

# Thermodynamics of Ion Association and Solvation in 2-Methoxyethanol: Behavior of Tetraphenylarsonium, Picrate, and Tetraphenylborate Ions from Conductivity and Ultrasonic Data

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Precise measurements on electrical conductances and ultrasonic velocities of solutions of potassium picrate (KPic), potassium tetraphenylborate (KBPh<sub>4</sub>), tetrabutylammonium tetraphenylborate (Bu<sub>4</sub>NBPh<sub>4</sub>), and tetraphenylarsonium picrate (Ph<sub>4</sub>AsPic) in 2-methoxyethanol (ME) at temperatures 288.15 ≤ T/K ≤ 308.15 have been reported. The conductance data have been analyzed by the 1978 Fuoss conductance–concentration equation. Thermodynamics of the association processes have also been studied and the Coulombic forces are found to play a major role in the association processes. The limiting ionic conductances have been estimated from the appropriate division of the limiting molar conductivity values of the “reference electrolyte” Bu<sub>4</sub>NBPh<sub>4</sub>. Strong association was found for all these salts in this solvent medium. The results strongly suggest the electrostriction of the solvent molecules around the potassium and picrate ions, while for the larger tetrabutylammonium and tetraphenylarsonium ions they are accommodated inside the space between the alkyl or aryl chains attached to the nitrogen or arsenic atom; for tetraphenylborate ion, however, neither electrostriction nor penetration of the solvent molecules is found to be important.

## 1. Introduction

2-Methoxyethanol (ME) is an amphiprotic dipolar solvent of low dielectric constant ( $D = 16.94$  at 298.15 K)<sup>1</sup> with large dipole moment ( $\mu = 2.36$  D).<sup>2</sup> But, unfortunately, it is hygroscopic, fairly toxic, a weak narcotic, and a systemic poison; and for these reasons, careful handling of this solvent is essential.<sup>3</sup> ME could be considered as a moderate Lewis acid ( $pK_{\text{autoprot}} = 20.5$  at 298.15 K),<sup>4</sup> and is a probable solvent for anions through its hydrogen-bonding network and dipole-induced interactions. It has unique solvating properties associated with its “quasiaprotic” character and is widely used for electrochemical investigations and various industrial processes.<sup>5–7</sup>

Even though ME has drawn much attention in recent years as a solvent for electroanalytical investigations,<sup>8,9</sup> very few reliable studies on the electrolytic behavior in this nonaqueous medium have so far been made. Therefore, as a part of a series of investigations on the chemical nature of structure of ions on their mutual and specific interactions with solvent molecules,<sup>10–18</sup> we have performed conductivity and ultrasonic velocity measurements on 2-methoxyethanol solutions of potassium picrate (KPic), potassium tetraphenylborate (KBPh<sub>4</sub>), tetrabutylammonium tetraphenylborate (Bu<sub>4</sub>NBPh<sub>4</sub>), and tetraphenylarsonium picrate (Ph<sub>4</sub>AsPic) as functions of temperature (288.15 ≤ T/K ≤ 308.15). The results have been interpreted in terms of specific constitutional and structural factors of the solvent molecules and of the solutes.

## 2. Experimental Section

**2.1 Materials.** 2-Methoxyethanol (ME, G. R.E Merck) was dried with potassium carbonate and distilled twice in an all glass distillation set immediately before use and the middle fraction collected. The purified solvent had a density of 0.96002 g cm<sup>-3</sup>, a coefficient of viscosity of 1.5414 mPa s, and a specific

TABLE 1: Physical Properties of 2-Methoxyethanol

T/K	$\rho/\text{g cm}^{-3}$	$\eta/\text{mPa s}$	D
288.15	0.96960	1.9377	17.77
293.15	0.96490	1.7287	17.35
298.15	0.96002	1.5414	16.94
308.15	0.95356	1.2579	16.15

conductance of ca.  $1.01 \times 10^{-6}$  S cm<sup>-1</sup> at 298.15 K. These values are in good agreement with the literature data.<sup>19</sup> The solvent properties are recorded in Table 1.

Potassium picrate (KPic) was prepared<sup>20</sup> by neutralizing picric acid (A.R., BDH) with an equal molar amount of potassium hydroxide (A.R., BDH) in ethanol. The resulting potassium picrate, which precipitated, was recrystallized from water and dried in vacuo for 3–4 weeks.

Potassium tetraphenylborate (KBPh<sub>4</sub>) was precipitated by mixing equimolar aqueous solutions of potassium nitrate (KNO<sub>3</sub>) and sodium tetraphenylborate (NaBPh<sub>4</sub>). The product was recrystallized from 30 mass % aqueous acetone and dried in vacuo for several weeks.

Tetraphenylarsonium picrate (Ph<sub>4</sub>AsPic) was prepared by the metathesis between potassium picrate obtained as above and tetraphenylarsonium chloride (Ph<sub>4</sub>AsCl) both dissolved in 50 mass % aqueous ethanol. The precipitate was washed with water, repeatedly crystallized from ethanol, and dried in vacuo for several weeks.

Tetrabutylammonium tetraphenylborate (Bu<sub>4</sub>NBPh<sub>4</sub>) was prepared by mixing equimolar quantities of sodium tetraphenylborate and tetrabutylammonium bromide (Bu<sub>4</sub>NBr) in water. The salt was dried in vacuo at 353.15 K for 48 h.

**2.2. Apparatus and Procedures.** Conductance measurements were carried out on a pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell of cell constant 1.14 cm<sup>-1</sup> and having an accuracy of 0.1%. Measurements were made in an oil bath maintained within ± 0.005 K of the desired

TABLE 2: Molar Conductivities of Electrolytes in 2-Methoxyethanol at 288.15, 293.15, 298.15, and 308.15 K

T = 288.15 K		T = 293.15 K		T = 298.15 K		T = 308.15 K	
$c \times 10^4$ mol dm <sup>-3</sup>	$\Lambda$ S cm <sup>2</sup> mol <sup>-1</sup>	$c \times 10^4$ mol dm <sup>-3</sup>	$\Lambda$ S cm <sup>2</sup> mol <sup>-1</sup>	$c \times 10^4$ mol dm <sup>-3</sup>	$\Lambda$ S cm <sup>2</sup> mol <sup>-1</sup>	$c \times 10^4$ mol dm <sup>-3</sup>	$\Lambda$ S cm <sup>2</sup> mol <sup>-1</sup>
KPic							
3.5164	27.41	4.0216	30.07	3.0172	33.67	3.0065	39.39
4.5456	26.80	5.5090	29.17	4.0230	32.93	4.0287	38.46
5.5748	26.26	6.2802	28.75	5.0287	32.22	5.0509	37.65
6.5182	25.82	6.9964	28.38	6.0344	31.59	6.0130	36.97
7.5474	25.37	7.7126	28.04	7.0402	31.02	7.0352	36.31
8.5766	24.96	8.5389	27.67	8.0459	30.47	7.9973	35.74
9.5200	24.62	9.0347	27.46	9.0516	29.98	9.0195	35.19
10.5492	24.26	10.0263	27.06	10.0574	29.51	10.0417	34.67
11.5784	23.93	11.0180	26.68	11.0631	29.04	11.0037	34.21
		12.0096	26.33	12.0689	28.67	11.9057	33.81
KBPh <sub>4</sub>							
3.0274	22.05	2.9546	23.94	3.4658	25.65	3.0584	31.80
4.0365	21.55	3.9774	23.42	5.0412	24.91	4.1704	31.12
5.0456	21.11	5.0002	22.97	6.0495	24.51	5.0111	30.66
6.0547	20.73	6.0231	22.56	7.0971	24.13	6.0443	30.16
7.0639	20.37	7.0459	22.19	8.0030	23.82	7.0258	29.73
8.0057	20.07	8.0119	21.88	9.0112	23.51	8.0070	29.33
9.0148	19.77	9.0347	21.56	10.0195	23.21	9.0620	28.93
10.0240	19.49	10.0007	21.29	11.0277	22.94	10.0221	28.59
11.0331	19.23	11.0234	21.01	12.0186	22.76	11.0392	28.25
12.0422	18.99	12.0458	20.78			11.5804	27.98
Bu <sub>4</sub> NBPh <sub>4</sub>							
3.2400	18.99	3.3104	21.11	5.6183	22.42	4.1616	27.70
4.0621	18.58	4.0460	20.75	6.6039	22.02	5.0176	27.33
5.0242	18.16	5.5174	20.07	7.5896	21.65	6.0516	26.78
5.9863	17.79	7.0623	19.47	8.5753	21.32	7.0421	26.31
7.0018	17.43	8.0187	19.14	9.5609	21.00	8.0571	25.87
8.0173	17.10	9.1957	18.76	10.5466	20.71	8.9453	25.51
8.9794	16.82	10.0785	18.50	11.5323	20.44	10.0238	25.11
9.9950	16.54	11.0348	18.24	12.5179	20.18	11.0389	24.76
11.0639	16.30	11.8441	18.03	13.5036	19.94	12.0540	24.42
Ph <sub>4</sub> AsPic							
2.9869	23.59	2.9801	26.30	2.9909	29.29	4.0011	32.54
4.0025	23.00	4.0286	25.58	3.4992	28.94	4.9425	31.87
5.0181	22.48	5.0220	24.99	4.7198	28.09	5.8839	31.24
5.9739	22.04	6.0153	24.46	5.9818	27.33	6.8842	30.65
6.9894	21.62	7.0087	23.99	7.0150	26.79	7.8256	30.13
8.0050	21.24	8.0021	23.55	7.9938	26.31	8.8259	29.63
8.9906	20.90	8.9954	23.16	9.0271	25.86	9.8262	29.16
9.9764	20.58	10.0440	22.77	10.0059	25.45	10.7676	28.75
10.9913	20.27	10.9821	22.54	11.0391	25.05	11.5325	28.43
11.5296	20.20						

temperature. The details of the experimental procedure have been described earlier.<sup>10,21</sup> Solutions were prepared by mass for the conductance runs, the molalities being converted to molarities by the use of densities measured with an Ostwald-Sprengel type pycnometer of about 25 mL capacity. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent at all temperatures.

Sound velocities were measured using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi) working at 4 MHz, which was calibrated with water, methanol, and benzene at each temperature. The temperature stability was maintained within  $\pm 0.01$  K by circulating thermostated water around the cell by a circulating pump.

The dielectric constants of 2-methoxyethanol at different temperatures were taken from the literature.<sup>1</sup>

### 3. Results

**3.1. Conductance.** The measured molar conductances ( $\Lambda$ ) of electrolyte solutions as a function of molar concentration ( $c$ ) at 288.15, 293.15, 298.15, and 308.15 K are given in Table 2.

The conductance data have been analyzed by the 1978 Fuoss conductance-concentration equation.<sup>22,23</sup> For a given set of conductivity values ( $c_j$ ,  $\Lambda_j$ ;  $j = 1, \dots, n$ ), three adjustable parameters, the limiting molar conductivity ( $\Lambda^\circ$ ), association constant ( $K_A$ ), and the cosphere diameter ( $R$ ), are derived from the following set of equations:

$$\Lambda = p[\Lambda^\circ(1 + R_X) + E_L] \quad (1)$$

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

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

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

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

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

where  $R_X$  is the relaxation field effect,  $E_L$  is the electrophoretic countercurrent,  $k^{-1}$  is the radius of the ion atmosphere,  $D$  is the dielectric constant of the solvent,  $e$  is the electron charge,  $k_B$  is the Boltzmann constant,  $\gamma$  is the fraction of solute present

TABLE 3: Conductance Parameters of Electrolytes in 2-Methoxyethanol at 288.15, 293.15, 298.15, and 308.15 K

electrolyte	T/K	$\Lambda^\circ/\text{S cm}^2 \text{ mol}^{-1}$	$K_A/\text{dm}^3 \text{ mol}^{-1}$	$R/\text{\AA}$	$\sigma\%$
KPic	288.15	31.80 ± 0.04	347 ± 5	10.00	0.07
	293.15	35.54 ± 0.05	373 ± 5	10.01	0.07
	298.15	38.94 ± 0.12	381 ± 11	10.02	0.18
	308.15	45.29 ± 0.07	347 ± 5	10.03	0.09
KBPh <sub>4</sub>	288.15	25.20 ± 0.03	308 ± 4	10.60	0.07
	293.15	27.23 ± 0.03	275 ± 5	10.60	0.08
	298.15	29.37 ± 0.04	237 ± 4	10.61	0.07
	308.15	36.17 ± 0.08	240 ± 7	10.62	0.15
Bu <sub>4</sub> NBPh <sub>4</sub>	288.15	22.32 ± 0.02	430 ± 4	14.20	0.05
	293.15	24.82 ± 0.04	410 ± 6	14.21	0.10
	298.15	27.57 ± 0.03	371 ± 3	14.22	0.04
	308.15	33.03 ± 0.11	354 ± 11	14.23	0.15
Ph <sub>4</sub> AsPic	288.15	27.24 ± 0.04	395 ± 5	12.87	0.09
	293.15	30.51 ± 0.04	426 ± 5	12.88	0.08
	298.15	34.05 ± 0.06	426 ± 7	12.89	0.11
	308.15	38.93 ± 0.06	421 ± 6	12.89	0.07

as unpaired ion,  $c$  is the molarity of the solution,  $f$  is the activity coefficient,  $T$  is the temperature in absolute scale, and  $\beta$  is twice the Bjerrum distance. The computations were performed on a computer using the program as suggested by Fuoss. The initial  $\Lambda^\circ$  values for the iteration procedure were obtained from Shedlovsky extrapolation<sup>24</sup> of the data. Input for the program is the set ( $c_j, \Lambda_j, j = 1, \dots, n$ ),  $n, D, \eta, T$ , initial value of  $\Lambda^\circ$ , and an instruction to cover a preselected range of  $R$  values.

In practice, calculations are made by finding the values of  $\Lambda^\circ$  and  $\alpha$  which minimize the standard deviation,  $\sigma$ :

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

for a sequence of  $R$  values and then plotting  $\sigma$  against  $R$ ; the best-fit  $R$  corresponds to the minimum in  $\sigma$  vs  $R$  curve. However, since a rough scan using unit increment of  $R$  values from 4 to 20 gave no significant minima in the  $\sigma$  (%) vs  $R$  curves, the  $R$  value was assumed to be  $R = a + d$ , where  $a$  is the sum of the ionic crystallographic radii and  $d$  is given by<sup>23</sup>

$$d = 1.183(M/\rho_0)^{1/3} \quad (8)$$

where  $M$  is the molecular weight of the solvent and  $\rho_0$  is its density.

The values of  $\Lambda^\circ$ ,  $K_A$ , and  $R$  obtained by this procedure are reported in Table 3.

3.2. Compressibility. Adiabatic compressibility coefficients ( $\beta$ ) were derived from the relation

$$\beta = 1/u^2 \rho \quad (9)$$

where  $\rho$  is the solution density and  $u$  is the sound velocity in the solution.

The apparent molar adiabatic compressibility ( $\phi_K$ ) of liquid solutions was calculated from the relation

$$\phi_K = \frac{1000}{m\rho\rho_0}(\beta\rho_0 - \beta_0\rho) + \beta \frac{M}{\rho_0} \quad (10)$$

where  $m$  is the molality of the solution and the other symbols have their usual significance.

The molar concentration ( $c$ ), density ( $\rho$ ), and the adiabatic compressibility coefficient ( $\beta$ ) of the solutions of KPic, KBPh<sub>4</sub>, and Ph<sub>4</sub>AsPic at 298.15 K are given in Table 4.

The limiting apparent molar adiabatic compressibilities ( $\phi_K^\circ$ ) were obtained<sup>25</sup> by extrapolating the plots of  $\phi_K$  versus

TABLE 4: Ultrasonic Velocities and Adiabatic Compressibilities of Electrolytes in 2-Methoxyethanol at 298.15 K

$c$ mol dm <sup>-3</sup>	$u$ cm s <sup>-1</sup>	$\beta \times 10^{12}$ cm <sup>2</sup> dyn <sup>-1</sup>	$c$ mol dm <sup>-3</sup>	$u$ cm s <sup>-1</sup>	$\beta \times 10^{12}$ cm <sup>2</sup> dyn
KPic					
0.03536	135385	56.437	0.09862	135827	55.556
0.04732	135478	56.261	0.12601	135988	55.206
0.05928	135567	56.089	0.15340	136135	54.870
0.07124	135650	55.923			
KBPh <sub>4</sub>					
0.01010	135002	56.905	0.03510	135405	56.361
0.02516	135257	56.567	0.04503	135537	56.166
0.03013	135333	56.463	0.04967	135612	56.072
Ph <sub>4</sub> AsPic					
0.00501	135431	56.658	0.02045	136354	55.702
0.00835	135651	56.432	0.02588	136626	55.415
0.01169	135859	56.217	0.03131	136884	55.143
0.01503	136052	56.015			

TABLE 5: Coefficients of the Polynomial, Eq 12

electrolyte	$a_0$	$a_1$	$a_2$	$\sigma\%$
KPic	38.97	-0.6735	0.04209	0.054
KBPh <sub>4</sub>	29.49	-0.5459	0.01196	0.217
Bu <sub>4</sub> NBPh <sub>4</sub>	27.53	-0.5369	0.00141	0.075
Ph <sub>4</sub> AsPic	33.89	-0.5900	0.00828	0.287

the square root of molal concentration of the solute to zero concentration:

$$\phi_K = \phi_K^\circ + S_K m^{1/2} \quad (11)$$

where  $S_K$  is the experimental slope.

#### 4. Discussion

4.1. Limiting Molar Conductance and Association Constant. Table 3 shows that for all salts the limiting molar conductances ( $\Lambda^\circ$ ) increase as the temperature increases. The  $\Lambda^\circ$  values were fitted to the following polynomial:

$$\Lambda^\circ = a_0 + a_1(298.15 - T) + a_2(298.15 - T)^2 \quad (12)$$

and the coefficients of these fits are given in Table 5 together with the standard percentage errors ( $\sigma\%$ ).

The single ion conductivities at different temperatures have been evaluated from the division of the  $\Lambda^\circ$  value of Bu<sub>4</sub>NBPh<sub>4</sub> using the following relationship:

$$\frac{\lambda^\circ(\text{Bu}_4\text{N}^+)}{\lambda^\circ(\text{Ph}_4\text{B}^-)} = \frac{r_{\text{Ph}_4\text{B}^-}}{r_{\text{Bu}_4\text{N}^+}} = 1.07 \quad (13)$$

The ionic radii of Bu<sub>4</sub>N<sup>+</sup> and Ph<sub>4</sub>B<sup>-</sup> ions were taken from the work of Gill and Sekhri.<sup>25,26</sup>

The single-ion conductivities ( $\lambda^\circ_\pm$ ) along with the Walden products ( $\lambda^\circ_\pm \eta_0$ ) of all the ions are reported in Table 6.

The single-ion conductivities have also been fitted to the following polynomial equation:

$$\lambda^\circ_\pm = b_0 + b_1(298.15 - T) + b_2(298.15 - T)^2 \quad (14)$$

and the coefficients of the fits along with the  $\sigma\%$  values are recorded in Table 7.

The Walden products for these salts in 2-methoxyethanol are substantially lower than those in aqueous solutions.<sup>27</sup> The apparent excess of mobility in aqueous solution has been attributed to far greater solvation in the nonaqueous media.

TABLE 6: Limiting Ionic Conductances ( $\lambda_{\pm}^0/S \text{ cm}^2 \text{ mol}^{-1}$ ) and Ionic Walden Products ( $\lambda_{\pm}^0 \eta_0/S \text{ cm}^2 \text{ mol}^{-1} \text{ Pa s}$ ) in 2-Methoxyethanol at 288.15, 293.15, 298.15, and 308.15 K

ion	288.15 K		293.15 K		298.15 K		308.15 K	
	$\lambda_{\pm}^0$	$\lambda_{\pm}^0 \eta_0$						
K <sup>+</sup>	14.39	0.279	15.24	0.263	16.05	0.247	20.21	0.254
Bu <sub>4</sub> N <sup>+</sup>	11.54	0.224	12.43	0.215	14.25	0.220	17.07	0.215
Ph <sub>4</sub> As <sup>+</sup>	9.83	0.190	10.21	0.176	11.16	0.172	13.85	0.174
Pic <sup>-</sup>	17.41	0.337	20.30	0.351	22.89	0.353	25.08	0.315
Ph <sub>4</sub> B <sup>-</sup>	10.78	0.209	11.99	0.207	13.32	0.205	15.96	0.201

TABLE 7: Coefficients of the Polynomial, Eq 14

ion	$b_0$	$b_1$	$b_2$	$\sigma\%$
K <sup>+</sup>	16.19	-0.2862	0.01129	0.254
Bu <sub>4</sub> N <sup>+</sup>	14.05	-0.2831	0.00219	0.344
Ph <sub>4</sub> As <sup>+</sup>	11.11	-0.2026	0.00722	0.088
Pic <sup>-</sup>	22.78	-0.3873	-0.01550	0.199
Ph <sub>4</sub> B <sup>-</sup>	13.30	-0.2579	0.00067	0.036

TABLE 8: Coefficients of the Polynomial, Eq 18, and Thermodynamic Standard Data of the Association

electrolyte	$c_0$	$c_1$	$10^2 c_2$	$\sigma\%$	$c_0 + 298.15c_1$
	$\Delta G_{298.15}^{\ddagger}$ J mol <sup>-1</sup>	$\Delta S_{298.15}^{\ddagger}$ J K <sup>-1</sup> mol <sup>-1</sup>	J K <sup>-2</sup> mol <sup>-1</sup>		$\Delta H_{298.15}^{\ddagger}$ J mol <sup>-1</sup>
KPic	-14734.6	48.59	234.85	0.028	-248.3
KBPh <sub>4</sub>	-13614.1	14.00	-274.93	0.073	-9442.9
Bu <sub>4</sub> NBPh <sub>4</sub>	-14709.1	24.13	-77.81	0.162	-7513.2
Ph <sub>4</sub> AsPic	-15034.3	56.72	126.88	0.106	1877.5

We find (cf.  $K_A$  values from Table 3) that all these salts are moderately associated in 2-methoxyethanol at all the temperature investigated. This is quite expected owing to the low dielectric constant ( $D = 16.94$  at 298.15 K)<sup>1</sup> of the solvent.

4.2. Thermodynamics of Ion Pair Formation. The standard Gibbs energy changes for the ion association process,  $\Delta G^{\ddagger}$ , can be calculated from the equation

$$\Delta G^{\ddagger} = -RT \ln K_A \quad (15)$$

The values of the standard enthalpy change,  $\Delta H^{\ddagger}$ , and the standard entropy change,  $\Delta S^{\ddagger}$ , can be evaluated from the temperature dependence of  $\Delta G^{\ddagger}$  values as follows:

$$\Delta H^{\ddagger} = -T^2 \left[ \frac{d(\Delta G^{\ddagger}/T)}{dT} \right]_p \quad (16)$$

$$\Delta S^{\ddagger} = - \left( \frac{d\Delta G^{\ddagger}}{dT} \right)_p \quad (17)$$

The  $\Delta G^{\ddagger}$  values can be fitted with the help of a polynomial of the type

$$\Delta G^{\ddagger} = c_0 + c_1(298.15 - T) + c_2(298.15 - T)^2 \quad (18)$$

and the coefficients of the fits are compiled in Table 8, together with the  $\sigma\%$  values of the fits.

The standard values at 298.15 K are then

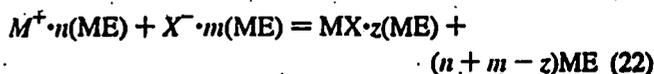
$$\Delta G_{298.15}^{\ddagger} = c_0 \quad (19)$$

$$\Delta S_{298.15}^{\ddagger} = c_1 \quad (20)$$

$$\Delta H_{298.15}^{\ddagger} = c_0 + 298.15c_1 \quad (21)$$

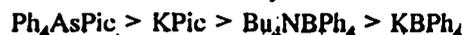
It is observed from Table 8 that the  $\Delta S^{\ddagger}$  values of ion association for all these electrolytes are positive. These positive  $\Delta S^{\ddagger}$  values may be attributed to the increasing number of degrees of freedom upon association mainly due to the release

of solvent molecules



In other words, the solvation of ions is weakened as soon as the ion pair is formed.

The  $\Delta S^{\ddagger}$  values of the electrolytes are found to decrease in the following order:



which indicates that the degree of weakening of the ion solvation due to the formation of ion pair also decreases in the same order.

The main factors which govern the standard entropy of ion association of electrolytes are (i) the size and shape of the ions, (ii) charge density on the ions, (iii) electrostriction of the solvent molecules around the ions, and (iv) penetration of the solvent molecules inside the space of the ions, and the influence of these factors is discussed in section 4.3.

The variation of  $\Delta H^{\ddagger}$  from one salt to another is quite interesting. For Ph<sub>4</sub>AsPic, the  $\Delta H^{\ddagger}$  value is sufficiently positive. It is obvious, therefore, that, for this salt, the enthalpic term is counterbalanced by a favorable entropy change which comes from the short- and long-range desolvation of both ions. The attribution of  $\Delta S^{\ddagger}$  to desolvation is also supported by the positive enthalpies indicating lack of covalent bonds.

The  $\Delta H^{\ddagger}$  value of KPic is very small. The enthalpic term for the ion association process here is so small that it plays a negligible role in the association equilibrium, which is mainly determined by the positive entropic term which comes from the desolvation of the cations.

It is especially noteworthy that the  $\Delta H^{\ddagger}$  values for KBPh<sub>4</sub> and Bu<sub>4</sub>NBPh<sub>4</sub> are negative. The electrostatic theories of ionic association,<sup>29</sup> however, never give negative values for  $\Delta H^{\ddagger}$ , since the theoretical equation for  $\Delta H^{\ddagger}$  contains the  $[1 + (d \ln D/d \ln T)_p]$  term; thus, the experimental value of  $(d \ln D/d \ln T)_p$  makes the theoretical  $\Delta H^{\ddagger}$  value positive, contrary to the expectation.

The negative values of  $\Delta H^{\ddagger}$  can be explained by considering the participation of specific covalent interaction in the ion association process. Here, in this case, the covalent interaction somewhat works between the ions, and hence, the binding enthalpy between the ions is sufficiently negative to compensate for the positive contribution from the weakening of ion solvation. In this case,  $\Delta G^{\ddagger}$  of the ion association should have a large negative value (a large  $K_A$  value) and should depend on the kind of ions, and this is found to be true here.

The non-Coulombic part of the Gibbs energy,  $\Delta G^*$ , has also been calculated using the following equation<sup>30</sup>:

$$\Delta G^* = N_A W_{\pm}^* \quad (23)$$

$$K_A = (4\pi N_A / 1000) \int_a^R r^2 \exp\left(\frac{2q}{r} - \frac{W_{\pm}^*}{kT}\right) dr \quad (24)$$

where the symbols have their usual significance. The quantity  $2q/r$  is the Coulombic part of the interionic mean force potential and  $W_{\pm}^*$  is its non-Coulombic part.

The procedure for the evaluation of the non-Coulombic part of the entropy and enthalpy (and  $\Delta S^*$  and  $\Delta H^*$ , respectively) is the same as that used for obtaining  $\Delta S^{\ddagger}$  and  $\Delta H^{\ddagger}$ .

TABLE 9: Coefficients of the Polynomial, Eq 25, for the Non-Coulombic Contribution to the Association Process

electrolyte	$c_0^*$ $\Delta G_{298.15}^*$ J mol <sup>-1</sup>	$c_1^*$ $\Delta S_{298.15}^*$ J K <sup>-1</sup> mol <sup>-1</sup>	$c_2^*$ J K <sup>-2</sup> mol <sup>-1</sup>	$\sigma$ %	$c_0^* + 298.15c_1^*$ $\Delta H_{298.15}^*$ J mol <sup>-1</sup>
KPic	-3805.9	1.03	242.50	0.023	-3497.2
KBPh <sub>4</sub>	-2712.7	-33.60	-267.27	0.487	-12729.8
Bu <sub>4</sub> NBPh <sub>4</sub>	-4170.9	-23.97	-77.81	0.162	-7513.2
Ph <sub>4</sub> AsPic	-1504.3	8.92	134.96	0.390	-1655.5

The  $\Delta G^*$  values at different temperatures were fitted to the polynomial

$$\Delta G^* = c_0^* + c_1^*(298.15 - T) + c_2^*(298.15 - T)^2 \quad (25)$$

and the coefficients of the fits along with the  $\sigma$ % values are given in Table 9.

The values of  $\Delta G^*$ ,  $\Delta S^*$ , and  $\Delta H^*$  at 298.15 K are then easily obtained from the following equations:

$$\Delta G_{298.15}^* = c_0^* \quad (26)$$

$$\Delta S_{298.15}^* = c_1^* \quad (27)$$

$$\Delta H_{298.15}^* = c_0^* + 298.15c_1^* \quad (28)$$

The non-Coulombic parts of the Gibbs energy,  $\Delta G_{298.15}^*$ , of all the salts are found to be small (Table 9), 20% (KBPh<sub>4</sub>), 26% (KPic), 29% (Ph<sub>4</sub>AsPic), and 28% (Bu<sub>4</sub>NPh<sub>4</sub>) in 2-methoxyethanol. This indicates that the Coulombic forces play a major role in the association processes. This is further supported by the fairly higher values of the Coulombic parts of  $\Delta S^*$  and  $\Delta H^*$  compared to their non-Coulombic counterparts.

**4.3. Compressibility Behavior.** The limiting apparent molar adiabatic compressibilities ( $\phi_K^*$ ) of KPic, KBPh<sub>4</sub>, and Ph<sub>4</sub>AsPic are found to be negative ( $\phi_K^*$  values at 298.15 K for KPic, KBPh<sub>4</sub>, and Ph<sub>4</sub>AsPic are  $-164.22 \times 10^{-10}$ ,  $-139.41 \times 10^{-10}$ , and  $-617 \times 10^{-10}$  cm<sup>3</sup> mol<sup>-1</sup> dyn<sup>-1</sup>, respectively). These negative  $\phi_K^*$  values of the electrolytes can be interpreted in terms of loss of compressibility of the solvent 2-methoxyethanol due to the presence of these solutes in solution.

A comparison of the  $\phi_K^*$  values of these three salts can unravel some interesting and intricate aspects of electrostriction of the solvent molecules around the small sized ions and penetration of those molecules into the larger ions and their influence on the compressibility of the medium.

For small ions with higher surface charge density on them, there will be loss of compressibility in solution arising out of the electrostriction of the solvent molecules around those ions. Electrostriction will, however, be negligible in the vicinity of larger ions with low charge density on their surface. But, in these cases also the loss of compressibility might be effected by other factors; one effect that can play an important role for the large tetraphenylborate and tetraphenylarsonium ions is the penetration of the solvent molecules (ME) into the space between the phenyl chains attached to the boron atom of the former or arsenic atom of the later ion. This obviously will cause constriction of the solution volumes resulting in a more compact and hence less compressible medium. The possibility of penetration of the 2-methoxyethanol molecules into the tetraphenylborate ions is rather less due mainly to (i) the repulsive effect of the negatively charged boron atom upon the 2-methoxyethanol molecules (arsenic is positively charged, in contrast) and (ii) the less available space between the phenyl groups

attached to the smaller boron atom compared to the bigger arsenic atom.

Among KPic and KBPh<sub>4</sub> solutions, the former solution is more compressible than the later (Table 4) indicating that the loss of compressibility of the medium is less in the presence of KPic. In these two salts, K<sup>+</sup> ion being common, the anions are evidently making the difference. In case of picrate ion, electrostriction will be predominant, whereas in the case of tetraphenylborate ion, neither electrostriction nor penetration is expected to affect compressibility of the medium. From the observed trend in the compressibility (and also in the apparent molar adiabatic compressibility), it appears that electrostrictive effect plays a major role here. In case of picrate ion, more solvent was associated with the ion compared to the tetraphenylborate ion; hence on association, a greater number of solvent molecules are released into the bulk, thereby making the medium more compressible. This observation also gets support from the  $\Delta S^*$  value of the association process. Greater desolvation for KPic solution helps make the system more compressible.

Among KPic and Ph<sub>4</sub>AsPic solutions, once again the former solution has higher compressibility. The plausible reason for this observation is similar to that described for the pair KPic and KBPh<sub>4</sub> except that some amount of penetration is possible for tetraphenylarsonium ion. But, the most striking observation is that though KPic is more compressible, Ph<sub>4</sub>AsPic has a higher  $\Delta S^*$  value of the ion association. A possible explanation for this might be that the solvent molecules which are released from the tetraphenylarsonium ion upon association will remain trapped inside the tetraphenyl chains around the arsenic atom. These trapped solvent molecules are, thus, free to move within the territory of the phenyl chains to increase the entropic term; but, since these remain inside the chains, these are not sufficiently compressible under applied pressure.

It may thus be concluded that all these electrolytes remain strongly associated in 2-methoxyethanol to form ion pairs and the solvation of the ions is weakened as soon as the ion pair is formed. The results indicate that the Coulombic forces play a major role in the association process. Electrostriction is found to be important for potassium and picrate ions while penetration of the solvent molecules occurs inside the space between the alkyl or aryl chains attached to the nitrogen or arsenic atom of the tetrabutylammonium or tetraphenylarsonium ion. For tetraphenylborate ion, on the other hand, neither electrostriction nor penetration is found to be operative.

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# Thermodynamics of Ionic Association of Tetraphenylphosphonium, Tetraphenylarsonium, and Some Common Cations in 2-Methoxyethanol Using Conductometry and FT-Raman Spectroscopy

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Precise measurements on electrical conductances and Fourier Transform (FT) Raman spectra of solutions of tetraphenylarsonium chloride ( $\text{Ph}_4\text{AsCl}$ ), tetraphenylphosphonium chloride ( $\text{Ph}_4\text{PCl}$ ), tetraphenylphosphonium bromide ( $\text{Ph}_4\text{PBr}$ ), lithium tetrafluoroborate ( $\text{LiBF}_4$ ), and sodium tetrafluoroborate ( $\text{NaBF}_4$ ) in 2-methoxyethanol (ME) at temperatures  $288.15 \leq T/\text{K} \leq 308.15$  are reported. The conductance data were analyzed by the 1978 Fuoss conductance–concentration equation. Thermodynamics of the association processes were also studied, and the Coulombic forces are found to play a major role in the association processes. The Raman spectra suggest the presence of “spectroscopically free”  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{BF}_4^-$  ions in solution, thus substantiating the moderate ion-pair formation constants for these electrolytes obtained from conductometric measurements. The observed processes were interpreted by an Eigen multistep mechanism. Raman spectra also indicate that the cations get attached to the ME molecules through the ethereal oxygen atom rather than through the alcoholic oxygen of the solvent molecules.

## 1. Introduction

In recent years, 2-methoxyethanol (ME)—commonly known as methyl cellosolve—has drawn much attention as a solvent medium for various electrochemical investigations, as well as for various industrial processes.<sup>1,2</sup> It has unique solvating properties associated with its quasiaprotic character.<sup>3</sup> As it is a monomethyl ether of ethylene glycol, it is very likely to show physicochemical properties midway between protic and aprotic solvents. Hence, it is of much interest to study the behavior of electrolytes in such a solvent medium.

Recently, we have initiated a comprehensive program to study the solvation and association behavior of 1:1 electrolytes in different nonaqueous solvents from the measurements of various transport, thermodynamic, and spectroscopic properties.<sup>4–6</sup> In this paper, an attempt is made to unravel the nature of various types of interactions prevailing in solutions of tetraphenylarsonium chloride ( $\text{Ph}_4\text{AsCl}$ ), tetraphenylphosphonium chloride ( $\text{Ph}_4\text{PCl}$ ), tetraphenylphosphonium bromide ( $\text{Ph}_4\text{PBr}$ ), lithium tetrafluoroborate ( $\text{LiBF}_4$ ), and sodium tetrafluoroborate ( $\text{NaBF}_4$ ) in 2-methoxyethanol from precise conductivity and Fourier Transform (FT) Raman spectral measurements.

## 2. Experimental Section

**2.1 Materials.** 2-Methoxyethanol (ME, G. R.E Merck) was dried with potassium carbonate and distilled twice in an all glass distillation set immediately before use, and the middle fraction was collected. The purified solvent had a density of  $0.96002 \text{ g cm}^{-3}$ , a coefficient of viscosity of  $1.5414 \text{ mPa}\cdot\text{s}$ , and a specific conductance of  $\text{ca. } 1.01 \times 10^{-6} \text{ S cm}^{-1}$  at  $298.15 \text{ K}$ . These values are in good agreement with the literature data.<sup>7</sup>

Tetraphenylarsonium chloride,  $\text{Ph}_4\text{AsCl}$  (Fluka) was recrystallized from absolute ethanol solution by dry ether and dried in a vacuum.<sup>8</sup>

Tetraphenylphosphonium chloride,  $\text{Ph}_4\text{Cl}$ , and tetraphenylphosphonium bromide,  $\text{Ph}_4\text{PBr}$  (Fluka, puriss grade) were dissolved in absolute ethanol, reprecipitated by the addition of dry ether, and vacuum-dried at  $373 \text{ K}$ .<sup>8</sup>

Lithium tetrafluoroborate,  $\text{LiBF}_4$ , and sodium tetrafluoroborate,  $\text{NaBF}_4$  (Fluka, purum grade) were dried under vacuum at high temperatures for 48 h and were used without further purification.

**2.2. Apparatus and Procedures.** Conductance measurements were carried out on a pye-Unicam PW 9509 conductivity meter at a frequency of  $2000 \text{ Hz}$  using a dip-type cell of cell constant  $1.14 \text{ cm}^{-1}$  and having an accuracy of  $0.1\%$ . Measurements were made in an oil bath maintained within  $\pm 0.005 \text{ K}$  of the desired temperature. The details of the experimental procedure have been described earlier.<sup>3,9</sup> Solutions were prepared by mass for the conductance runs, the molalities being converted to molarities by the use of densities measured with an Ostwald-Sprengel type pycnometer of about  $25 \text{ cm}^3$  capacity. Several independent solutions were prepared, and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent at all temperatures.

FT Raman spectra were excited at  $1064 \text{ nm}$  using a Nd:YAG laser and a Bruker IFS 66V optical bench with an FRA 106 Raman module attached to it. Laser power was set at  $200 \text{ mW}$ , and 256 (averaged) scans were accumulated with a resolution of  $2 \text{ cm}^{-1}$ . The spectra were recorded by the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras.

The dielectric constants of 2-methoxyethanol at different temperatures were taken from the literature.<sup>10</sup>

## 3. Results

**3.1. Conductance.** The measured molar conductances ( $\Lambda$ ) of electrolyte solutions as a function of molar concentration ( $c$ ) at  $288.15$ ,  $293.15$ ,  $298.15$ , and  $308.15 \text{ K}$  are given in Table 1.

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TABLE 1: Molar Conductivities of Electrolytes in 2-Methoxyethanol at 288.15, 293.15, 298.15, and 308.15 K

T = 288.15 K		T = 293.15 K		T = 298.15 K		T = 308.15 K	
$c \times 10^4/\text{mol dm}^{-3}$	$\Lambda/S \text{ cm}^2 \text{ mol}^{-1}$	$c \times 10^4/\text{mol dm}^{-3}$	$\Lambda/S \text{ cm}^2 \text{ mol}^{-1}$	$c \times 10^4/\text{mol dm}^{-3}$	$\Lambda/S \text{ cm}^2 \text{ mol}^{-1}$	$c \times 10^4/\text{mol dm}^{-3}$	$\Lambda/S \text{ cm}^2 \text{ mol}^{-1}$
Ph <sub>4</sub> AsCl							
6.5187	23.54	4.2025	26.87	4.0000	29.52	3.8416	34.47
7.5372	23.21	5.1756	26.44	5.0625	29.01	5.0176	33.87
8.5558	22.91	6.0530	26.08	6.2413	28.52	5.9524	33.44
9.5743	22.65	7.0618	25.73	7.0195	28.22	7.0602	32.96
10.5929	22.39	8.0034	25.39	8.0620	27.84	8.0015	32.60
11.0003	22.27	9.0123	25.07	9.4899	27.38	9.0101	32.23
12.0188	22.01	10.0211	24.74	10.4250	27.05	10.0187	31.87
13.0374	21.79	11.0299	24.46	11.4675	26.73	11.0273	31.55
14.0559	21.56	12.0388	24.18	12.4405	26.40	12.0359	31.22
Ph <sub>4</sub> PCl							
5.0625	24.35	3.4596	27.54	5.2900	29.09	3.0276	35.00
6.0784	23.97	4.6447	26.95	6.8270	28.48	3.6100	34.63
7.0071	23.64	6.0520	26.36	7.8151	28.12	5.0842	33.81
8.0201	23.33	6.9999	25.98	8.8033	27.79	6.5459	33.09
9.0332	23.01	8.0208	25.62	9.7914	27.50	7.5628	32.65
10.0463	22.70	9.1145	25.24	10.7795	27.23	8.5161	32.26
11.0594	22.44	10.0624	24.94	11.7676	26.95	9.5329	31.87
12.0724	22.17	11.0103	24.65	12.7557	26.67	10.5497	31.49
13.5076	21.81	12.0639	24.34	13.7439	26.44	11.5030	31.18
Ph <sub>4</sub> PBr							
2.1408	29.14	4.6656	29.76	2.0991	34.36	2.1377	40.70
3.1743	28.38	5.6644	29.22	3.1825	33.46	3.1437	39.74
4.2077	27.74	6.5487	28.79	4.1982	32.71	4.2125	38.86
5.2412	27.17	7.5053	28.36	5.2816	32.04	5.2185	38.14
6.2747	26.69	8.5354	27.93	6.2973	31.47	6.2873	37.41
7.3082	26.20	9.5656	27.51	7.3130	30.95	7.3562	36.79
8.4155	25.73	10.5221	27.16	8.3965	30.41	8.3622	36.24
9.4490	25.35	10.5522	26.77	9.4122	29.95	9.4310	35.67
10.4824	24.92	12.5088	26.43	10.4956	29.48	10.4370	35.17
LiBF <sub>4</sub>							
4.4944	30.22	4.2436	33.10	4.1616	35.30	4.1616	40.34
5.5697	29.58	5.0271	32.58	5.0544	34.71	5.0667	39.72
6.0540	29.30	6.0261	31.97	6.0067	34.14	6.0213	39.13
7.0226	28.80	7.0231	31.43	7.0322	33.56	7.0493	38.51
8.0720	28.29	8.0581	30.89	8.0577	33.02	8.0039	38.01
9.0406	27.84	9.0192	30.44	9.0100	32.56	9.0319	37.48
10.0092	27.42	10.0542	29.97	9.9623	32.10	10.0599	37.02
11.0586	26.98	11.0153	29.54	11.0611	31.63	11.0145	36.58
12.0272	26.59	12.0502	29.13	12.0134	31.20	12.0425	36.14
NaBF <sub>4</sub>							
1.0250	30.94	1.0250	32.62	5.6644	31.53	2.0437	38.47
2.0505	29.92	2.0505	31.58	6.5832	31.10	3.0655	37.58
3.0785	29.17	3.0758	30.79	7.5237	30.70	4.0088	36.88
4.0222	28.59	4.0222	30.16	8.5817	30.28	5.0306	36.24
5.0475	28.00	5.0475	29.54	9.5222	29.93	6.0525	35.61
6.0727	27.53	6.0727	29.04	10.5802	29.54	7.0743	35.04
7.0980	27.06	7.0980	28.55	11.5207	29.21	8.0175	34.58
8.0444	26.60	8.0444	28.05	12.5787	28.85	9.0394	34.07
9.0697	26.25	9.0697	27.67	13.5191	28.56	10.2184	33.54
10.2527	25.77	10.2527	27.20				

The conductance data were analyzed by the 1978 Fuoss conductance-concentration equation.<sup>11,12</sup> For a given set of conductivity values ( $c_j$ ,  $\Lambda_j$ ;  $j = 1, \dots, n$ ), three adjustable parameters, the limiting molar conductivity ( $\Lambda^0$ ), association constant ( $K_A$ ), and the cosphere diameter ( $R$ ), are derived from the following set of equations:

$$\Lambda = p[\Lambda^0(1 + R_X) + E_L] \quad (1)$$

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

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

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

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

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

where the symbols have their usual significance. The computations were performed on a computer using the program as suggested by Fuoss. The initial  $\Lambda^0$  values for the iteration

procedure were obtained from Shedlovsky extrapolation<sup>13</sup> of the data. Input for the program is the set ( $c_j$ ,  $\Lambda_j$ ;  $j = 1, \dots, n$ ),  $n$ ,  $D$ ,  $\eta$ ,  $T$ , the initial value of  $\Lambda^0$ , and an instruction to cover a preselected range of  $R$  values.

In practice, calculations are made by finding the values of  $\Lambda^0$  and  $\alpha$  which minimize the standard deviation,  $\sigma$ ,

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

for a sequence of  $R$  values and then plotting  $\sigma$  against  $R$ ; the best-fit  $R$  corresponds to the minimum in  $\sigma$  versus  $R$  curve. However, since a rough scan using unit increment of  $R$  values from 4 to 20 gave no significant minima in the  $\sigma(\%)$  versus  $R$  curves, the  $R$  value was assumed to be  $R = a + d$ , where  $a$  is the sum of the ionic crystallographic radii and  $d$  is given by<sup>12</sup>

$$d = 1.183(M/\rho_0)^{1/3} \quad (8)$$

where  $M$  is the molecular weight of the solvent and  $\rho_0$  its density.

**TABLE 2: Conductance Parameters of Electrolytes in 2-Methoxyethanol at 288.15, 293.15, 298.15, and 308.15 K**

electrolyte	<i>T</i> /K	$\Lambda^0/S$ cm <sup>2</sup> mol <sup>-1</sup>	$K_A/dm^3$ mol <sup>-1</sup>	$R/\Lambda^0$	$\sigma\%$
Ph <sub>4</sub> AsCl	288.15	28.33 ± 0.07	254 ± 6	10.91	0.08
	293.15	31.08 ± 0.06	246 ± 6	10.91	0.10
	298.15	33.98 ± 0.10	233 ± 9	10.92	0.16
	308.15	39.26 ± 0.07	186 ± 5	10.93	0.10
Ph <sub>4</sub> PCl	288.15	28.78 ± 0.07	274 ± 7	10.81	0.11
	293.15	31.47 ± 0.07	257 ± 7	10.81	0.13
	298.15	34.03 ± 0.05	213 ± 4	10.82	0.06
	308.15	39.41 ± 0.07	208 ± 5	10.83	0.12
Ph <sub>4</sub> PBr	288.15	32.48 ± 0.07	336 ± 9	10.97	0.17
	293.15	35.36 ± 0.10	340 ± 9	10.97	0.12
	298.15	38.25 ± 0.08	317 ± 8	10.98	0.16
	308.15	45.31 ± 0.09	297 ± 8	10.99	0.15
LiBF <sub>4</sub>	288.15	36.26 ± 0.12	388 ± 12	7.70	0.13
	293.15	39.21 ± 0.11	350 ± 9	7.70	0.12
	298.15	41.52 ± 0.13	313 ± 10	7.71	0.14
	308.15	46.86 ± 0.09	224 ± 6	7.72	0.10
NaBF <sub>4</sub>	288.15	33.07 ± 0.06	280 ± 7	8.26	0.18
	293.15	34.93 ± 0.07	276 ± 7	8.26	0.19
	298.15	37.66 ± 0.10	253 ± 8	8.27	0.11
	308.15	42.54 ± 0.09	228 ± 8	8.28	0.17

The values of  $\Lambda^0$ ,  $K_A$ , and  $R$  obtained by this procedure are reported in Table 2.

**3.2. FT Raman Spectra.** The Raman spectra of pure 2-methoxyethanol and of the solutions of Ph<sub>4</sub>AsCl, Ph<sub>4</sub>PBr, LiBF<sub>4</sub>, and NaBF<sub>4</sub> in 2-methoxyethanol in the range 3500–100 cm<sup>-1</sup> are presented in Figures 1 to 5. The principal bands observed are listed in Table 3.

#### 4. Discussion

**4.1. Limiting Molar Conductance and Association Constant.** Table 2 shows that for all salts, the limiting molar conductances  $\Lambda^0$  increase as the temperature increases. The  $\Lambda^0$  values were fitted to the following polynomial:

$$\Lambda^0 = a_0 + a_1(298.15 - T) + a_2(298.15 - T)^2 \quad (9)$$

The coefficients of these fits are given in Table 4, together with the standard percentage errors ( $\sigma\%$ ).

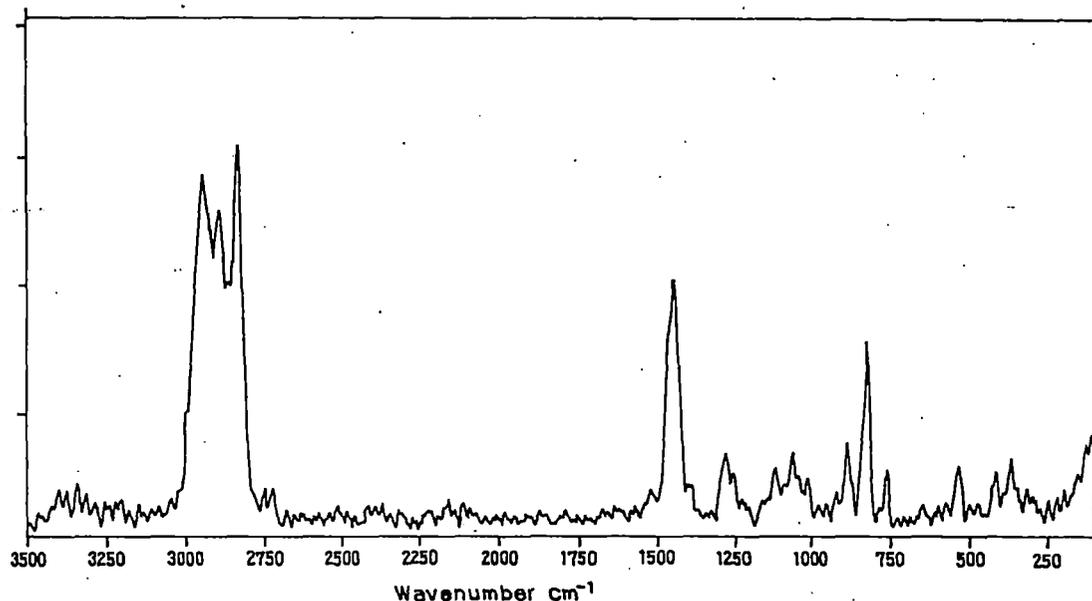


Figure 1. FT Raman spectrum of 2-methoxyethanol.

**TABLE 3: Raman Frequencies in cm<sup>-1</sup><sup>a</sup>**

ME	Ph <sub>4</sub> AsCl	Ph <sub>4</sub> PBr	LiBF <sub>4</sub>	NaBF <sub>4</sub>
—	238.1(m)	253.8(m)	—	—
—	—	—	376.8(m)	375.3(w)
—	—	—	425.8(m)	427.7(w)
—	—	—	541.5(m)	542.7(w)
—	—	—	766.4(m)	770.2(w)
834.7(s)	833.1(m)	832.9(s)	833.7(s)	834.5(s)
891.4(m)	894.6(w)	892.2(w)	892.6(m)	889.5(m)
1019.4(w)	1001.9(vs)	1001.3(s)	—	—
1074.6(w)	1023.6(m)	1027.3(m)	1065.4(m)	1069.0(w)
1457.0(s)	sh	1455.8(s)	1457.9(s)	1454.1(s)
1470.6(s)	1463.5(s)	1470.0(s)	sh	sh
—	1580.6(s)	1586.6(s)	—	—
2829.7(vs)	2828.4(s)	2829.1(m)	2835.5(vs)	2832.8(vs)
2890.3(m)	2896.5(m)	2891.0(m)	2895.1(m)	2892.1(m)
2942.4(s)	2937.0(s)	2923.1(s)	2943.5(s)	2944.8(s)
—	3063.0(vs)	3065.8(s)	—	—

<sup>a</sup> sh = shoulder, w = weak, m = medium, s = strong, vs = very strong.

**TABLE 4: Coefficients of the Polynomial, Eq 9**

electrolyte	$a_0$	$a_1$	$a_2$	$\sigma\%$
Ph <sub>4</sub> AsCl	33.93	-0.5481	-0.0015	0.066
Ph <sub>4</sub> PCl	34.07	-0.5302	-0.0003	0.055
Ph <sub>4</sub> PBr	38.32	-0.6390	0.0058	0.089
LiBF <sub>4</sub>	41.67	-0.5236	-0.0010	0.162
NaBF <sub>4</sub>	37.49	-0.4792	0.0029	0.209

The single-ion conductivities at different temperatures were calculated from the reference electrolyte Bu<sub>4</sub>NBPh<sub>4</sub>.<sup>14</sup> The single-ion conductivities  $\lambda_{\pm}^0$  along with the Walden products  $\lambda_{\pm}^0 \eta_0$  are reported in Table 5.

The single-ion conductivities were also fitted to the following polynomial equation:

$$\lambda_{\pm}^0 = b_0 + b_1(298.15 - T) + b_2(298.15 - T)^2 \quad (10)$$

The coefficients of the fits, along with the  $\sigma\%$  values, are recorded in Table 6.

All these electrolytes are found to be moderately associated (cf.  $K_A$  values from Table 2) in 2-methoxyethanol at all the temperatures investigated. These electrolyte solutions, in general,

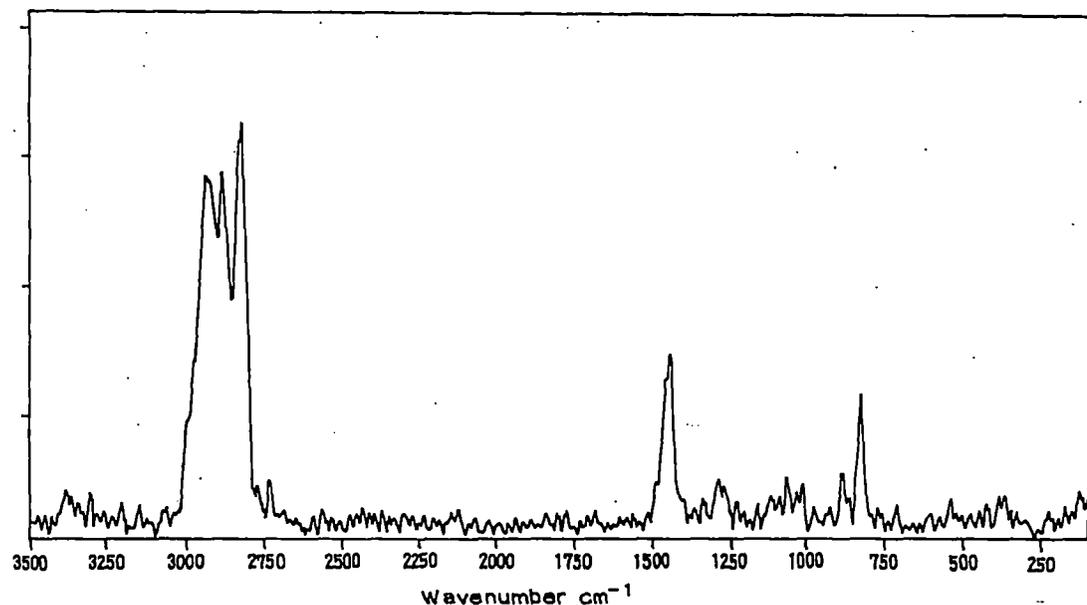
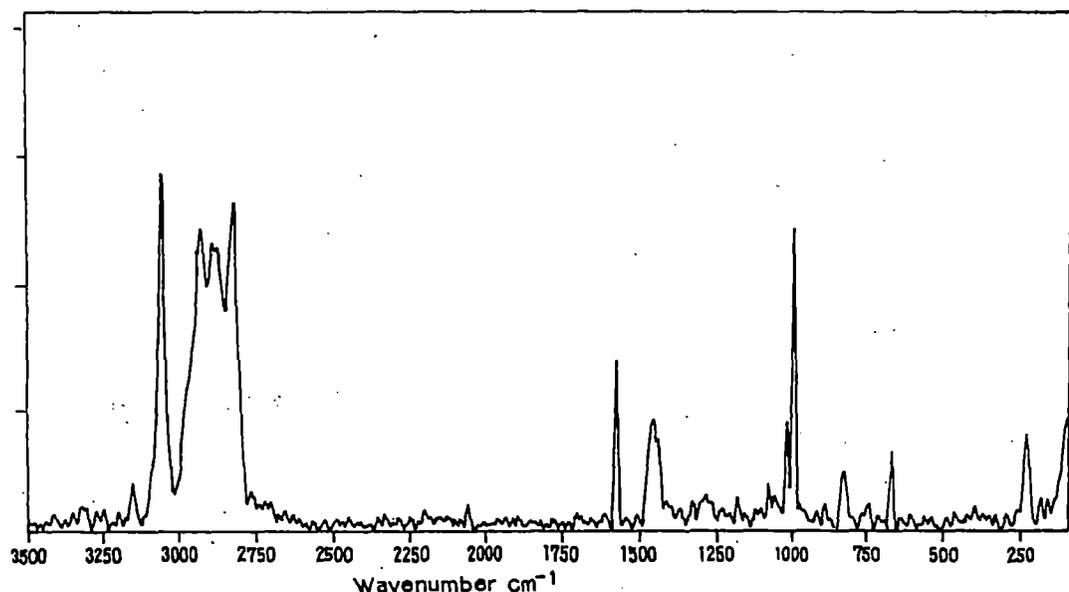
Figure 2. FT Raman spectrum of Ph<sub>4</sub>AsCl in 2-methoxyethanol.Figure 3. FT Raman spectrum of Ph<sub>4</sub>PBr in 2-methoxyethanol.

TABLE 5: Limiting Ionic Conductances ( $\lambda_{\pm}^0/S \text{ cm}^2 \text{ Mol}^{-1}$ ) and Ionic Walden Products ( $\lambda_{\pm}^0/S \text{ cm}^2 \text{ Mol}^{-1} \text{ Pa S}$ ) in 2-Methoxyethanol at 288.15, 293.15, 298.15, and 308.15 K

ion	288.15 K		293.15 K		298.15 K		308.15 K	
	$\lambda_{\pm}^0$	$\lambda_{\pm}^0 \eta_0$						
Ph <sub>4</sub> As <sup>+</sup>	9.83	0.019	10.21	0.018	11.16	0.017	13.85	0.017
Ph <sub>4</sub> P <sup>+</sup>	10.28	0.020	10.60	0.018	11.21	0.017	14.00	0.018
Cl <sup>-</sup>	18.50	0.036	20.87	0.036	22.82	0.035	25.41	0.032
Br <sup>-</sup>	22.20	0.043	24.76	0.043	27.04	0.042	31.31	0.039

TABLE 6: Coefficients of the Polynomial, Eq 10

ion	$b_0$	$b_1$	$b_2$	$\sigma\%$
Ph <sub>4</sub> As <sup>+</sup>	11.11	-0.2026	0.00721	0.204
Ph <sub>4</sub> P <sup>+</sup>	11.25	-0.1847	0.00898	0.158
Cl <sup>-</sup>	22.82	-0.3455	-0.00866	0.002
Br <sup>-</sup>	27.07	-0.4544	-0.00313	0.059

show a small negative temperature dependence of  $K_A$ , which is a quite normal behavior for molecular ions with nonelectrostatic contributions to the interionic potential; this behavior is also

known to occur for acetate and fluoroacetate salts in dimethyl sulfoxide<sup>15</sup> and tetraalkylammonium salts in acetonitrile<sup>16</sup> and methanol.<sup>17</sup>

**4.2. Thermodynamics of Ion-Pair Formation.** The standard Gibbs energy changes for the ion association process,  $\Delta G^0$ , can be calculated from the association constants using the equation:

$$\Delta G^0 = -RT \ln K_A \quad (11)$$

To evaluate the standard enthalpy change,  $\Delta H^0$ , and the standard entropy change,  $\Delta S^0$ , we fitted the  $\Delta G^0$  values to a polynomial of T of the type:

$$\Delta G^0 = c_0 + c_1(298.15 - T) + c_2(298.15 - T)^2 \quad (12)$$

The coefficients of the fits are compiled in Table 7, together with the  $\sigma\%$  values of the fits.

The  $\Delta H^0$ , and  $\Delta S^0$  values of the ion association process can then be evaluated from the temperature dependence of  $\Delta G^0$

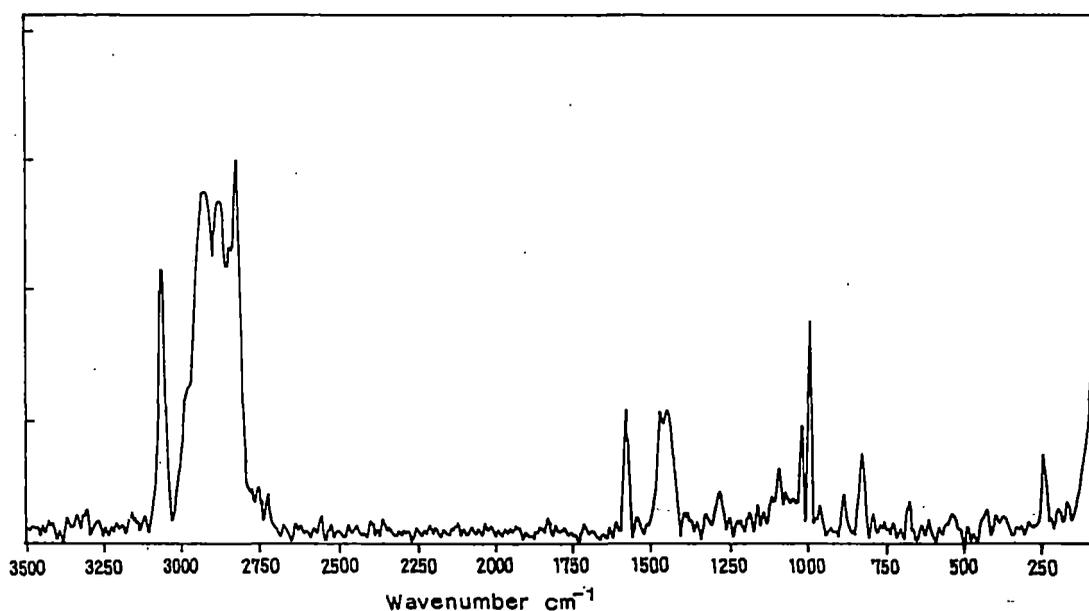
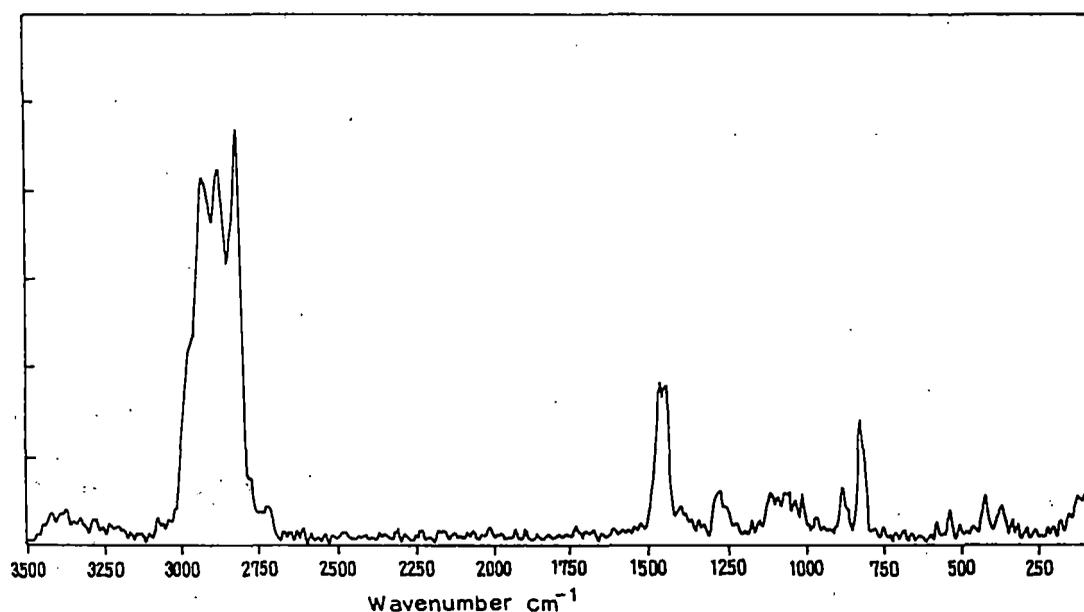
Figure 4. FT Raman spectrum of LiBF<sub>4</sub> in 2-methoxyethanol.Figure 5. FT Raman spectrum of NaBF<sub>4</sub> in 2-methoxyethanol.

TABLE 7: Coefficients of the Polynomial, Eq 12, and Thermodynamic Standard Data of the Association

electrolyte	$c_0$ $\Delta G_{298.15}^0$ J mol <sup>-1</sup>	$c_1$ $\Delta S_{298.15}^0$ J K <sup>-1</sup> mol <sup>-1</sup>	$10^2 c_2$ J K <sup>-2</sup> mol <sup>-1</sup>	$\sigma\%$	$c_0 + 298.15c_1$ $\Delta H_{298.15}^0$ J mol <sup>-1</sup>
Ph <sub>4</sub> AsCl	-13504.9	6.38	178.80	0.025	-11602.7
Ph <sub>4</sub> PCl	-13387.1	8.11	-190.62	0.316	-10969.1
Ph <sub>4</sub> PBr	-14318.2	31.14	48.99	0.131	-5033.8
LiBF <sub>4</sub>	-14241.4	-11.88	-80.44	0.009	-17783.4
NaBF <sub>4</sub>	-13754.7	19.26	43.38	0.121	-8012.3

values as follows:

$$\Delta H^0 = -T^2 \left[ \frac{d(\Delta G^0/T)}{dT} \right]_p \quad (13)$$

$$\Delta S^0 = - \left( \frac{d\Delta G^0}{dT} \right)_p \quad (14)$$

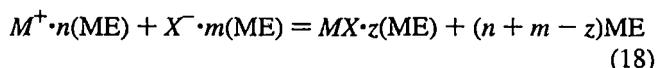
The standard values of the thermodynamic parameters at 298.15 K can, therefore, be expressed as:

$$\Delta G_{298.15}^0 = c_0 \quad (15)$$

$$\Delta S_{298.15}^0 = c_1 \quad (16)$$

$$\Delta H_{298.15}^0 = c_0 + 298.15c_1 \quad (17)$$

It is observed from Table 7 that the  $\Delta S^0$  values of ion association for all these electrolytes (LiBF<sub>4</sub> being an exception) are positive. These positive  $\Delta S^0$  values may be attributed to the increasing number of degrees of freedom upon association mainly due to the release of solvent molecules as shown below



In other words, the solvation of the individual ions is weakened as soon as these ion pairs are formed. A decrease in the entropy for LiBF<sub>4</sub> solution, on the other hand, suggests that the ion pairs that are formed organize the solvent molecules in their vicinity better than the ions.

TABLE 8: Coefficients of the Polynomial, Eq 21, for the Non-Coulombic Contribution to the Association Process

electrolyte	$c_0^*$ $\Delta G_{298.15}^*/\text{J mol}^{-1}$	$c_1^*$ $\Delta S_{298.15}^*/\text{J K}^{-2}\text{ mol}^{-1}$	$10^2 c_2^*/\text{J K}^{-2}\text{ mol}^{-1}$	$\sigma\%$	$c_0^* + 298.15c_1^*$ $\Delta H_{298.15}^*/\text{J mol}^{-1}$
Ph <sub>4</sub> AsCl	-2616.2	-41.29	182.33	0.094	-14926.8
Ph <sub>4</sub> PCl	-2496.5	-39.49	-182.95	1.578	-14270.4
Ph <sub>4</sub> PBr	-3437.0	-16.47	56.72	0.531	-8347.5
LiBF <sub>4</sub>	-3255.2	-59.38	87.96	0.037	-20959.3
NaBF <sub>4</sub>	-2776.3	-28.15	50.90	0.578	-11199.0

It is especially noteworthy that the  $\Delta H^0$  values for all the electrolytes are negative. The electrostatic theories of ionic association,<sup>18</sup> however, never give negative values for  $\Delta H^0$ , because the theoretical equation for  $\Delta H^0$  contains the  $[1 + (d \ln D/d \ln T)]_p$  term; thus the experimental value of  $(d \ln D/d \ln T)_p$  makes the theoretical  $\Delta H^0$  value positive, contrary to the expectation.

The negative values of  $\Delta H^0$  can be explained by considering the participation of specific covalent interaction in the ion association process. Here in this case, the covalent interaction somewhat works between the ions and hence, the binding enthalpy between the ions is sufficiently negative to compensate for the positive contribution from the weakening of ion solvation. In this case,  $\Delta G^0$  of the ion association should have a large negative value (a large  $K_A$  value) and should depend on the kind of ions and this is found to be true here.

The non-Coulombic contribution to the Gibbs energy,  $\Delta G^*$ , was calculated from the following equation:<sup>15</sup>

$$\Delta G^* = N_A W_{\pm}^* \quad (19)$$

$$K_A = (4\pi N_A / 1000) \int_a^R r^2 \exp\left(\frac{2q}{r} - \frac{W_{\pm}^*}{kT}\right) dr \quad (20)$$

where the symbols have their usual meaning. The quantity  $2q/r$  is the Coulombic part of the interionic mean force potential, and  $W_{\pm}^*$  is its non-Coulombic part.

The procedure for the evaluation of the non-Coulombic contribution to the entropy and enthalpy ( $\Delta S^*$  and  $\Delta H^*$  respectively) is similar to that used for obtaining  $\Delta S^0$  and  $\Delta H^0$ .

The  $\Delta G^*$  values at different temperatures were fitted to the polynomial

$$\Delta G^* = c_0^* + c_1^*(298.15 - T) + c_2^*(298.15 - T)^2 \quad (21)$$

and the coefficients of the fits along with the  $\sigma\%$  values are given in Table 8.

The values of  $\Delta G^*$ ,  $\Delta S^*$ , and  $\Delta H^*$  at 298.15 K are then easily obtained from the following equations:

$$\Delta G_{298.15}^* = c_0^* \quad (22)$$

$$\Delta S_{298.15}^* = c_1^* \quad (23)$$

$$\Delta H_{298.15}^* = c_0^* + 298.15c_1^* \quad (24)$$

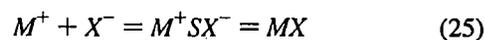
The non-Coulombic parts of the Gibbs energy,  $\Delta G_{298.15}^*$ , of all the salts were found to be small (Table 8): 19% (Ph<sub>4</sub>AsCl), 19% (Ph<sub>4</sub>PCl), 24% (Ph<sub>4</sub>PBr), 23% (LiBF<sub>4</sub>), and 20% (NaBF<sub>4</sub>) in 2-methoxyethanol. This indicates that the Coulombic forces play a major role in the association processes. This is further supported by the fairly high values of the Coulombic parts of  $\Delta S^0$  and  $\Delta H^0$  in comparison with their non-Coulombic counterparts.

**4.3. Raman Spectral Behavior.** Partial band assignments for the pure solvent as well as of the electrolyte solutions were made and are discussed accordingly. From Figures 1 through 5, we see that 2-methoxyethanol (ME) shows  $\nu_s(\text{C—O})$  in the range 800–900  $\text{cm}^{-1}$  and  $\nu_s(\text{O—H})$  in the range 100–1100  $\text{cm}^{-1}$ . The  $\text{CH}_3\text{—O}$  symmetric and asymmetric bending vibrations of ME appear as a closely spaced doublet at 1457 and 1471  $\text{cm}^{-1}$ , respectively. The solvent also exhibits its stretching modes in the wavenumber range 2800–2950  $\text{cm}^{-1}$ . It can be seen from Table 3 that the spectra of the salt solutions show several remarkable changes from that of pure solvent. For LiBF<sub>4</sub> solution, three new bands of medium intensity appear in the range 375–550  $\text{cm}^{-1}$ . These bands may be assigned to the vibration primarily involving the lithium ion. Similar types of bands in this frequency range have also been observed in 1,2-dimethoxyethane solutions.<sup>5</sup> Sodium ion in NaBF<sub>4</sub> also exhibits similar bands, however, with very low intensity.

Phosphorus and arsenic atoms present in tetraphenylphosphonium and tetraphenylarsonium ions, respectively, show Raman peaks at 254 and 238  $\text{cm}^{-1}$ , respectively, in this lower frequency range.

From the spectra, we see that LiBF<sub>4</sub> and NaBF<sub>4</sub> solutions of 2-methoxyethanol show new bands with maxima around 700  $\text{cm}^{-1}$ . The strong bands at 1587  $\text{cm}^{-1}$  for Ph<sub>4</sub>PBr and at 1581  $\text{cm}^{-1}$  for Ph<sub>4</sub>AsCl solutions are also observed in their Raman spectra. The appearance of these new bands for these salts have been assigned to the "spectroscopically free" anion  $X^-$  ( $X = \text{BF}_4, \text{Cl}, \text{Br}$ ) in 2-methoxyethanol, that is, to the solvent-separated ion pair  $M^+SX^-$  ( $S$  is the solvent molecule) and/or to the solvent-separated dimer  $M^+SX^- \dots M^+SX^-$ , spectroscopically indistinguishable from each other.

The above observations can be interpreted in terms of the following eigen multistep mechanism:



Thus, for these electrolytes, one would expect the presence of an equilibrium between the solvent-separated and contact ion pairs as represented by eq 25, which is strongly shifted toward the left due to the presence of "spectroscopically free" anions. The equilibrium represented by eq 26 for forming the solvent-separated dimer may also exist since  $M^+SX^-$  and  $M^+SX^- \dots M^+SX^-$  are indistinguishable from each other by Raman spectra. However, no contact quadrupole is expected to form through eq 27 for the electrolytes for the reasons just mentioned above. This also supports the moderate association of these salts, as manifested by the conductivity study.

The complexation of 2-methoxyethanol with the cations was manifested by the shifts of the Raman band of the symmetric C—O stretching mode as well as by that of the symmetric O—H mode of pure solvent. The  $\nu_s(\text{C—O})$  band of 2-methoxyethanol in salt solutions shifts slightly from the corresponding peak in pure 2-methoxyethanol. This indicates the coordination of the lithium, sodium, tetraphenylphosphonium, and tetraphenylarsonium ions to the oxygen atom of 2-methoxyethanol molecules. But the shifts are too small to draw any definitive conclusion as to which of the two oxygen atoms in 2-methoxyethanol molecules get coordinated to the cations. This is, however, nicely demonstrated by the sizable shifts of  $\nu_s(\text{O—H})$  bands in the electrolyte solutions compared to the solvent  $\nu_s(\text{O—H})$  peak. The  $\nu_s(\text{O—H})$  peak appears at 1074.6  $\text{cm}^{-1}$  in pure 2-methoxy-

ethanol, and those in all the salt solutions shift to the shorter wavenumber region. The probability of complexation of the cations with 2-methoxyethanol molecules through the  $-\text{OCH}_3$  group (with higher electron density on the oxygen atom arising due to the electron-repelling inductive effect of the  $\text{CH}_3$  group compared to the alcoholic oxygen atom) makes the  $-\text{OH}$  moiety rather free, and in this case, the band shifts to the shorter wavenumber region. In the case of linkage through the  $-\text{OH}$  group, the reverse trend should have been observed. The red-shift of the  $\nu_s(\text{O}-\text{H})$  band in solutions amply indicated the complexation through the ethereal oxygen atom.

In the higher wavenumber region, the pure solvent shows three peaks at 2829.7, 2890.3, and 2942.4  $\text{cm}^{-1}$ . The peak at 2829.7  $\text{cm}^{-1}$  may be assigned to the  $\text{C}-\text{O}-\text{C}$  symmetric stretching, and that at 2942.4  $\text{cm}^{-1}$  has been assigned to the  $\text{C}-\text{O}-\text{H}$  symmetric stretching of 2-methoxyethanol. The peak of medium intensity at 2890.3  $\text{cm}^{-1}$  appears due to the intramolecular hydrogen bonding of alcoholic hydrogen with the ethereal oxygen atom. For the alkali metal salts, it is observed that all these three peaks appear at higher wavenumbers in the spectra. As a result of coordination of alkali metal ions with the lone pair of electrons on the ethereal oxygen atom, the lone pairs get shifted to the alkali cations, thus increasing the stretching frequency of the  $\text{C}-\text{O}-\text{C}$  mode in salt solutions. Due to this displacement of the lone pairs toward the alkali metal ions, the intramolecular hydrogen bonding will be weaker which results in a shift of both  $\text{C}-\text{O}-\text{H}$  symmetric stretching mode and  $\text{O}-\text{H}\cdots\text{O}$  band to longer wavenumbers. The shifting of the  $\text{C}-\text{O}-\text{C}$  and  $\text{O}-\text{H}\cdots\text{O}$  bands are found to be in the order  $\text{LiBF}_4 > \text{NaBF}_4$ . This may be ascribed to the greater displacement of the ethereal oxygen lone pair toward the lithium ion, with higher surface charge density compared to the sodium ion. The anomalous order in shifting of the  $\text{C}-\text{O}-\text{H}$  bands might possibly be due to the greater interaction of sodium ion with 2-methoxyethanol molecules, as demonstrated conductometrically.

For  $\text{Ph}_4\text{PBr}$  and  $\text{Ph}_4\text{AsCl}$  solutions, the  $\text{C}-\text{O}-\text{C}$  and  $\text{C}-\text{O}-\text{H}$  bands of pure 2-methoxyethanol shift toward the shorter wavenumbers, whereas the  $\text{O}-\text{H}\cdots\text{O}$  band exhibits a blue shift. Both the larger tetraphenylphosphonium and tetraphenylarsonium ions coordinate with the ethereal oxygen atom, though the strength of coordination is sufficiently weaker compared to the alkali metal ions because of larger size and smaller charge density of these cations. Thus, the  $\text{C}-\text{O}-\text{C}$  and  $\text{C}-\text{O}-\text{H}$  bands of pure 2-methoxyethanol do not shift to the higher wavenumber regions as do the alkali metal ions in these cases. A possible explanation may be that though the electron pairs of the ethereal oxygen atom coordinate with these cations (extent of displacement of lone pairs is small enough compared to the alkali cations), but their bulky sizes hinder the  $\text{C}-\text{O}-\text{C}$  and  $\text{C}-\text{O}-\text{H}$  stretching vibrations, resulting in red shifts for these bands in salt solutions. The shift of the  $\text{O}-\text{H}\cdots\text{O}$  bands to the longer wavenumbers may be ascribed to the loosening of the intramolecular hydrogen bonding arising out of this coordination.

The four  $\text{P}-\text{Ph}$   $\sigma$ -bonds are  $\text{sp}^3$  hybridized. The phenyl groups show strong peaks in the 3060  $\text{cm}^{-1}$  region. As the phosphorus atom has a positive charge, the vacant 3d orbitals are compact and shaped to participate in bonding as acceptors of electrons, the ethereal oxygen atom lone pairs being the donors. The d-orbitals in phosphorus are usually diffuse. But when phosphorus consists of a positive charge and its ligands

are electronegative, its five vacant d-orbitals are compact and shaped to accept electrons—in this case from ethereal oxygen atom lone pairs. In the case of tetraphenylarsonium ions, due to the larger size of the arsenic atom, it will be less compact compared to tetraphenylphosphonium ion, and so coordination through lone pairs will be easier in this case. This is manifested by the spectral shifts. As arsenic atom appears to be more metallic in nature compared to phosphorus, the tetraphenylarsonium ion pulls the ethereal oxygen lone pair more effectively toward it, causing greater loosening of the intramolecular hydrogen bonding; thus, the shift of the  $\text{O}-\text{H}\cdots\text{O}$  bands will be higher with tetraphenylarsonium ion than with tetraphenylphosphonium ion. For the other bands, that is,  $\text{C}-\text{O}-\text{C}$  and  $\text{C}-\text{O}-\text{H}$  vibrations, the red shifts are found to be in the order: tetraphenylphosphonium ion > tetraphenylarsonium ion. Thus, lower shifting with tetraphenylarsonium ion may be due to the greater size of the tetraphenylarsonium ion, which makes free movement of  $\text{C}-\text{O}-\text{C}$  and  $\text{C}-\text{O}-\text{H}$  bands quite restricted.

It may thus be concluded that all these electrolytes remain strongly associated in 2-methoxyethanol to form ion pairs, and the solvation of the ions is weakened as soon as the ion pair is formed. The results indicate that the Coulombic forces play a major role in the association process. All these electrolytes are found to exist in ME solution as solvent-separated ion pairs and/or solvent-separated dimers, thus exhibiting a very intense peak for the "spectroscopically free" anion. Moreover, the chelation of ME with the cations is taking place through the lone pairs of electrons on the ethereal oxygen atom.

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