

## **CHAPTER VIII**

### **Electrical Conductances of Some Ammonium and Tetraalkylammonium Halides in Aqueous Binary Mixtures of 1,4-Dioxane at 298.15 K\***

#### **8.1. Introduction**

Studies on ionic solvation of ammonium and tetraalkylammonium salts in solvents of low permitivity are very few. Such studies have major importance because of their applications in modern technology.<sup>1</sup>

1, 4-dioxane and its aqueous binary mixtures are very important solvents widely used in various industries. It is a good industrial solvent and figures prominently in the high-energy battery technology<sup>1</sup> and has also found its application in the organic syntheses as manifested from the physico-chemical studies in these media.<sup>2-5</sup> With a system of varying dielectric constant, in the mixed solvents there is scope of variation of solvent-solvent interaction since composition of the solvents in a binary mixture is varied. Thus, studies in mixed solvents may provide information regarding both the specific and non-specific solvent effects on the ion-association phenomena.

In the present chapter, an attempt has been made to ascertain the complete nature of ion-solvent, solvent-solvent interactions of ammonium and tetraalkylammonium halides measured in different mass% of 1,4-dioxane + water mixtures (20%, 40%, 60% and 80%) at 298.15 K. The limiting molar conductivity ( $\Lambda_0$ ), the association constant ( $K_A$ ) and association distance ( $R$ ) in the solvent mixtures have been evaluated using Fuoss conductance equation (1978).

#### **8.2. Experimental Section**

##### **8.2.1. Chemicals**

1,4-dioxane (Merck, India) was kept several days over KOH, refluxed for 24 hours and distilled over  $\text{LiAlH}_4$ , as described earlier.<sup>2</sup> The purified solvent has a density of  $1.03052 \text{ g.cm}^{-3}$  and a co-efficient of viscosity of  $1.20011 \text{ cp}$  at 298.15 K compared well with literature values.<sup>6</sup>

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The salts  $\text{Me}_4\text{NCl}$ ,  $\text{Et}_4\text{NBr}$ ,  $\text{Pr}_4\text{NBr}$ ,  $\text{Bu}_4\text{NBr}$  and  $\text{Bu}_4\text{NI}$  of A.R grade (Aldrich) were purified by dissolving in mixed alcohol medium and re-crystallized from solvent ether medium. After filtration, the salts were dried in an oven for few hours. The salts  $\text{NH}_4\text{F}$ ,  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{Cl}$  were dried at about 80-100°C in a vacuum oven for 48 hours before use.<sup>7</sup>

### 8.2.2. Measurements

A stock solution for each salt was prepared by mass and the working solutions were obtained by mass dilution. The values of dielectric constant ( $\epsilon$ ) were taken from the literature<sup>6</sup> and the densities ( $\rho_0$ ) and viscosities ( $\eta_0$ ) of the solvent mixtures were measured by an Ostwald-Sprengel type pycnometer and suspended-level Ubbelohde type viscometer respectively, as described in detail earlier.<sup>2</sup> The conductance measurements were carried out in a systronic 306 conductivity bridge (accuracy  $\pm 0.1\%$ ) using a dip-type immersion conductivity cell, CD-10 having cell constant  $1.0 \pm 10\%$ . Measurements were made in a water bath maintained within  $298.15 \pm 0.01$  K.

### 8.3. Results and Discussion

The solvent properties of the different aqueous binary mixtures of 1,4-dioxane are given in Table 1, where  $\epsilon$  is the dielectric constant,  $\rho_0$  the density ( $\text{g.cm}^{-3}$ ),  $\eta_0$  the viscosity (cp),  $x_1$  the mole fraction of 1,4-dioxane. Molar conductances ( $\Lambda$ ) of the electrolyte solutions as a function of molar concentration ( $c$ ) are given in Table 2 for the different solvent mixtures at 298.15 K.

The analysis of conductance data in terms of limiting molar conductance,  $\Lambda_0$  and ion-association constant,  $K_A$  of the electrolytes have been carried out iteratively according to Shedlovsky equation using least square treatment for the reasons described earlier.<sup>8</sup> Shedlovsky method involves the linear extrapolation using equation,<sup>9</sup>

$$1/\Lambda S(z) = 1/\Lambda_0 + [K_A/\Lambda_0^2]c\Lambda f_{\pm}^2 S(z) \quad (1)$$

where  $\Lambda$  is the equivalent conductance at a concentration  $c$  ( $\text{mol.lit}^{-1}$ ),  $\Lambda_0$  is the limiting equivalent conductance and  $K_A$  is the observed association constant. The other symbols are given by,

$$S(z) = [(z/2) + \sqrt{1 + (z/2)^2}]^2, z = [(\alpha\Lambda_0 + \beta)/\Lambda_0^{3/2}](c\Lambda)^{1/2}$$

$$\alpha = 0.8204 \times 10^6 / (\epsilon T)^{3/2}; \beta = 82.0501 / \eta (\epsilon T)^{1/2} \quad (2)$$

where  $\epsilon$  is the dielectric constant and  $\eta$  is the viscosity of the medium. The degree of dissociation ( $t$ ) is related to  $S(z)$  by,

$$\tau = \Lambda S(z) / \Lambda_0$$

$f_{\pm}$ , the mean activity co-efficient of the free ions was calculated by the following equation-

$$-\log f_{\pm} = A(\tau c)^{1/2} / [1 + BR(\tau c)^{1/2}] \quad (3)$$

where  $A = 1.8246 \times 10^6 / (\epsilon T)^{3/2}$ ;  $B = 0.5029 \times 10^{10} / (\epsilon T)^{1/2}$  and  $R$  = association distance.

The initial  $\Lambda_0$  values for the iteration procedure were, thus obtained from Shedlovsky extrapolation of the data.<sup>10</sup>

The conductance data was analyzed using Fuoss conductance equation,<sup>11</sup> which has been programmed in a computer. So with a given set of conductivity values ( $\sigma_j, \Lambda_j; j=1, \dots, n$ ), three adjustable parameters, i.e.  $\Lambda_j, K_A$  and  $R$  were derived from the Fuoss equation. Here  $R$  is the association distance, i.e. the maximum centre-to-centre distance between the ions in the solvent separated ion-pairs. There is no precise method for determining the  $R$ -value<sup>12</sup> but in order to treat the data in our system,  $R$ -value is assumed to be,  $R = a + d$ ; where  $a$  is the sum of the crystallographic radii of ions, which varies from 2 to 7 Å and  $d$  is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance  $d$ (Å) is given by,<sup>11</sup>

$$d = 1.183(M/\rho_0)^{1/3} \quad (4)$$

where  $M$  is the molecular weight and  $\rho_0$  is the density of the solvent. For mixed solvents,  $M$  is replaced by the mole fraction average molecular weight ( $M_{AV}$ ), which is given by,

$$M_{AV} = M_1 M_2 / [W_1 M_2 + W_2 M_1] \quad (5)$$

where  $W_1$  is the weight fraction of the first component of molecular weight  $M_1$  and  $W_2$  is the weight fraction of the second component of molecular weight  $M_2$ . Though, this is an over simplification which ignores

possible selective solvation, it at least provides a self-consistent way to obtain an acceptable value for the parameters when a broad range of  $R$ -values fit the data.

Thus, the Fuoss conductance equation may be represented as follows:

$$\Lambda = p[\Lambda_0(1+R_x) + E_L] \quad (6)$$

$$p = 1 - \alpha(1 - \gamma) \quad (7)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (8)$$

$$-\ln f = \beta \kappa / 2(1 + K_R) \quad (9)$$

$$\beta = e^2 / \epsilon K_B T \quad (10)$$

$$K_A = K_R / (1 - \alpha) = K_R(1 + K_S) \quad (11)$$

where  $R_x$  is the relaxation field effect,  $E_L$  is the electrophoretic counter current constant,  $\kappa^{-1}$  is the radius of the ionic atmosphere,  $\epsilon$  is the relative permittivity of the solvent,  $e$  is the electric charge,  $K_B$  is the Boltzmann constant,  $\gamma$  is the fraction of solute present as unpaired ion,  $c$  is the molarity of the solution,  $f$  is the activity coefficient,  $T$  is the temperature in absolute scale,  $\beta$  is twice the Bjerrum distance,  $K_R$  describes the formation and separation of solvent separated pairs by diffusion in and out of sphere of diameter  $R$  around cations and  $K_S$  is a constant describing the short-range process by which contact pairs forms and dissociates.

We input for the program the number of data,  $n$ ; followed by dielectric constant of the solvent mixture,  $\epsilon$ ; initial  $\Lambda_0$  values,  $T$ ,  $\rho$ , molecular weight of the solvents along with  $c_j$ ,  $\Lambda_j$  values where  $j=1, 2, \dots, n$  and an instruction to cover pre-selected range of  $R$ -values.

In practice calculations, were performed by finding the values of  $\Lambda_0$  and  $\sigma$ , which minimized the standard deviation ( $\sigma$ ),

$$\sigma^2 = \sum_{j=1}^n \frac{[\Lambda_j(\text{calc}) - \Lambda_j(\text{obs})]^2}{(n - 2)} \quad (12)$$

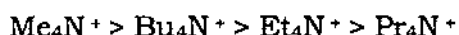
for a sequence of  $R$ -values and then plotting  $\sigma$  against  $R$ .

The best-fit  $R$  corresponds to the minimum of the  $\sigma$  versus  $R$  curve. First, approximate run over a fairly wide range of  $R$ -values were made to locate the minimum, and then a fine scan around the minimum was made. Thus,

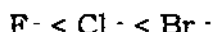
the corresponding  $\Lambda_0$  and  $K_A$  values were noted. The  $\Lambda_0$ ,  $K_A$ ,  $R$  and Walden products ( $\Lambda_0 \eta_0$ ) for the ammonium and tetraalkylammonium halides in different aqueous binary mixtures of 1,4-dioxane were thus reported in Table 3.

The association constant,  $K_A$  recorded in Table 3 indicates that all the electrolytes are highly associated in these solvent mixtures. This is quite expected due to the low dielectric constant (2.209) of 1,4-dioxane. The most outstanding feature is that the electrolytes containing smaller cations show almost considerable amount of association. Here, values of  $K_A$  decrease as the size of the cation increases with the exception of  $\text{Bu}_4\text{N}^+$  ion whereas  $\Lambda_0$  increases. The possible explanation may be due to the larger size of the cations, which are less solvated than the smaller one. Similar results were reported earlier by some workers<sup>13</sup> in the conductance study of 1-ethyl-4-cyano pyridinium iodide in aqueous binary mixtures of 1,4-dioxane.

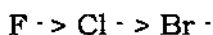
The  $K_A$  values of various tetraalkylammonium halides in these solvent mixtures follow the order:



However, in case of ammonium halides the value of  $\Lambda_0$  is enhanced by the order:



This trend of variation indicates the relative actual sizes of these anions having common ammonium ion as they exist in the solution. Thus the sizes of these anions as they exist in these solutions follow the order:



This shows that  $\text{F}^-$  is the most solvated and  $\text{Br}^-$  is the least solvated one in any mole fraction of 1,4-dioxane. Roy et al<sup>14</sup> found similar trends for many of the alkali metal halides in THF +  $\text{H}_2\text{O}$  mixtures. In case of  $\text{Bu}_4\text{NI}$ , the value of  $K_A$  is greater than that of  $\text{Bu}_4\text{NBr}$ . This may be expected owing to the larger size of  $\text{I}^-$  as compared to  $\text{Br}^-$ .

From Table 3 it is observed that  $K_A$  values are found to increase whereas  $\Lambda_0$  values are found to decrease in aqueous binary mixtures of 1,4-dioxane with the increase of the mole fraction of 1,4-dioxane.

This indicates that association of ions increase with the addition of 1,4-dioxane to the mixture rendering to the decrease of the mobility of ions in the mixture. The significantly large values of  $K_A$  and exothermic ion-pair formation in the solvent mixtures indicates the presence of specific short-range interaction within the ion-pair.

The variation of Walden product,  $\Lambda_0\eta_0$  with  $x_1$ , the mole fraction of 1,4-dioxane for the electrolytes studied at 298.15 K are shown in figure 1. The values of Walden product pass through a maximum at about  $x_1 = 0.11996$  mole fraction of 1,4-dioxane whereas the maximum viscosity of the aqueous binary mixtures at 298.15 K is observed at about  $x_1 = 0.23472$  mole fraction of 1,4-dioxane. It is known that the variation of Walden product indicates the change of solvation.<sup>12</sup> The increase of Walden products indicates weak solvation of ions, which attains a maximum value at a particular solvent composition ( $x_1 = 0.11996$ ). Such results have been interpreted in terms of microheterogeneity<sup>15</sup> in the mixtures.

On water rich side, there exists a region where the water structure remains more or less intact as the 1,4-dioxane molecules are added into the cavities in this structure. The cluster of water molecule has lower ability to donate a hydrogen atom to the solvation of ions. This may cause hydrophobic dehydration of cations<sup>13</sup> or may reduce the ability of hydrophobic ions to promote the structure in water rich region resulting in excess mobility, which in turn results an increase in Walden products to attain a maximum. As the percentage of 1,4-dioxane in the mixture increases the self-associated structure gradually breaks at an increased mole fraction of 1,4-dioxane and there is preferential solvation<sup>16</sup> due to specific ion-solvent interaction leading to a decrease of Walden product. However, this decrease in large part may be due to the Zwanzig<sup>17</sup> solvent relaxation effect also.

#### 8.4. Conclusion

The study revealed that all the electrolytes under investigation are highly associated in these solvent mixtures. Smaller cations are relatively more solvated than the larger ones. The same trend was observed for the anions too. Also the variation of Walden product indicated preferential solvation at higher mole fraction of 1,4-dioxane justifying specific ion-solvent interactions in these media.

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Table 1.

Physical properties of 1, 4-dioxane + water mixtures at 298.15 K.

$x_1$	$\varepsilon$	$\rho_0/\text{g.cm}^{-3}$		$\eta_0/\text{cp}$	
		Expt.	Lit.	Expt.	Lit.
0	78.3	0.99707	0.9971 <sup>6</sup>	0.89041	0.8903 <sup>6</sup>
0.04863	63.5	1.01612	1.0143 <sup>6</sup>	1.29671	1.30 <sup>6</sup>
0.11996	44.4	1.03127	1.0284 <sup>6</sup>	1.69701	1.74 <sup>6</sup>
0.23472	27.5	1.04011	1.0360 <sup>6</sup>	1.98712	1.98 <sup>6</sup>
0.44991	12.1	1.04053	1.0350 <sup>6</sup>	1.78589	1.73 <sup>6</sup>
1	2.209	1.03052	1.0269 <sup>6</sup>	1.20011	1.196 <sup>6</sup>



Table 2.

Molar Conductances ( $\Lambda$ ) and Corresponding Molarities ( $c$ ) of Some Tetraalkylammonium Halides and Ammonium Halides in Different Aqueous Binary Mixtures of 1,4-Dioxane at 298.15 K.

$c \times 10^4$ /mol.lit <sup>-1</sup>	$\Lambda$ /S.cm <sup>2</sup> .mol <sup>-1</sup>	$c \times 10^4$ /mol.lit <sup>-1</sup>	$\Lambda$ /S.cm <sup>2</sup> .mol <sup>-1</sup>	$c \times 10^4$ /mol.lit <sup>-1</sup>	$\Lambda$ /S.cm <sup>2</sup> .mol <sup>-1</sup>	$c \times 10^4$ /mol.lit <sup>-1</sup>	$\Lambda$ /S.cm <sup>2</sup> .mol <sup>-1</sup>
$x_1 = 0.04863$							
NH <sub>4</sub> F		NH <sub>4</sub> Cl		NH <sub>4</sub> Br		Me <sub>4</sub> NCl	
42.7	49.26	48.1	71.93	48.5	81.44	46.2	55.63
55.9	48.65	61.9	71.24	62.4	80.77	56.5	54.69
68.6	48.00	74.8	70.59	75.4	80.24	65.2	54.45
80.8	47.82	86.9	70.20	87.6	79.79	72.6	53.86
92.6	47.55	98.2	69.55	99.0	79.19	79.0	53.67
104.0	47.31	108.8	69.39	109.7	78.85	84.6	53.31
125.7	46.61	118.8	69.02	119.8	78.71	89.6	53.01
136.0	46.40	128.2	68.49	129.3	78.50	94.0	52.66
Et <sub>4</sub> NBr		Pr <sub>4</sub> NBr		Bu <sub>4</sub> NBr		Bu <sub>4</sub> NI	
44.8	66.96	45.6	78.24	51.7	87.62	47.1	60.65
57.6	65.97	54.2	77.47	67.8	86.92	61.6	59.64
69.6	65.09	69.1	76.52	75.2	86.51	66.1	59.33
80.8	64.36	75.6	74.04	82.1	86.25	74.7	58.78
91.3	63.86	81.6	75.76	88.6	86.07	78.8	58.53
101.2	63.34	92.2	75.28	94.8	85.91	82.8	58.48
110.5	62.81	96.9	74.99	97.8	85.82	97.6	57.62
119.3	62.45	101.3	74.91	100.7	85.67	104.4	57.24
$x_1 = 0.11996$							
NH <sub>4</sub> F		NH <sub>4</sub> Cl		NH <sub>4</sub> Br		Me <sub>4</sub> NCl	
25.6	45.31	22.5	59.11	20.2	72.65	17.8	47.49
34.8	43.97	25.8	58.02	26.0	71.08	21.2	46.45

Contd...

38.4	43.75	33.8	57.24	29.8	70.89	26.6	45.63
43.7	43.25	38.5	57.15	39.1	69.84	37.0	44.35
55.5	42.34	48.9	55.51	48.1	68.67	43.9	43.34
71.4	41.18	56.1	55.18	73.6	65.31	48.7	42.69
79.0	40.76	69.7	53.68	89.3	63.92	57.8	41.79
93.4	39.83	82.4	52.80	104.2	62.66	66.4	41.04
Et <sub>4</sub> NBr		Pr <sub>4</sub> NBr		Bu <sub>4</sub> NBr		Bu <sub>4</sub> NI	
17.9	59.74	24.5	72.68	19.4	82.62	16.8	53.88
21.1	59.58	29.6	71.86	23.2	82.26	31.8	52.06
24.2	58.97	34.4	71.24	26.7	81.66	36.5	51.22
30.1	57.76	36.7	70.76	28.4	81.37	45.3	50.24
32.9	57.34	43.1	70.10	35.8	80.75	49.5	49.87
35.6	56.91	50.8	69.63	37.1	80.73	53.5	49.36
43.1	55.77	54.3	69.40	38.4	80.49	61.2	48.75
47.8	55.29	57.6	69.06	40.8	80.38	68.4	48.18
$x_1 = 0.23472$							
NH <sub>4</sub> F		NH <sub>4</sub> Cl		NH <sub>4</sub> Br		Me <sub>4</sub> NCl	
9.7	23.09	3.7	35.07	5.4	40.37	3.7	37.45
11.4	22.81	10.9	33.39	7.2	39.58	6.1	36.52
13.1	22.44	14.5	32.76	9.0	39.33	7.8	35.82
16.3	21.90	18.1	31.99	12.6	37.62	9.4	35.55
19.3	21.45	23.3	31.33	16.2	36.98	13.5	34.74
24.7	20.69	28.4	30.99	23.2	35.78	16.4	34.34
27.1	20.48	31.8	30.50	28.3	35.69	17.8	34.18
34.6	19.94	35.2	29.83	33.4	34.73	19.2	33.94
Et <sub>4</sub> NBr		Pr <sub>4</sub> NBr		Bu <sub>4</sub> NBr		Bu <sub>4</sub> NI	
3.7	48.56	5.2	51.69	4.1	56.76	4.3	43.88
6.1	47.62	6.7	51.49	5.9	56.32	6.2	43.19

Condt...

7.1	46.97	10.3	51.08	6.4	56.22	7.1	42.94
8.8	46.14	11.2	51.00	7.4	56.02	10.5	41.76
10.3	45.87	13.9	50.81	8.4	55.93	11.3	41.48
11.8	45.59	15.2	50.68	10.3	55.45	14.1	41.13
16.1	44.50	18.8	50.56	11.1	55.38	15.4	40.88
21.3	43.74	22.1	50.39	11.9	55.24	16.6	40.75
$x_1 = 0.44991$							
NH <sub>4</sub> F		NH <sub>4</sub> Cl		NH <sub>4</sub> Br		Me <sub>4</sub> NCl	
1.9	2.12	0.3	5.88	0.5	5.98	0.6	23.12
3.2	1.85	0.7	5.51	0.7	5.80	0.9	22.30
3.7	1.79	1.4	5.08	1.2	5.51	1.0	21.40
4.9	1.65	1.7	4.78	1.7	5.32	1.2	20.90
6.8	1.50	2.1	4.55	2.2	5.07	1.9	18.80
7.9	1.46	2.9	4.51	2.5	4.94	2.4	17.33
9.5	1.41	3.3	4.27	3.2	4.69	2.7	17.11
9.9	1.39	3.9	4.36	3.5	4.54	2.8	16.82
Et <sub>4</sub> NBr		Pr <sub>4</sub> NBr		Bu <sub>4</sub> NBr		Bu <sub>4</sub> NI	
0.4	33.40	0.7	39.71	1.2	41.50	0.7	31.60
0.6	31.50	1.5	34.93	1.7	40.32	0.9	31.22
1.2	27.83	1.7	34.53	2.0	39.90	1.2	29.50
1.5	26.80	2.0	33.85	2.5	39.12	1.4	28.50
1.8	25.44	2.2	33.68	2.8	38.86	1.6	27.63
2.3	24.78	2.5	32.88	3.3	38.24	1.9	26.32
2.7	23.80	3.2	32.13	3.6	37.89	2.0	26.25
3.1	21.60	3.5	31.57	4.1	37.37	2.2	25.68

**Electrical Conductances of Some Ammonium ....at 298.15 K**

Table 3.

Values of  $\Lambda_0$ ,  $K_A$ ,  $\Lambda_0\eta_0$ ,  $R$  and  $\sigma$  for Some Ammonium and Tetraalkylammonium Halides in Different Aqueous Binary Mixtures of 1, 4-Dioxane at 298.15 K.

$x_1$	$\Lambda_0$ /S.cm <sup>2</sup> .mol <sup>-1</sup>	$K_A$ /dm <sup>3</sup> .mol <sup>-1</sup>	$R$ /Å	$\Lambda_0\eta_0$	$\sigma$
NH <sub>4</sub> F					
0.04863	51.53 ± 0.12	8.42	6.18	66.82	0.12
0.11996	49.36 ± 0.11	36.45	6.41	78.89	0.11
0.23472	26.27 ± 0.08	149.62	6.71	52.20	0.08
0.44991	3.14 ± 0.02	4535.07	7.21	5.61	0.02
NH <sub>4</sub> Cl					
0.04863	75.58 ± 0.10	8.03	6.66	98.01	0.10
0.11996	63.67 ± 0.26	32.92	6.88	108.05	0.26
0.23472	37.76 ± 0.30	107.84	7.19	75.03	0.30
0.44991	6.36 ± 0.11	2500.04	7.68	11.36	0.11
NH <sub>4</sub> Br					
0.04863	84.87 ± 0.11	5.85	6.69	110.05	0.11
0.11996	78.14 ± 0.28	33.76	7.02	132.60	0.28
0.23472	42.96 ± 0.36	100.72	7.33	85.37	0.36
0.44991	6.72 ± 0.06	2247.41	7.82	12.00	0.06
Me <sub>4</sub> NCl					
0.04863	59.98 ± 0.12	16.78	8.65	77.78	0.12
0.11996	52.12 ± 0.15	59.64	8.67	88.45	0.15
0.23472	39.07 ± 0.16	90.51	9.17	77.64	0.16
0.44991	29.94 ± 0.28	6215.89	9.67	53.47	0.28
Et <sub>4</sub> NBr					
0.04863	71.59 ± 0.07	14.79	9.32	92.83	0.07
0.11996	65.19 ± 0.16	47.24	9.53	110.63	0.16
0.23472	50.77 ± 0.24	94.19	9.85	100.89	0.24
0.44991	39.69 ± 0.49	5682.46	10.34	70.88	0.49
Pr <sub>4</sub> NBr					
0.04863	82.65 ± 0.11	11.19	9.84	107.17	0.11
0.11996	77.21 ± 0.19	22.65	10.06	131.03	0.19
0.23472	53.10 ± 0.01	73.70	10.37	105.52	0.01
0.44991	44.74 ± 0.59	2253.78	10.86	79.90	0.59
Bu <sub>4</sub> NBr					
0.04863	91.13 ± 0.06	5.56	10.26	118.17	0.06
0.11996	86.37 ± 0.11	16.39	10.48	146.57	0.11
0.23472	58.63 ± 0.01	30.94	10.79	116.50	0.01
0.44991	45.68 ± 0.08	659.09	11.28	81.58	0.08
Bu <sub>4</sub> NI					
0.04863	65.18 ± 0.01	15.63	10.47	84.52	0.01
0.11996	57.80 ± 0.11	39.08	10.69	98.09	0.11
0.23472	46.17 ± 0.16	91.24	11.01	91.75	0.16
0.44991	40.57 ± 0.31	5107.55	11.49	72.45	0.31