A Study on the Solvation Phenomena of Some Sodium Salts in 1,2-Dimethoxyethane from Conductance, Viscosity, Ultrasonic Velocity, and FT-Raman Spectral Measurements

Pitchai J. Victor, Bijan Das,* and Dilip K. Hazra*

Department of Chemistry, North Bengal University, Darjeeling 734 430, India

Received: February 8, 2001

Electrical conductances, viscosity, apparent molar adiabatic compressibilities and Fourier transform (FT)-Raman spectra of sodium perchlorate ($NaClO_4$), sodium tetrafluoroborate ($NaBF_4$), and sodium tetraphenylborate ($NaBPh_4$) in 1,2-dimethoxyethane have been reported. All these electrolytes are found to be strongly associated in this solvent medium. Both ion pairs and triple ions are found to be formed though an overwhelming fraction of each of these electrolytes exists as ion pairs. For $NaClO_4$, the solvent-separated ion pairs predominate over the contact species. For $NaBF_4$ and $NaBPh_4$, on the other hand, the contact species are also formed in significant amounts. FT-Raman studies indicate the presence of "spectroscopically free" ClO_4^-, BF_4^-, and BPh_4^- ions in 1,2-dimethoxyethane solution. The ClO_4^- ion is found to be significantly solvated, whereas BF_4^- and BPh_4^- ions are poorly solvated in DME solution.

1. Introduction

In nonaqueous batteries, the choice of electrolyte solution and optimization of its salt concentration are two important factors. An electrolyte solution possessing high specific conductivity and hence with minimal ion−ion interactions is required to maintain the cell at low internal resistance. Knowledge of the state of association of the electrolytes and their interaction with the solvent molecules is essential for the optimal choice of solvent and electrolyte. To this end, various classical methods such as electrical conductivity, viscosity and ultrasonic velocity measurements have been employed to study the status of association of the electrolytes. Such studies are complemented with structural studies of the metal ion solvates using Raman spectroscopy. Hopefully, this would give a molecular rationale for the choice of a given electrolyte in battery construction.

Recently, we have initiated a comprehensive program to study the solvation and association behavior of several 1:1 alkali metal salts in different nonaqueous solvents from the measurements of various transport, thermodynamic, and spectroscopic properties.[1−4] In this paper, an attempt is made to unravel the nature of various types of interactions prevailing in solutions of sodium perchlorate ($NaClO_4$), sodium tetraphenylborate ($NaBPh_4$), and sodium tetrafluoroborate ($NaBF_4$) in 1,2-dimethoxyethane (DME) from precise conductivity and Raman spectroscopic techniques.

2. Experimental Section

2.1. Materials. 1,2-Dimethoxyethane (Fluka, purum) was shaken well with ferrous sulfate, $FeSO_4$ (AR, BDH), for 1−2 h, decanted, and distilled. The distillate was refluxed for 12 h and redistilled over metallic sodium, and the middle fraction was collected.[5] The purity of the solvent as checked by gas chromatography was found to be greater than 99.8%. The boiling point (357.5 K) and density (0.8613 g cm^{-3}) at 298.15 K also compared fairly well with the literature values:[6] 358.15 K and 0.8612 g cm^{-3}, respectively.

The salts were of Fluka purum or puriss grade. Sodium perchlorate ($NaClO_4$) was recrystallized several times from water + methanol mixtures and dried in vacuo at 423.15 K for 96 h. Sodium tetraphenylborate ($NaBPh_4$) was recrystallized three times from acetone and then dried in vacuo at 353.15 K for 72 h. Sodium tetrafluoroborate ($NaBF_4$) was dried under vacuum at high temperatures for 48 h and was 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 Hz using a dip-type cell (cell constant 1.14 cm^{-1}) with an accuracy of 0.01%. The cell was calibrated by the method of Lind and co-workers.[7] Measurements were made at 298.15 ± 0.005 K, as described earlier.[8] Several independent solutions were prepared, and conductance measurements were performed with each of these to ensure the reproducibility of the results. Corrections were made for the specific conductance of the solvent.

The kinematic viscosities were measured at the desired temperature using a suspended Ubbelohde-type viscometer. The densities were measured with an Ostwald-Sprengal type pycnometer of about 25 cm^3 capacity. The precisions of the density and viscosity measurements were $3 \times 10^{-5} \text{ g cm}^{-3}$ and 0.05 %, respectively. The kinematic viscosities were converted into absolute viscosities by multiplying the former with density. From the absolute viscosities of the solutions and the solvent, the relative viscosities were obtained. In all cases the experiments were performed at least in five replicates and the results were averaged.

Ultrasonic velocity measurements were carried out 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 298.15 K. The temperature stability was maintained within ±0.01 K by circulating thermostated water around the cell by a circulating pump.

FT Raman spectra were excited at 1064 nm using a Nd:YAG laser and a Bruker IFS 66 V optical bench with an FRA 106 Raman module attached to it. Laser power was set at 200 mW, and 250 (averaged) scans were accumulated with a resolution

10.1021/jp010510v CCC: \$20.00

TABLE 1: Equivalent Conductances (S cm^2 mol^{-1}) and Corresponding Molarities (mol^{-1} dm^{-3}) of the Sodium Salts in 1,2-Dimethoxyethane at 298.15 K

$NaClO_4$		$NaBF_4$		$NaBPh_4$	
10^4c	Λ	10^4c	Λ	10^4c	Λ
17.02	2.40	7.07	1.15	9.55	4.321
102.72	1.89	8.06	1.08	15.92	3.492
135.41	1.78	9.04	1.03	31.84	2.662
172.76	1.70	10.03	0.98	63.68	2.102
200.78	1.67	11.02	0.95	79.61	1.971
238.15	1.67	12.01	0.91	89.16	1.913
270.88	1.66	13.07	0.88	95.52	1.880
303.50	1.66	30.41	0.63	101.90	1.852
406.22	1.75	60.19	0.51	108.26	1.826
508.95	1.84	90.61	0.47	111.45	1.815
607.00	1.96	158.41	0.45	127.37	1.768
705.06	2.08			159.21	1.707
				191.05	1.676
				254.74	1.666
				302.50	1.686
				401.22	1.773
				796.07	2.401

of 2 cm^{-1}. The spectra were recorded by the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras.

The relative permittivity of the pure solvent ($\epsilon = 7.075$ at 298.15 K) was taken from the literature.[6]

3. Results

3.1. Electrical Conductance. The equivalent conductance (Λ) vs the concentration (c) data of $NaClO_4$, $NaBF_4$, and $NaBPh_4$ in 1,2-dimethoxyethane at 298.15 K are recorded in Table 1. The variation of equivalent conductance with the concentration of the salt solutions is represented in Figure 1a–c.

The conductance data have been analyzed by the Fuoss-Krauss' theory[9] of triple ion formation in the form

$$\Lambda g(c)c^{1/2} = (\Lambda_0/K_P^{1/2}) + \Lambda_0^T(K_T/K_P^{1/2})(1 - \Lambda/\Lambda_0)c \quad (1)$$

where $g(c)$ is a factor that lumps together all the intrinsic interaction terms and is defined by

$$g(c) = \frac{\exp[-(2.303/\Lambda_0^{1/2})\beta'(c\Lambda^{1/2})]}{[1 - (S/\Lambda_0^{3/2})(c\Lambda)^{1/2}](1 - \Lambda/\Lambda_0)^{1/2}} \quad (2)$$

Here, $\beta' = 1.8247 \times 10^6/(\in T)^{3/2}$ is the Debye–Hückel term of the activity coefficient, $f = \exp[-(2.303/\Lambda_0^{1/2})\beta'(c\Lambda^{1/2})]$ and $S = [0.8204 \times 10^6/(\in T)^{3/2}]\Lambda_0 + 82.501/\eta(\in T)^{1/2}$ is the Onsagar coefficient of the conductance equation $\Lambda = \Lambda_0 - S(c\Lambda/\Lambda_0)^2$. Also Λ_0 is the sum of the limiting equivalent conductances of the simple ions Na^+ and B^- ($B = ClO_4$, BF_4, and BPh_4) and Λ_0 is the sum of the values for the two possible triple ions, NaB_2^- and Na_2B^+; K_P and K_T are the ion-pair and triple-ion formation constants, respectively. The symmetrical approximation of considering the two possible formation constants of triple ions equal to each other has been considered.

Neglect of Λ/Λ_0 and $(S\Lambda_0^{3/2})(c\Lambda)^{3/2}$ together with the assumption of $f_\pm = 1$ leads to $g(c) = 1$ and hence

$$\Lambda c^{1/2} = (\Lambda_0/K_P^{1/2}) + \Lambda_0^T(K_T/K_P^{1/2}) \quad (3)$$

For the present data, it was found that eq 3 was inadequate, the data showing a downward curvature when plotted as $\Lambda c^{1/2}$ vs c. On the contrary, eq 1 gives reasonably straight lines, the curvature having almost disappeared.

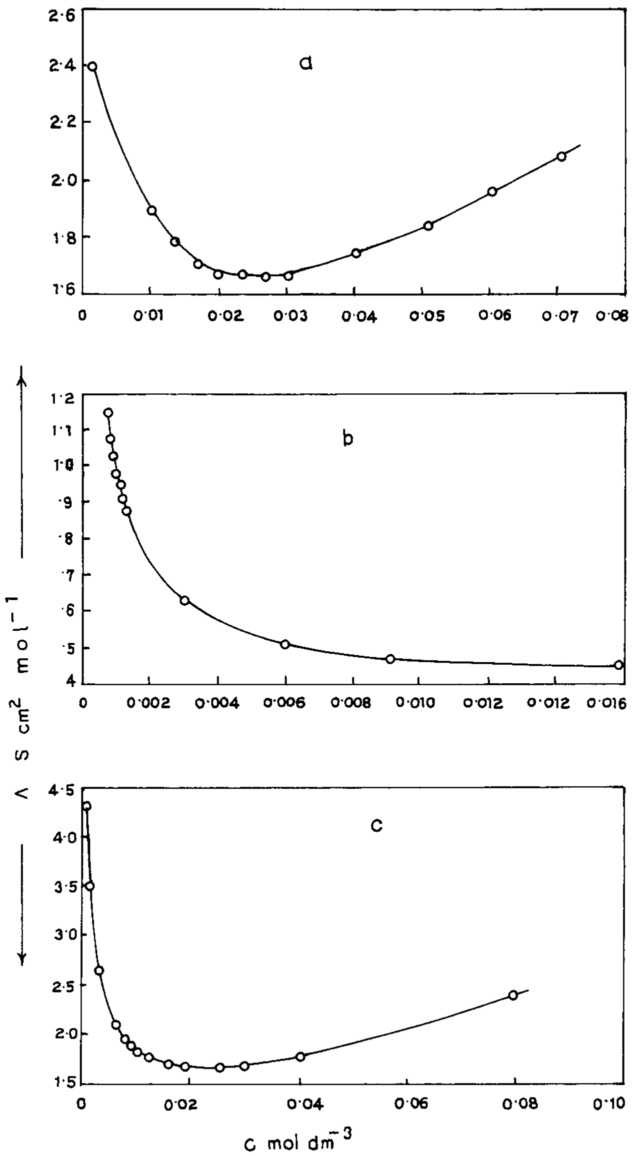

Figure 1. Variation of equivalent conductance as a function of salt concentration in 1,2-dimethoxyethane at 298.15 K: (a) $NaClO_4$; (b) $NaBF_4$; (c) $NaBPh_4$).

To apply eq 1, it is necessary to have estimates of Λ_0 and to assume a value of Λ_0^T. Λ_0^T was assumed to be equal to $2\Lambda_0/3$. An average value of 0.637 S cm^2 equiv^{-1} P was used for the walden product ($\Lambda_0\eta_0$) of $NaClO_4$ at 298.15 K (the solvents include methanol, acetonitrile, pyridine, and dimethylformamide[10]). The corresponding $\Lambda_0\eta_0$ value for $NaBF_4$ was estimated from that of $NaClO_4$ as given above and those for $LiBF_4$ and $LiClO_4$ as reported in our previous work[2] using the following equation:

$$\Lambda_0\eta_0(NaBF_4) = \Lambda_0\eta_0(NaClO_4) + \Lambda_0\eta_0(LiBF_4) - \Lambda_0\eta_0(LiClO_4) \quad (4)$$

The Λ_0 values were then estimated from the coefficient of viscosity of DME (0.0042 mPa•s) and are found to be 151.7 and 148.6 S cm^2 mol^{-1} for $NaClO_4$ and $NaBF_4$, respectively. Table 2 reports Λ_0, K_P, K_T, and r^2 values for these salts.

The concentrations of the ion pairs and triple ions (c_P and c_T, respectively) at the highest concentration for each electrolyte

TABLE 2: Conductance Parameters in 1,2-Dimethoxyethane at 298.15 K

electrolyte	Λ_0	K_P	K_T	r^2	10^4c_P	10^6c_T
$NaClO_4$	151.7	1.88×10^6	22.96	0.9896	693.68	313.50
$NaBF_4$	148.6	2.88×10^7	61.08	0.9999	157.49	22.70
$NaBPh_4$	106.9	9.43×10^5	20.37	0.9827	779.03	471.15

TABLE 3: Concentration (mol dm^{-3}), Density (g cm^{-3}), and Relative Viscosity of the Sodium Salts in 1,2-Dimethoxyethane at 298.15 K

c	ρ	η_r
	$NaClO_4$	
0.02028	0.86346	1.0139
0.04025	0.86566	1.0285
0.06021	0.86789	1.0436
0.08018	0.87004	1.0589
0.10295	0.87257	1.0773
	$NaBF_4$	
0.02018	0.86433	1.0424
0.03014	0.86572	1.0643
0.05008	0.86856	1.1067
0.06005	0.86992	1.1291
0.07001	0.87126	1.1517
	$NaBPh_4$	
0.00705	0.86226	1.0069
0.010204	0.86256	1.0087
0.01504	0.86294	1.0107
0.01668	0.86316	1.0118
0.01832	0.86337	1.0128

solution have been calculated using the following relations:

$$c_P = c(1 - \alpha - 3\alpha_T) \qquad (5)$$

$$\alpha = (K_Pc)^{-1/2} \qquad (6)$$

$$\alpha_T = (K_T/K_P^{1/2})c^{1/2} \qquad (7)$$

$$c_T = (K_T/K_P^{1/2})c^{3/2} \qquad (8)$$

and are reported in Table 2. From this table we see that a preponderant fraction of these electrolytes exist as ion pairs with only a minor portion as triple ions.

From Table 2, we also see that the K_P and K_T values for $NaBF_4$ are significantly higher than those for $NaClO_4$. This indicates far greater solvation of ClO_4^- compared to BF_4^- ion in DME. Studies on lithium salts also support this view. Again, the sodium ion, with smaller surface charge density upon it than the lithium ion, is expected to be less solvated than the lithium ion in view of higher degrees of association of the sodium salts. The ion pairs in $NaBF_4$ solutions will, therefore, be predominantly the contact species/contact ion pair (CIP). $NaClO_4$ solution, on the other hand, is expected to have the solvent separated ion pair (SSIP) in greater amount. $NaBPh_4$ is least associated among the three. The behavior of this salt gives some important insight regarding its solution properties when its conductivity parameters will be analyzed in conjunction with its spectral information (see later).

3.2. Viscosity. Viscometric investigations indicate complex solvation-association interactions in these systems. A steep increase in dynamic viscosity (Table 3) in the range of higher concentrations causes a deviation from the Jones−Dole law,[11] indicating a process of intermolecular association. The isotherms of dynamic viscosity in the whole studied range of concentrations behave exponentially according to the following relationship:

$$\eta = \eta_0 e^{Bm} \qquad (9)$$

Such a dependence is typical for solutions of electrolytes in aprotic solvents with low and medium relative permittivities and is a particular case of the Einstein−Vand−Stocks equation as described in the literature.[12] For the solutions of $NaClO_4$, $NaBF_4$, and $NaBPh_4$ in DME we have:
for $NaBF_4$

$$\ln(\eta/\text{mPa·s}) = 0.6362(c/\text{mol·dm}^{-3}) - 5.4698 \quad \text{with} \quad \sigma = 0.0001 \text{ mPa·s} \qquad (10)$$

for $NaClO_4$,

$$\ln(\eta/\text{mPa·s}) = 0.7330(c/\text{mol·dm}^{-3}) - 5.4722 \quad \text{with} \quad \sigma = 0.0003 \text{ mPa·s} \qquad (11)$$

and for $NaBPh_4$,

$$\ln(\eta/\text{mPa.s}) = 1.9940\ (\text{c/mol.dm}^{-3}) - 5.4703 \text{ with} \quad \sigma = 0.0004 \text{ mPa·s} \qquad (12)$$

The values of B were determined for the region of the Jones−Dole equation validity. These are 0.7845 dm^3·mol^{-1} for $NaClO_4$, 0.5589 dm^3·mol^{-1} for $NaBF_4$ and 2.2233 dm^3·mol^{-1} for $NaBPh_4$ at 298.15 K. Large positive values of these coefficients indicate the big size of moving particles presumably because of the solvation of the constituting ions of these electrolytes as evidenced from the conductivity study. The viscosity B coefficients suggest that the perchlorate ion is present as a bigger entity than the fluoroborate ion in DME solutions. This has also been found to be true from our conductivity study.

3.3. Compressibility. The adiabatic compressibility coefficients (β) were derived from the relation

$$\beta = u^{-2}\rho^{-1} \qquad (13)$$

where ρ is the solution density and u is the velocity of sound in the solution.

The apparent molar adiabatic compressibility (ϕ_K) of liquid solutions was calculated from the relation

$$\phi_K = (10060/m\rho\rho_0)(\beta\rho_0 - \beta_0\rho) + \beta(M/\rho_0) \qquad (14)$$

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

The molar concentration (c), density (ρ) and the adiabatic compressibility coefficient (β) of the solutions of $NaClO_4$, $NaBF_4$, and $NaBPh_4$ at 298.15 K are given in Table 4.

The limiting apparent molar adiabatic compressibilities (ϕ_K^0) were obtained by extrapolating the plots of ϕ_K vs the square root of the solute molality to zero concentration:

$$\phi_K = \phi_K^{\ 0} + S_K m^{1/2} \qquad (15)$$

where S_K is the experimental slope.

The limiting apparent molar adiabatic compressibilities (ϕ_K^0) of $NaClO_4$ and $NaBP_4$ are found to be negative. The ϕ_K^0 values at 298.15 K for $NaClO_4$ and $NaBF_4$ are $+116.96 \times 10^{-10}$ and -123.99×10^{-10} cm^5 mol^{-1} dyne^{-1}, respectively. These negative ϕ_K^0 values of these electrolytes can be interpreted in terms of loss of compressibility of the solvent 1,2-dimethoxyethane in the presence of these solutes arising out of the

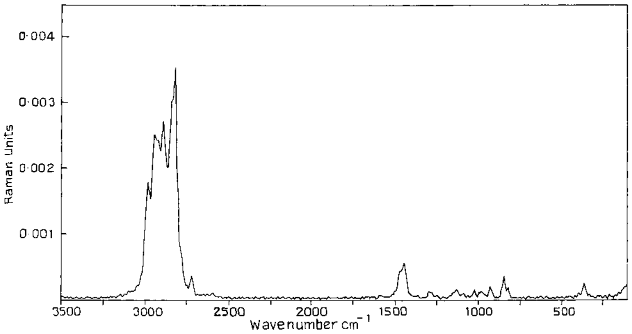

Figure 2. FT-Raman spectrum of 0.05 M $NaClO_4$ in 1,2-dimethoxyethane.

TABLE 4: Concentration (mol dm^{-3}), Density (g cm^{-3}), Ultrasonic Velocity (m s^{-1}), Adiabatic Compressibility (Pa^{-1}), and Apparent Molar Adiabatic Compressibility (m^3 mol^{-1} Pa^{-1}) of the Sodium Salts in 1,2-Dimethoxyethane at 298.15 K

c	ρ	u	$\beta \times 10^{12}$	$10^{10}\phi_K$
		$NaClO_4$		
0.03014	0.86477	1169.71	84.52	−154.0
0.05000	0.86669	1171.25	84.11	−169.5
0.06029	0.86806	1171.62	83.92	−181.9
0.08015	0.87016	1173.24	83.49	−171.9
0.09610	0.87192	1174.57	83.13	−183.1
0.10639	0.87306	1175.48	82.89	−182.8
		$NaBF_4$		
0.00505	0.86171	1168.44	85.00	−179.1
0.00640	0.86186	1168.54	84.97	−186.0
0.00803	0.86205	1168.64	84.93	−193.5
0.01101	0.86243	1168.85	84.87	−205.3
0.01404	0.86284	1169.05	84.80	−215.9
0.01685	0.86315	1169.35	84.73	−224.6
		$NaBPh_4$		
0.03014	0.86592	1175.57	83.56	−314.6
0.04007	0.86730	1178.03	83.08	−306.8
0.05002	0.86856	1180.62	82.60	−300.0
0.06024	0.86993	1183.12	82.12	−293.7
0.07182	0.87161	1185.74	81.60	−287.1
0.08068	0.87289	1187.70	81.21	−282.4

electrostriction of the solvent molecules around the small-sized ions (particularly the sodium ions) because of high charge density on their surface.

Between the $NaClO_4$ and $NaBF_4$ solutions, the former solution is more compressible than the latter (Table 4), indicating that the loss of compressibility of the medium is less in the presence of $NaClO_4$. In these two salts, Na^+ ion being common, the anions are evidently making the difference. Since the BF_4^- ion is smaller in size ($r = 2.02$ Å) compared to ClO_4^- ($r = 2.40$ Å), the former will have higher surface charge density.

3.4. Raman Spectra. The Raman spectrum of pure 1,2-dimethoxyethane has been reported earlier;[2] the Raman spectra of the solutions of $NaClO_4$ (at three different molarities, e.g., 0.05, 1, and 2 M) and $NaBF_4$ (0.02 M) and $NaBPh_4$ (0.1 M) in 1,2-dimethoxyethane in the range 3500−100 cm^{-1} have been presented in Figures 2−6. The principal bands observed have been listed in Table 5. Partial band assignments for the pure solvent as well as for the salt solutions have been made and discussed accordingly. It has been shown earlier[2] that 1,2-dimethoxyethane (DME) shows ν_s(C−O) and ν_{as}(C−O) in the range 1150−1100 and 950−800 cm^{-1}, respectively. The ν_{as}(C−H) stretching mode of the solvent appears in the wavenumber range 1150−1100 cm^{-1}, and the ν_s(C−H) mode in the range 3000−2700 cm^{-1}. It can be seen from Table 5 and Figures 2−6 that the spectra of the salt solutions show several remarkable changes from that of the pure solvent.

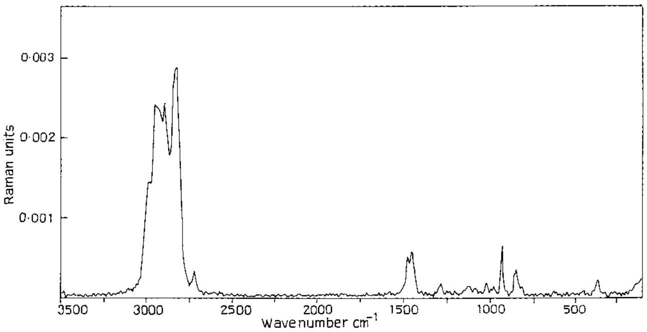

Figure 3. FT-Raman spectrum of 1 M $NaClO_4$ in 1,2-dimethoxyethane.

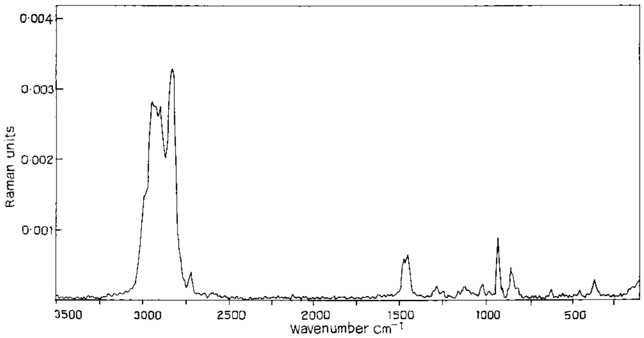

Figure 4. FT-Raman spectrum of 2 M $NaClO_4$ in 1,2-dimethoxyethane.

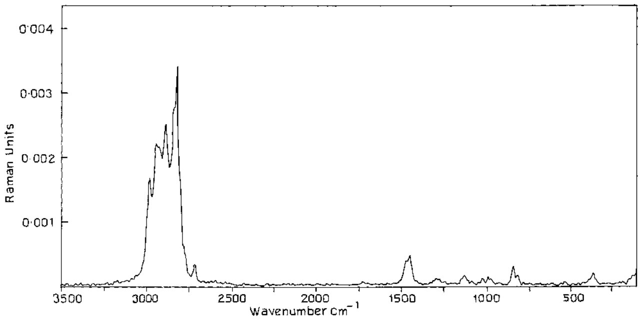

Figure 5. FT-Raman spectrum of ~0.02 M $NaBF_4$ in 1,2-dimethoxyethane.

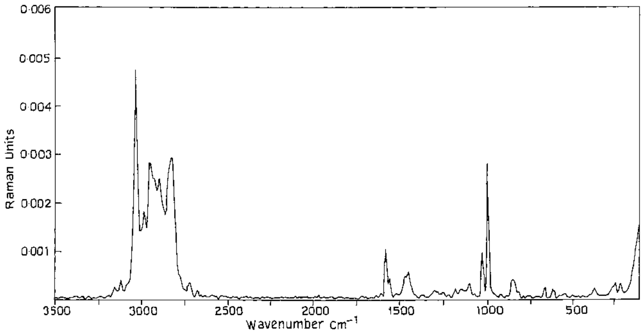

Figure 6. FT-Raman spectrum of ~0.10 M $NaBPh_4$ in 1,2-dimethoxyethane.

For all the salt solutions, a broad band near 370 cm^{-1} appears. This band has been assigned to the vibration primarily involving the sodium ion. This cation band frequency is found to be anion dependent. This observation is similar to those found in other weakly solvating nonpolar solvents such as tetrahydrofuran[13,14] and pyridine[15]—a phenomenon also reported earlier by us[2] for several lithium salt solutions in DME. The variation of this band for Na^+ ion with different counteranions indicates that the cation is associated with the anion in an intimate way in DME solutions, and this association may be primarily in the form of

TABLE 5: Raman Frequencies (cm^{-1}) [a]

DME	$NaClO_4$ (0.05 M)	$NaClO_4$ (1 M)	$NaClO_4$ (2 M)	$NaBPh_4$ (∼0.1 M)	$NaBF_4$ (∼0.02 M)
385.4 (m)	365.0 (m)	368.0 (m)	369.0 (m)	369.0 (w)	366.6 (w)
867.0 (m)	850.0 (m)	850.0 (m)	862.0 (m)	855.0 (m)	850.0 (w)
	933.0 (w)	933.6 (s)	933.3 (s)		
					991.0 (w)
				999.0 (s)	
				1031.5 (m)	1025.0 (w)
				1105.0 (w)	
1146.2 (w)	1133.0 (vw)	1128.0 (w)	1127.0 (w)		1133.0 (vw)
	1299.5 (vw)	1287.7 (m)	1287.0 (vw)		
1452.5 (s)	1450.5 (m)	1452.7 (m)	1449.5 (m)	1450.0 (m)	1451.0 (m)
		1473.0 (w)	1474.0 (w)		
	2722.0 (w)	2724.0 (w)	2722.0 (m)	2723.0 (w)	2720.5 (w)
2805.0 (vs)	2821.0 (s)	2826.0 (s)	2832.0 (s)	2828.5 (s)	2820.0 (vs)
2878.0 (m)	2891.0 (m)	2895.0 (m)	2898.0 (m)	2896.0 (m)	2891.0 (m)
2937.0 (w)	2945.0 (w)	2945.5 (w)	2947.0 (w)	2947.0 (m)	2944.0 (w)
2979.0 (w)	2964.0 (w)	hump		2986.0 (m)	2984.5 (m)
				3038.0 (vs)	

[a] vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

contact ion pairs. However, one can also expect that the cation might have some solvent molecules in its near-neighbor environment on geometrical grounds. If the vibrations were due to unsolvated ion pairs, much greater dependence on the mass of the anion would have been observed. A comparison of cation frequency in DME with that in other solvents, e.g., acetone,[16] methyl acetate,[17] methyl formate,[17] pyridine,[15] tetrahydrofuran,[13,14] 2-methoxyethanol,[1] etc., shows that the frequency of the cation vibration also varies with the solvent. This implies that the solvent affects the vibration of Na^+ ions in DME solutions. Thus, one is led to the view that the cation vibrates in a cage composed of anion and solvent molecules in DME solutions and that all elements in this cage contribute (although not necessarily to an equal extent) to the factors that determine this band frequency.

For $NaClO_4$, a new nondegenerate band appearing at ∼933 cm^{-1} is attributed to the infrared forbidden totally symmetric stretching vibration of the perchlorate ion.[16,18] The Raman spectrum of the $NaBF_4$ solution shows two very weak new bands peaking around 1025 and 991 cm^{-1} due to an internal vibration of the anion.[14] The $NaBPh_4$ solution exhibits a band of medium intensity centering at 1582 cm^{-1}, presumably due to symmetrical stretching mode of the BPh_4 ion. Another new band appears at 999 cm^{-1}. The appearance of these new bands (∼933 cm^{-1} for $NaClO_4$, ∼991 cm^{-1} for $NaBF_4$, and ∼999 cm^{-1} for $NaBPh_4$) for these electrolytes can be assigned to the "spectroscopically free" anion B^- ($B = ClO_4$, BF_4, and BPh_4) in DME, that is to the solvent-separated ion pair Li^+SB^- (S is solvent molecule) and/or to the solvent-separated dimer, $Li^+SB^-\cdots LiSB^-$, spectroscopically indistinguishable from each other.

No contact ion pairs are detectable for the $NaClO_4$ solution. Indeed, these species, if present, would cause the appearance of an additional band in the neighborhood of the band for the "spectroscopically free" perchlorate ion toward the higher wavenumber region. But for $NaBF_4$ and $NaBPh_4$ solutions, the bands at 991 and 999 cm^{-1}, respectively, have been assigned to contact ion pairs.

The above observation indicates that ClO_4^- ions significantly solvated, thus rendering the formation of $Na^+ClO_4^-$ contact ion pairs impossible. The formation of contact ion pairs for $NaBF_4$ and $NaBPh_4$ indicates poor solvation of the anions BF_4^- and BPh_4^-.

All these above observations may be interpreted in terms of the following, eigen multistep mechanism:

$$Na^+ + B^- \rightleftharpoons Na^+SB^- \rightleftharpoons Na^+B^- \qquad (16)$$

$$2Na^+SB^- \rightleftharpoons NaSB^-\cdots Na^+SB^- \qquad (17)$$

$$2NaB \rightleftharpoons (NaB)_2 \qquad (18)$$

For $NaClO_4$, one would therefore expect only the presence of an equilibrium between the solvent-separated and contact ion pairs represented by eq 16 that is strongly shifted toward the left. The equilibrium represented by eq 17, to form the solvent-separated dimer may also exist since Na^+SB^- and $Na^+SB^-\cdots Na^+SB^-$ are indistinguishable by Raman spectra. However, no contact quadrupole is expected to form through eq 18 for $NaClO_4$. For both $NaBF_4$ and $NaBPh_4$, where contact ion pairs are also found to be present, the formation of contact quadrupoles or dimers via eq 18 is possible.

Acknowledgment. We thank the University of North Bengal for financial assistance. P.J.V. thanks the University Grants Commission for a fellowship under the Faculty Improvement Program.

References and Notes

(1) Das, B.; Hazra, D. K. *J. Phys. Chem.* **1995**, *99*, 269.
(2) Muhuri, P. K.; Das, B.; Hazra, D. K. *J. Phys. Chem. B* **1997**, *101*, 3329.
(3) Victor, P. J.; Muhuri, P. K.; Das, B.; Hazra, D. K. *J. Phys. Chem. B* **1999**, *103*, 11227.
(4) Victor, P. J.; Muhuri, P. K.; Das, B.; Hazra, D. K. *J. Phys. Chem. B* **2000**, *104*, 5350.
(5) Ghosh, S. K.; Hazra, D. K.; Lahiri, S. C. *Thermochim. Acta* **1989**, *147*, 41.
(6) Renard, E.; Justice, J. C. *J. Solution Chem.* **1974**, *3*, 633.
(7) Lind, J. E., Jr.; Zwolenik, J. J.; Fuoss, R. M. *J. Am. Chem Soc.* **1959**, *81*, 1557.
(8) Dasgupta, D.; Das, S.; Hazra, D. K. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1057.
(9) Fuoss, R. M.; Accascina, F. *Electrolytic Conductance*; Interscience: New York, 1959.
(10) Covington, A. K., Dickinson, T., Eds. *Physical Chemistry of Organic Solvent Systems*; Plenum Press: London, New York, 1973.
(11) Jones, G.; Dole, M. *J. Am. Chem. Soc.* **1920**, *51*, 2950.
(12) Afarasayev, V.; Zyatkova, L. *J. Chem. Eng. Data* **1996**, *41*, 1315.
(13) Edgell, W. F.; Lyford, J., IV; Wright, R.; Risen, W., Jr.; Watts, A. *J. Am. Chem. Soc.* **1970**, *92*, 2240.
(14) Chang, S.; Severson, M. W.; Schmidt, P. P. *J. Phys. Chem.* **1985**, *89*, 2892.
(15) Mckinney, W. J.; Popov, A. I. *J. Phys. Chem.* **1970**, *74*, 535.
(16) Pullin, A. D. E.; Pollock, J. M. *Trans. Faraday Soc.* **1958**, *54*, 11.
(17) Dang, Z.; Irish, D. E. *Can. J. Chem.* **1991**, *69*, 1966.
(18) Maaser, H.; Xu, M.; Hemmes, P.; Petrucci, S. *J. Phys. Chem.* **1987**, *91*, 3047.