670
0.04968	0.78670	1.0723

$x_2 = 0.60$

	Et_4NBr			Pr_4NBr	
0.00456	0.78255	1.0042	0.00422	0.78252	1.0044
0.00639	0.78272	1.0056	0.00805	0.78288	1.0079
0.01253	0.78329	1.0102	0.01265	0.78331	1.0119
0.01665	0.78367	1.0132	0.01512	0.78354	1.0141
0.02024	0.78400	1.0157	0.01695	0.78371	1.0156
0.02450	0.78439	1.0188	0.01943	0.78394	1.0177
0.02702	0.78462	1.0206	0.02355	0.78432	1.0213
0.03461	0.78531	1.0259	0.02799	0.78473	1.0250
0.03925	0.78573	1.0291	0.03180	0.78508	1.0282
0.04224	0.78600	1.0312	0.03573	0.78544	1.0304
0.04646	0.78638	1.0342	0.03945	0.78578	1.0346
0.05069	0.78676	1.0371	0.04274	0.78608	1.0374

	Bu_4NBr			Pen_4NBr	
0.00426	0.78254	1.0054	0.00474	0.78258	1.0064
0.00763	0.78287	1.0091	0.00806	0.78290	1.0103
0.01122	0.78322	1.0129	0.01181	0.78326	1.0146
0.01606	0.78369	1.0180	0.01505	0.78357	1.0182
0.01947	0.78402	1.0216	0.01935	0.78398	1.0230
0.02320	0.78438	1.0255	0.02324	0.78435	1.0274
0.02746	0.78479	1.0299	0.02767	0.78477	1.0320
0.03121	0.78515	10337	0.03063	0.78505	1.0355
0.03600	0.78558	10.386	0.03508	0.78547	1.0404
0.03905	0.78590	1.0417	0.03876	0.78581	1.0444
0.04314	0.78629	1.0459	0.04252	0.78617	1.0485
0.0787	0.78674	1.0507	0.04860	0.78674	1.0552

Hex_4NBr

0.00352	0.78247	1.0056
0.00822	0.78293	1.0120
0.0113	0.78322	1.0161
0.01603	0.78370	1.0223
0.01941	0.78403	1.0267
0.02362	0.78444	1.0321
0.02743	0.78481	1.0370
0.03135	0.78519	1.0420
0.03466	0.78551	1.0462
0.03870	0.78590	1.0513
0.04306	0.78630	1.0569
0.04618	0.78662	1.0608
0.04993	0.78698	1.0655

Hep_4NBr

0.01537	0.78365	1.0242
0.01618	0.78373	1.0254
0.01912	0.78402	1.0298
0.02247	0.78435	1.0347
0.02644	0.78474	1.0441
0.03052	0.78514	1.0464
0.03471	0.78555	1.0525
0.03727	0.78580	1.0562
0.03973	0.78604	1.0598
0.04093	0.78627	1.0615
0.04620	0.78667	1.0691
0.04939	0.78698	1.0737

Bu_4NBPh_4

0.00772	0.78248	1.0128
0.01544	0.78283	1.0244
0.01926	0.78300	1.0301
0.02697	0.78334	1.0414
0.03064	0.78350	1.0443
0.03457	0.78367	1.0524
0.03829	0.78383	1.0578
0.04580	0.78415	1.0686
0.04936	0.78430	1.0738

x =0.80

Et_4NBr			Pr_4NBr		
0.0075	0.78025	1.0065	0.01176	0.78066	1.0108
0.01561	0.78103	1.0128	0.01666	0.78113	1.0149
0.02011	0.78146	1.0162	0.01959	0.78141	1.0173
0.02505	0.78193	1.0199	0.02526	0.78195	1.0219
0.02758	0.78217	1.0218	0.02842	0.78225	1.0245
0.03170	0.78256	1.0249	0.03127	0.78252	1.0268
0.03456	0.78283	1.0270	0.03476	0.78285	1.0296
0.04019	0.78336	1.0312	0.03847	0.78320	1.0326
0.04200	0.78358	1.0325	0.04272	0.78360	1.0361
0.04616	0.78392	1.0356	0.04486	0.78380	1.0378

Bu_4NBr			Pen_4NBr		
0.01017	0.78054	1.0117	0.00849	0.78038	1.0104
0.01238	0.78076	1.0140	0.01227	0.78076	1.0145
0.01530	0.78105	1.0170	0.02107	0.78164	1.0241
0.01944	0.78146	1.0213	0.02368	0.78190	1.0269
0.02349	0.78186	1.0254	0.02720	0.78225	1.0305
0.02745	0.78225	1.0294	0.03204	0.78273	1.0359
0.03142	0.78217	1.0334	0.03406	0.78293	1.0380
0.03499	0.78299	1.0370	0.03831	0.78335	1.0425
0.03918	0.78340	1.0412	0.04135	0.78365	1.0457
0.04215	0.78369	1.0442	0.04531	0.78404	1.0499
0.04615	0.78408	1.0482	0.04714	0.78422	1.0519
0.05026	0.78448	1.0523			

	Hex_4NBr	
0.00400	0.77993	1.0059
0.00830	0.78037	1.0114
0.01125	0.78067	1.0150
0.01559	0.78111	1.0204
0.01925	0.78148	1.0249
0.02292	0.78185	1.0293
0.02819	0.78238	1.0357
0.03108	0.78267	1.0392
0.04048	0.78361	1.0505
0.04419	0.78398	1.0549
0.04851	0.78441	1.0601

	Hep_4NBr	
0.00848	0.78040	1.0137
0.01168	0.78073	1.0184
0.01557	0.78113	1.0240
0.01905	0.78149	1.0290
0.02338	0.78193	1.0352
0.02818	0.78242	1.0420
0.03083	0.78269	1.0458
0.03427	0.78304	1.0506
0.03811	0.78343	1.0560
0.04166	0.78379	1.0610
0.04561	0.78417	1.0665
0.05026	0.78466	1.0720

	Bu_4NBPh_4	
0.00787	0.77991	1.0128
0.01554	0.78028	1.0240
0.01924	0.78046	1.0270
0.02303	0.78064	1.0348
0.02685	0.78082	1.0403
0.03069	0.78100	1.0458
0.03435	0.78117	1.0510
0.03824	0.78135	1.0565
0.04567	0.78169	1.0670
0.04918	0.78184	1.0747

308.15 K

x_2 = 0.00

Et_4NBr			Pr_4NBr		
0.00778	0.77790	1.0053	0.00780	0.77791	1.0070
0.01549	0.77860	1.0097	0.01547	0.77862	1.0128
0.01936	0.77895	1.0119	0.01939	0.77898	1.0157
0.02325	0.77930	1.0140	0.02322	0.77933	1.0857
0.02705	0.77964	1.0161	0.02706	0.77968	1.0214
0.03097	0.77999	1.0182	0.03091	0.78003	1.0242
0.03479	0.78033	1.0202	0.03466	0.78037	1.0269
0.03863	0.78067	1.0223	0.03854	0.78072	1.0297
0.04633	0.78135	1.0264	0.04611	0.78140	1.0352
0.05008	0.78168	1.0284	0.04990	0.78174	1.0379

Bu_4NBr			Pen_4NBr		
0.00772	0.77791	1.0085	0.00775	0.77793	1.0094
0.01543	0.77863	1.0159	0.01550	0.77867	1.0177
0.01930	0.77899	1.0196	0.01928	0.77903	1.0218
0.02319	0.77935	1.0232	0.02309	0.77939	1.0258
0.02698	0.77970	1.02670	0.02690	0.77975	1.0298
0.03079	0.78005	1.0302	0.03072	0.78011	1.0338
0.03460	0.78040	1.0337	0.03455	0.78047	1.0377
0.03843	0.78075	1.0372	0.03828	0.78082	1.0416
0.04600	0.78144	1.0441	0.04588	0.78153	1.0495
0.04974	0.78178	1.0475	0.04964	0.78188	1.0533

Hex_4NBr			Hep_4NBr		
0.00770	0.77793	1.0109	0.00770	0.77794	1.0124
0.01548	0.77868	1.0208	0.01547	0.77870	1.0236
0.01923	0.77904	1.0255	0.01927	0.77907	1.0290
0.02310	0.77941	1.0303	0.02309	0.77944	1.0345
0.02687	0.77977	1.0350	0.02681	0.77980	1.0397
0.03066	0.78013	1.0397	0.03064	0.78017	1.0451
0.03445	0.78049	1.0443	0.03439	0.78053	1.0504
0.03815	0.78084	1.0489	0.03813	0.78089	1.0556
0.04568	0.78155	1.0581	0.04555	0.78160	1.0660
0.04940	0.78190	1.0626	0.04921	0.78195	1.0710

Bu_4NBPh_4		
0.00775	0.77749	1.0113
0.01529	0.77778	1.0212
0.01925	0.77793	1.0262
0.02299	0.77807	1.0310
0.02678	0.77821	1.0358
0.03060	0.77835	1.0406
0.03418	0.77848	1.0451
0.03807	0.77862	1.0500
0.04670	0.77888	1.0607
0.04909	0.77901	1.0637

$x = 0.20$

Et_4NBr			Pr_4NBr		
0.0078	0.77819	1.0058	0.00778	0.77820	1.0071
0.01547	0.77889	1.0107	0.01554	0.77892	1.0132
0.01934	0.77924	1.0131	0.01934	0.77927	1.0161
0.02322	0.77959	1.0154	0.02315	0.77962	1.0190
0.02712	0.77994	1.0178	0.02708	0.77998	1.0220
0.03092	0.78028	1.0201	0.03093	0.78033	1.0249
0.03474	0.78062	1.0223	0.03467	0.78067	1.0277
0.03867	0.78099	1.0247	0.03853	0.78102	1.0305
0.04635	0.78165	1.0292	0.04617	0.78171	1.0362
0.05010	0.78198	1.0314	0.04995	0.78205	1.0390

Bu_4NBr			Pen_4NBr		
0.00768	0.77821	1.0088	0.00770	0.77821	1.0095
0.01548	0.77894	1.0166	0.01549	0.77895	1.0181
0.01931	0.77930	1.0203	0.01930	0.77931	1.0222
0.02316	0.77966	1.0241	0.02312	0.77967	1.0263
0.02701	0.78002	1.0278	0.02695	0.78003	1.0304
0.03077	0.78037	1.0314	0.03079	0.78039	1.0345
0.03465	0.78073	1.0352	0.03454	0.78074	1.0385
0.03843	0.78108	1.0388	0.03829	0.78109	1.0424
0.04602	0.78178	1.0460	0.04582	0.78179	1.0504
0.04983	0.78213	1.0496	0.04960	0.78214	1.0544

Hex_4NBr			Hep_4NBr		
0.00779	0.77823	1.0111	0.00770	0.77823	1.0124
0.01546	0.77897	1.0209	0.01538	0.77898	1.0236
0.01931	0.77934	1.0258	0.01928	0.77936	1.0293
0.02307	0.77970	1.0305	0.02300	0.77972	1.0346
0.02695	0.78007	1.0353	0.02683	0.78009	1.0400
0.03073	0.78043	1.0401	0.03066	0.78046	1.0455
0.03451	0.78079	1.0447	0.03440	0.78082	1.0508
0.03821	0.78114	1.0493	0.03815	0.78118	1.0561
0.04573	0.78185	1.0586	0.04557	0.78189	1.0665
0.04944	0.78220	1.0632	0.04924	0.78224	1.0717

Bu_4NBPh_4		
0.00770	0.77779	1.0120
0.01542	0.77810	1.0227
0.01922	0.77825	1.0279
0.02303	0.77840	1.0331
0.02668	0.77854	1.0380
0.03427	0.77883	1.0482
0.03798	0.77897	1.0531
0.04548	0.77925	1.0631
0.04900	0.77938	1.0678

χ = 0.40

Et_4NBr			Pr_4NBr		
0.00774	0.77587	1.0063	0.00771	0.77588	1.0075
0.01548	0.77658	1.0116	0.01540	0.77660	1.0139
0.01932	0.77693	1.0142	0.01927	0.77696	1.0171
0.02318	0.77728	1.0168	0.02316	0.77732	1.0203
0.02705	0.77763	1.0194	0.02695	0.77767	1.0233
0.030821	0.77797	1.0219	0.03075	0.77802	1.0264
0.034711	0.77832	1.0244	0.03456	0.77837	1.0294
0.03850	0.77866	1.0269	0.03839	0.77872	1.0325
0.046132	0.77934	1.0319	0.04605	0.77942	1.0385
0.04996	0.77968	1.0343	0.04979	0.77976	1.0415

Bu_4NBr			Pen_4NBr		
0.00779	0.77590	1.0091	0.00773	0.77590	1.0096
0.01545	0.77663	1.0170	1.01544	0.77664	1.0181
0.01925	0.77699	1.0209	0.01921	0.77700	1.0222
0.02305	0.77735	1.0247	0.02310	0.77737	1.0264
0.02687	0.77771	1.0285	0.02689	0.77773	1.0305
0.03070	0.77807	1.0324	0.03068	0.77809	1.0346
0.03454	0.77843	1.0362	0.03450	0.77845	1.0387
0.03829	0.77878	1.0399	0.03821	0.77880	1.0426
0.04590	0.77949	1.0475	0.04576	0.77951	1.0507
0.04967	0.77984	1.0512	0.04949	0.77986	1.0546

Hex_4NBr			Hep_4NBr		
0.00742	0.77591	1.0108	0.00770	0.77592	1.0126
0.01539	0.77666	1.0211	0.01538	0.77668	1.0239
0.01920	0.77703	1.0260	0.01924	0.77706	1.0295
0.02302	0.77740	1.0308	0.02301	0.77743	1.0350
0.02685	0.777777	1.0357	0.02678	0.77780	1.0404
0.03058	0.77813	1.0403	0.03056	0.77817	1.0458
0.03433	0.77849	1.0450	0.03425	0.77853	1.0511
0.03806	0.77883	1.0472	0.03806	0.77890	1.0565
0.04561	0.77957	1.0591	0.04548	0.77962	1.0671
0.04928	0.77994	1.0637	0.04909	0.77997	1.0722

Bu_4NBPh_4		
0.00764	0.77549	1.0124
0.01528	0.77582	1.0235
0.01928	0.77599	1.0293
0.02286	0.77614	1.0344
0.02669	0.77630	1.0398
0.03056	0.77646	1.0453
0.03789	0.77676	1.0556
0.04532	0.77706	1.0660
0.04907	0.77721	1.0712

x = 0.60

Et_4NBr			Pr_4NBr		
0.00768	0.77283	1.0064	0.00765	0.77284	1.0075
0.01536	0.77354	1.0120	0.01538	0.77357	1.0144
0.01928	0.77390	1.0148	0.019220	0.77393	1.0177
0.02310	0.77425	1.0175	0.02307	0.77429	1.0210
0.02691	0.77460	1.0202	0.02683	0.77464	1.0242
0.03078	0.77495	1.0229	0.03070	0.77500	1.0274
0.03454	0.77529	1.0255	0.03448	0.77535	1.0306
0.03841	0.77564	1.0282	0.03826	0.77570	1.0338
0.04596	0.77632	1.0334	0.04585	0.77640	1.0402
0.04975	0.77666	1.0360	0.04967	0.77675	1.0434

Bu_4NBr			Pen_4NBr		
0.00768	0.77286	1.0091	0.00767	0.77287	1.0096
0.01533	0.77360	1.0172	0.01531	0.77362	1.0182
0.01918	0.77397	1.0211	0.01921	0.77400	1.0225
0.02304	0.77434	1.0251	0.02301	0.77437	1.0267
0.02680	0.77470	1.0290	0.02671	0.77473	1.3070
0.03058	0.77506	1.0328	0.03053	0.77510	1.0348
0.03436	0.77542	1.0367	0.03436	0.77547	1.0390
0.03816	0.77578	1.0405	0.03809	0.77583	1.0430
0.04566	0.77649	1.0481	0.04557	0.77655	1.0511
0.04947	0.77685	1.0519	0.04933	0.77691	1.0551

Hex_4NBr			Hep_4NBr		
0.00770	0.77288	1.0111	0.00767	0.77289	1.0127
0.01538	0.77364	1.0211	0.01532	0.77366	1.0241
0.01913	0.77401	1.0259	0.01911	0.77404	1.0296
0.02289	0.77438	1.0306	0.02291	0.77442	1.0349
0.02667	0.77475	1.0354	0.02662	0.77479	1.0406
0.03043	0.77512	1.0376	0.03044	0.77517	1.0461
0.03421	0.77549	1.0449	0.03417	0.77554	1.0515
0.03800	0.77586	1.0497	0.03790	0.77591	1.0569
0.04541	0.77658	1.0539	0.04529	0.77664	1.0675
0.04912	0.77694	1.0635	0.04894	0.77700	1.0727

Bu_4NBPh_4		
0.00775	0.77248	1.0128
0.01529	0.77283	1.0240
0.01900	0.77300	1.0294
0.02274	0.77317	1.0349
0.02653	0.77334	1.0404
0.03032	0.77351	1.0450
0.03414	0.77308	1.0513
0.03779	0.77384	1.0565
0.04511	0.77416	1.0670
0.04880	0.77432	1.0723

x = 0.80

Et_4NBr			Pr_4NBr		
0.00765	0.76969	1.0064	0.00768	0.76971	1.0072
0.01529	0.77041	1.01210	0.01534	0.77045	1.0134
0.01914	0.77077	1.01490	0.01909	0.77081	1.0164
0.02300	0.77113	1.0177	0.02296	0.77118	1.0195
0.02676	0.77148	1.0203	0.02673	0.77154	1.0225
0.03065	0.77184	1.0231	0.03051	0.77190	1.0255
0.03444	0.77219	1.0258	0.03430	0.77226	1.0285
0.03823	0.77254	1.0285	0.03810	0.77262	1.0315
0.04586	0.77324	1.0339	0.04562	0.77333	1.0373
0.04958	0.77358	1.0365	0.04946	0.77369	1.0403

Bu_4NBr			Pen_4NBr		
0.00765	0.76972	1.00880	0.00762	0.76973	1.0091
0.01526	0.77047	1.0165	0.01532	0.77050	1.0173
0.01915	0.77085	1.0203	0.01913	0.77088	1.0213
0.02294	0.77122	1.0240	0.02285	0.77125	1.0252
0.02673	0.77159	1.0277	0.02668	0.77163	1.0291
0.03044	0.77195	1.0314	0.03043	0.77200	1.0330
0.03426	0.77232	1.0351	0.03417	0.77237	1.0368
0.03798	0.77268	1.0386	0.03794	0.77274	1.0407
0.04555	0.77341	1.0459	0.04536	0.77347	1.0482
0.04930	0.77377	1.0495	0.04914	0.77384	1.0521

Hex_4NBr

0.00769	0.76975	1.0102
0.0525	0.77052	1.0193
0.01909	0.77091	1.0238
0.02285	0.77129	1.0282
0.02661	0.77167	1.0326
0.03039	0.77205	1.0370
0.03407	0.77242	1.0412
0.3786	0.77280	1.0456
0.04528	0.77354	1.0541
0.04897	0.77391	1.0584

Hep_4NBr

0.00768	0.76976	1.0119
0.01523	0.77054	1.0224
0.01902	0.77093	1.0275
0.02283	0.77132	1.0327
0.02654	0.77170	1.0377
0.03027	0.77208	1.0427
0.03399	0.77246	1.0477
0.03773	0.77284	1.0527
0.04513	0.77359	1.0625
0.04879	0.77396	1.0674

Bu_4NBPh_4

0.00772	0.76936	1.0124
0.01525	0.76974	1.0233
0.01907	0.76993	1.0288
0.02271	0.77011	1.0339
0.02658	0.77030	1.0394
0.03027	0.77048	1.0446
0.03772	0.77084	1.0550
0.04497	0.77119	1.0651
0.04863	0.77136	1.0702

318.15 K

$x = 0.00$

Et_4NBr			Pr_4NBr		
0.00770	0.76845	1.0054	0.00766	0.76846	1.0070
0.01529	0.76914	1.0098	0.01532	0.76917	1.0129
0.01916	0.76949	1.0120	0.01913	0.76952	1.0158
0.02295	0.76983	1.0141	0.02295	0.76987	1.0187
0.02674	0.77017	1.0163	0.02667	0.77021	1.0215
0.03056	0.77051	1.0184	0.03051	0.77056	1.0244
0.03438	0.77085	1.0205	0.03426	0.77090	1.0271
0.03811	0.77118	1.0225	0.03802	0.77124	1.0299
0.04571	0.77185	1.0267	0.04556	0.77192	1.0354
0.04947	0.77218	1.0287	0.04935	077226	1.0382

Bu_4NBr			Pen_4NBr		
0.00771	0.76848	1.0087	0.00769	0.76849	1.0095
0.01528	0.76920	1.0160	0.01527	0.76922	1.0178
0.01910	01.76956	1.0197	0.01928	0.77958	1.0221
0.02293	0.76992	1.0233	0.02279	0.76994	1.0258
0.02666	0.77027	1.0268	0.02658	0.77030	1.0298
0.03040	0.77062	1.0303	0.03037	0.77066	1.0338
0.03416	0.77097	1.0338	0.03412	0.77101	1.0378
0.03792	0.77132	1.0373	0.03787	0.77137	1.0417
0.04547	0.77202	1.0443	0.04531	0.77207	1.0495
0.04916	0.77236	1.0477	0.04904	0.77242	1.0534

Hex_4NBr			Hep_4NBr		
0.00766	0.76850	1.0109	0.00765	0.76851	1.0121
0.01530	0.76925	1.0206	0.01529	0.76927	1.0232
0.01899	0.76961	1.0253	0.01902	0.76964	1.0285
0.02279	0.76998	1.0301	0.02276	0.77001	1.0338
0.02660	0.77035	1.0348	0.02652	0.77038	1.0392
0.03032	0.77071	1.0394	0.03019	0.77076	1.0443
0.03405	0.77107	1.0440	0.03396	0.77111	1.0496
0.03779	0.77143	1.0487	0.03765	0.77147	1.0548
0.04519	0.77217	1.0578	0.04502	0.77219	1.0651
0.04885	0.77249	1.0679	0.04863	0.77254	1.0702

Bu_4NBPh_4		
0.00758	0.76806	1.0113
0.01518	0.76837	1.0213
0.01893	0.76852	1.0262
0.02272	0.76867	1.0311
0.02654	0.76882	1.0360
0.03015	0.76896	1.0406
0.03379	0.76910	1.0452
0.04487	0.76952	1.0593
0.04862	0.76966	1.0640

$x_2 = 0.20$

Et_4NBr			Pr_4NBr		
0.00765	0.76879	1.0057	0.00764	0.76880	1.0069
0.01530	0.76949	1.0105	0.01528	075951	1.0129
0.01916	0.76984	1.0129	0.01916	0.76987	1.0159
0.02291	0.77018	1.0152	0.02296	0.77022	1.0187
0.02680	0.77053	1.0176	0.02677	0.77057	1.0216
0.03059	0.77089	1.0198	0.03050	0.77091	1.0244
0.03439	0.77121	1.0221	0.03433	0.77126	1.0272
0.03821	0.77155	1.0244	0.03435	0.77160	1.0300
0.04576	0.77222	1.0289	0.03808	0.77228	1.0356
0.04949	0.77255	1.0311	0.04559	0.77262	1.0383
			0.04936		

Bu_4NBr			Pen_4NBr		
0.00769	0.76882	1.0087	0.00766	0.76883	1.0095
0.01526	0.76954	1.0163	0.01530	0.76957	1.0179
0.01906	0.76990	1.0200	0.01904	0.76993	1.0220
0.02289	0.77026	1.0238	0.02289	0.77030	1.0261
0.02671	0.77062	1.0275	0.02665	0.77066	1.0301
0.03045	0.77097	1.0311	0.03042	0.77102	1.0341
0.03420	0.77132	1.0347	0.03410	0.77137	1.0380
0.03795	0.77167	1.0354	0.03788	0.77173	1.0420
0.04548	0.77237	1.0454	0.04528	0.77243	1.0498
0.04916	0.77271	1.0489	0.04900	0.77278	1.0537

Hex_4NBr			Hep_4NBr		
0.00764	0.76884	1.0110	0.00763	0.76885	1.0122
0.01527	0.76959	1.0208	0.01523	0.76961	1.0233
0.01905	0.76996	1.0256	0.0190	0.76999	1.0287
0.02283	0.77033	1.0303	0.02277	0.77036	1.0340
0.02654	0.77069	1.0349	0.02651	0.77073	1.0394
0.03035	0.77106	1.0397	0.03026	0.77110	1.0447
0.03407	0.77142	1.0443	0.03392	0.77146	1.0498
0.03780	0.77178	1.0489	0.03769	0.77183	1.0551
0.04517	0.77249	1.0580	0.04504	0.77255	1.0655
0.04882	0.77284	1.0625	0.04872	0.77291	1.0706

Bu_4NBPh_4		
0.00756	0.76841	1.0118
0.0515	0.76873	1.0223
0.01901	0.76889	1.0276
0.02267	0.76904	1.0325
0.02660	0.76920	1.0378
0.03008	0.76934	1.0425
0.03382	0.76949	1.0475
0.03761	0.76964	1.0526
0.04501	0.76993	1.0625
0.04861	0.77007	1.0672

$x_2 = 0.40$

Et_4NBr			Pr_4NBr		
0.00761	0.76631	1.0061	0.00765	0.76633	1.0074
0.01532	0.76702	1.0114	0.01531	0.76705	1.0138
0.01904	0.76736	1.0139	0.01903	0.76740	1.0169
0.02289	0.76771	1.0164	0.02289	0.76776	1.0200
0.02604	0.76805	1.0189	0.02666	0.76811	1.0230
0.03052	0.76840	1.0214	0.03044	0.76846	1.0260
0.03429	0.76874	1.0239	0.03422	0.76881	1.0290
0.03808	0.76908	1.0263	0.03791	0.76915	1.0319
0.04557	0.76975	1.0312	0.04543	0.76984	1.0379
0.04940	0.77009	1.0336	0.04925	0.77019	1.0408

Bu_4NBr			Pen_4NBr		
0.00762	0.76634	1.0088	0.00767	0.76636	1.0094
0.01523	0.76707	1.0166	0.01523	0.76710	1.0176
0.01899	0.70743	1.0204	0.01901	0.76747	1.0217
0.02277	0.76779	1.0242	0.02281	0.76784	1.0258
0.02657	0.76815	1.0281	0.02653	0.76820	1.0297
0.03038	0.76851	1.0319	0.03025	0.76856	1.0337
0.03409	0.76886	1.0354	0.03398	0.76892	1.0376
0.03780	0.76921	1.0390	0.03773	0.76928	1.0416
0.04537	0.76992	1.0464	0.04513	0.76999	1.0494
0.04901	0.77026	1.0500	0.04889	0.77035	1.0533

Hex_4NBr			Hep_4NBr		
0.00765	0.76637	1.0111	0.00760	0.76638	1.0123
0.01518	0.76712	1.0208	0.01516	0.76715	1.0233
0.01901	0.76750	1.0256	0.01892	0.76753	1.0287
0.02275	0.76787	1.0304	0.02274	0.76791	1.0342
0.02651	0.76824	1.0351	0.02646	0.76829	1.0395
0.03017	0.76860	1.0397	0.03014	0.76866	1.0447
0.033940	0.76897	1.0444	0.03383	0.76903	1.0499
0.03765	0.76933	1.0490	0.03753	0.76940	1.0551
0.04500	0.77005	1.0581	0.04485	0.77013	1.0655
0.04870	0.77041	1.0627	0.04857	0.77050	1.0707

Bu_4NBPh_4		
0.00753	0.76595	1.0120
0.01507	0.76629	1.0233
0.01890	0.76646	1.0288
0.02277	0.76663	1.0344
0.02645	0.76679	1.0396
0.03015	0.76695	1.0448
0.03377	0.76710	1.0499
0.03740	0.76726	1.0550
0.04474	0.76757	1.0653
0.04834	0.76772	1.0703

$x_2 = 0.60$

Et_4NBr			Pr_4NBr		
0.00765	0.76288	1.0064	0.00756	0.76289	1.0076
0.01517	0.76358	1.0118	0.01522	0.76362	1.0143
0.01903	0.76393	1.0145	0.01902	0.76398	1.0176
0.02275	0.76428	1.0171	0.02272	0.76433	1.0207
0.02657	0.76463	1.0197	0.02655	0.76469	1.0240
0.03040	0.76498	1.0223	0.03028	0.76504	1.0272
0.03413	0.76532	1.0249	0.03402	0.76539	1.0303
0.03787	0.76566	1.0275	0.03777	0.76574	1.0335
0.04539	0.76634	1.0326	0.04529	0.76644	1.0398
0.04916	0.76668	1.0351	0.04896	0.76678	1.0428

Bu_4NBr			Pen_4NBr		
0.00763	0.76291	1.0090	0.00758	0.76292	1.0095
0.01515	0.76364	1.0168	0.01513	0.76367	1.0179
0.01898	0.76401	1.0207	0.01888	0.76404	1.0220
0.02271	0.76437	1.0245	0.02264	0.76441	1.0261
0.02646	0.76473	1.0283	0.02640	0.76478	1.0301
0.03022	0.76509	1.0321	0.03018	0.76515	1.0342
0.03398	0.76545	1.0359	0.03386	0.76551	1.0382
0.03766	0.76580	1.0396	0.03755	0.76587	1.0421
0.04512	0.76651	1.0470	0.04496	0.76659	1.0500
0.04882	0.76686	1.0507	0.04868	0.776695	1.0539

Hex_4NBr			Hep_4NBr		
0.00760	0.76294	1.0108	0.00755	0.76295	1.0123
0.01519	0.76371	1.0206	0.01516	0.76374	1.0236
0.01894	0.76409	1.0253	0.01884	0.76412	1.0289
0.02259	0.76446	1.0298	0.02263	0.76451	1.0344
0.02640	0.76484	1.0346	0.02633	0.76489	1.0397
0.03008	0.76521	1.0391	0.03004	0.76527	1.0450
0.03378	0.76558	1.0437	0.03375	0.76565	1.0503
0.03748	0.76595	1.0483	0.03738	0.76602	1.0555
0.04482	0.76668	1.0573	0.04465	0.76676	1.0659
0.04844	0.76704	1.0617	0.04830	0.76713	1.0710

Bu_4NBPh_4		
0.00768	0.76255	1.0125
0.01516	0.76292	1.0235
0.01885	0.76310	1.0289
0.02258	0.76328	1.0343
0.02633	0.76346	1.0396
0.02990	0.76363	1.0447
0.03371	0.76381	1.0502
0.03732	0.76398	1.0553
0.04401	0.76432	1.0648
0.04829	0.76449	1.0708

x = 0.80

Et_4NBr			Pr_4NBr		
0.00754	0.75935	1.0063	0.00755	0.75937	1.0071
0.01518	0.76007	1.0118	0.01508	0.76010	1.0132
0.01893	0.76042	1.0145	0.01891	0.76047	1.0163
0.02268	0.76077	1.0171	0.02266	0.76083	1.0193
0.02644	0.76112	1.0197	0.02643	0.76119	1.0222
0.03022	0.76147	1.0224	0.03019	0.76155	1.0252
0.03401	0.76182	1.0250	0.03386	0.76190	1.0281
0.03770	0.76216	1.0276	0.03766	0.76226	1.0310
0.04523	0.76285	1.0327	0.04505	0.76296	1.0368
0.04523	0.76319	1.0353	0.04876	0.76331	1.0396

Bu_4NBr			Pen_4NBr		
0.00760	0.75939	1.0087	0.00753	0.75940	1.0089
0.01507	0.76013	1.0161	0.01514	0.76017	1.0169
0.01882	0.76050	1.0198	0.01881	0.76054	1.0207
0.02259	0.76087	1.0234	0.02259	0.76092	1.0245
0.02637	0.76124	1.0271	0.02629	0.76129	1.0283
0.03005	0.76160	1.0306	0.02999	0.76166	1.0320
0.03375	0.76196	1.0341	0.03370	0.76203	1.0358
0.03756	0.76233	1.0378	0.03742	0.76240	1.0395
0.04488	0.76304	1.0447	0.04478	0.76313	1.0469
0.04861	0.76340	1.0482	0.04842	0.76349	1.0505

Hex_4NBr			Hep_4NBr		
0.00757	0.75942	1.0100	0.00759	0.75944	1.0114
0.01510	0.76020	1.0188	0.01506	0.76023	1.0215
0.01879	0.76058	1.0231	0.01876	0.76062	1.0264
0.02250	0.76096	1.0274	0.02248	0.76101	1.0313
0.02620	0.76134	1.0316	0.02622	0.76140	1.0362
0.02993	0.76172	1.0359	0.03046	0.76179	1.0417
0.03365	0.76210	1.0401	0.03357	0.76217	1.0458
0.03728	0.76247	1.0442	0.03722	0.76255	1.0505
0.04469	0.76322	1.0526	0.04444	0.76330	1.0598
0.04823	0.76358	1.0566	0.04811	0.76368	1.0646

Bu_4NBr		
0.00761	0.75904	1.0121
0.01503	0.75943	1.0228
0.01870	0.75962	1.0280
0.02239	0.75981	1.0332
0.02608	0.76000	1.0389
0.02985	0.76019	1.0437
0.03342	0.76037	1.0487
0.03721	0.76056	1.0539
0.4444	0.76092	1.0640
0.04808	0.76110	1.0690

Table 3. Theoretical A / $dm^{3/2}$ $mol^{-1/2}$ Coefficients of Eleetrolytes in Methanol + Acetonitrile Mixtures at 298.15 K.

salt	x = 0.00	x = 0.20	x = 0.40	x = 0.60	x = 0.80
Et_4NBr	0.0166	0.0166	0.0167	0.0169	0.0166
Pr_4NBr	0.0190	0.0186	0.0187	0.0187	0.0184
Bu_4NBr	0.0204	0.0201	0.0201	0.0201	0.0196
Pen_4NBr	0.0215	0.0211	0.0210	0.0208	0.0204
Hex_4NBr	0.0227	0.0219	0.0220	0.0219	0.0214
Hep_4NBr	0.0234	0.0231	0.0229	0.0227	0.0222
Bu_4NBPh_4	0.0255	0.0252	0.0251	0.0252	0.0246

Table 4. Viscosity B-Coefficients ($dm^3.mol^{-1}$) of Tetraalkylammonium Salts in Methanol + Acetonitrile Mixtures at 298.15,308.15 and 318.15K

Salt	T/K	x_1=0.00	x_1=0.20	x_1=0.40	x_1=0.60	x_1=0.80
Et_4NBr	298.15	0.480	0.546	0.613	0.651	0.706
	308.15	0.492	0.549	0.607	0.653	0.669
	318.15	0.505	0.553	0.601	0.638	0.650
Pr_4NBr	298.15	0.663	0.689	0.750	0.783	0.762
	308.15	0.672	0.699	0.744	0.800	0.738
	318.15	0.684	0.692	0.737	0.794	0.731
Bu_4NBr	298.15	0.852	0.903	0.952	0.971	0.951
	308.15	0.859	0.900	0.941	0.941	0.909
	318.15	0.864	0.903	0.932	0.949	0.893
Pen_4NBr	298.15	0.978	0.998	1.024	1.040	1.011
	308.15	0.985	1.006	1.015	1.021	0.972
	318.15	0.992	1.001	1.004	1.013	0.954
Hex_4NBr	298.15	1.161	1.180	1.197	1.210	1.146
	308.15	1.171	1.181	1.191	1.191	1.100
	318.15	1.181	1.175	1.181	1.175	1.078
Hep_4NBr	298.15	1.332	1.350	1.370	1.380	1.342
	308.15	1.337	1.355	1.363	1.377	1.269
	318.15	1.349	1.350	1.350	1.364	1.233
Bu_4NBPh_4	298.15	1.185	1.278	1.346	1.382	1.357
	308.15	1.190	1.270	1.339	1.368	1.335
	318.15	1.202	1.268	1.337	1.360	1.333

Table 5. $\Delta\mu_2^{0*}$ / kJmol^{-1} Values of Electrolytes Methanol + Acetonitrile at 298.15, 308.15 and 318.15K

salt	T/K	x=0.00	x=0.20	x=0.40	x=0.60	x=0.80
Et_4NBr	298.15	33.09	35.24	37.19	37.75	39.23
	308.15	34.07	35.84	37.48	38.50	38.02
	318.15	35.26	36.64	37.77	38.34	37.67
Pr_4NBr	298.15	39.85	39.32	40.79	40.92	38.51
	308.15	41.86	40.52	41.17	42.54	37.95
	318.15	42.11	40.73	41.12	42.92	38.17
Bu_4NBr	298.15	47.19	47.14	48.16	47.18	44.51
	308.15	48.09	48.19	48.25	46.28	41.92
	318.15	49.01	49.10	48.48	47.43	42.84
Pen_4NBr	298.15	50.59	49.17	48.06	46.94	43.84
	308.15	51.53	50.25	48.37	46.72	42.58
	318.15	52.62	50.71	48.54	45.15	42.32
Hex_4NBr	298.15	56.64	55.54	53.74	52.18	47.10
	308.15	58.69	56.40	54.25	51.99	45.46
	318.15	60.10	56.89	54.59	51.95	45.04
Hep_4NBr	298.15	63.54	61.29	59.32	57.33	53.28
	308.15	64.61	62.44	59.89	58.08	50.39
	318.15	66.24	63.13	60.15	56.78	49.33
Bu_4NBPh_4	298.15	50.35	53.39	54.87	54.54	51.36
	308.15	51.30	53.75	55.25	54.57	50.98
	318.15	52.09	54.41	55.93	55.55	51.57

Table 6. Ionic Viscosity B-Coefficients ($dm^{-3}. mol^{-1}$) in Methanol + Acetonitrile Mixtures at 298.15, 308.15 and 318.15K

Salt	T/K	x =0.00	x =0.20	x =0.40	x =0.60	x =0.80
Et_4N^+	298.15	0.161	0.217	0.266	0.301	0.365
	308.15	0.158	0.220	0.268	0.327	0.360
	318.15	0.181	0.220	0.270	0.300	0.357
Pr_4N^+	298.15	0.344	0.360	0.403	0.433	0.421
	308.15	0.338	0.370	0.405	0.474	0.429
	318.15	0.360	0.359	0.406	0.456	0.438
Bu_4N^+	298.15	0.533	0.574	0.605	0.621	0.610
	308.15	0.535	0.571	0.602	0.615	0.600
	318.15	0.540	0.570	0.601	0.611	0.600
Pen_4N^+	298.15	0.659	0.669	0.677	0.690	0.670
	308.15	0.651	0.677	0.676	0.695	0.663
	318.15	0.668	0.668	0.673	0.675	0.661
Hex_4N^+	298.15	0.842	0.851	0.850	0.860	0.805
	308.15	0.837	0.852	0.852	0.865	0.791
	318.15	0.857	0.842	0.850	0.837	0.785
Hep_4N^+	298.15	1.013	1.021	1.023	1.030	1.001
	308.15	1.003	1.026	1.024	1.051	0.960
	318.15	1.025	1.017	1.019	1.026	0.940
Ph_4B^-	298.15	0.652	0.704	0.741	0.761	0.747
	308.15	0.655	0.699	0.737	0.753	0.735
	318.15	0.662	0.698	0.736	0.749	0.733
Br^-	298.15	0.319	0.329	0.347	0.350	0.341
	308.15	0.334	0.329	0.339	0.326	0.309
	318.15	0.324	0.333	0.331	0.338	0.293

Table 7 : Ionic Radii $R_\pm$ in Methanol + Acetonitrile Mixtures at 298.15 K

ion	r_c / nm[a]	$R_\pm$ / nm				
		x = 0.00	x = 0.20	x = 0.40	x = 0.60	x = 0.80
Et_4N^+	0.400	0.294	0.325	0.348	0.363	0.386
Pr_4N^+	0.452	0.379	0.385	0.400	0.409	0.406
Bu_4N^+	0.500	0.439	0.450	0.458	0.462	0.459
Pen_4N^+	0.529	0.471	0.473	0.475	0.478	0.474
Hex_4N^+	0.560	0.511	0.513	0.513	0.515	0.504
Hep_4N^+	0.586	0.547	0.545	0.545	0.547	0.541
Ph_4B^-	0.535	0.469	0.481	0.490	0.494	0.491
Br^-	0.195	0.370	0.374	0.380	0.381	0.378

[a]Crystallographic radii.

Table 8. Ionic $\Delta\mu_2^{0*}$ / kJmol^{-1} Values in Methanol + Acetonitrile Mixtures at 298.15, 308.15 and 318.15K

ion	T/K	x=0.00	x=0.20	x=0.40	x=0.60	x=0.80
Et_4N^+	298.15	8.53	11.49	13.69	15.08	17.80
	308.15	9.04	11.81	13.94	16.74	19.01
	318.15	10.05	11.99	14.43	15.88	18.01
Pr_4N^+	298.15	15.29	15.57	17.29	18.25	17.08
	308.15	16.83	16.49	17.63	20.78	18.94
	318.15	16.90	16.08	17.78	20.46	18.51
Bu_4N^+	298.15	22.63	23.99	24.66	24.51	23.08
	308.15	23.06	24.16	24.71	24.52	22.91
	318.15	23.80	24.45	25.14	24.97	23.18
Pen_4N^+	298.15	26.03	25.42	24.56	24.27	22.41
	308.15	26.50	26.22	24.83	24.96	23.57
	318.15	27.41	26.06	25.20	22.69	22.66
Hex_4N^+	298.15	32.08	31.79	30.24	29.51	25.67
	308.15	33.66	32.37	30.71	30.23	26.46
	318.15	34.89	32.24	31.25	29.49	25.38
Hep_4N^+	298.15	38.98	37.54	35.82	34.66	31.85
	308.15	39.58	38.41	36.35	36.32	31.38
	318.15	41.03	38.48	36.81	34.32	29.67
Ph_4B^-	298.15	27.72	29.40	30.21	30.03	28.28
	308.15	28.24	29.59	30.42	30.05	28.07
	318.15	28.89	29.96	30.79	31.03	28.39
Br^-	298.15	24.56	23.75	23.50	22.67	21.43
	308.15	25.03	24.03	23.54	21.76	19.01
	318.15	25.21	24.65	23.34	22.46	19.66