CHAPTER VII

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

In non-aqueous 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 will give a molecular rationale for the choice of a given electrolyte in battery construction.

As part of our efforts to study the solvation and association behaviour of several alkali metal salts in different non-aqueous solvents from the measurements of various transport, thermodynamic and spectroscopic properties,[1-4] we have attempted 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, viscosity, ultrasonic velocity and Raman spectroscopic techniques. The unique characteristics and physical properties of DME are presented in Chapter 3.

7.1 EXPERIMENTAL SECTION

7.1.1 Materials

1,2-dimethoxyethane (Fluka, purum) was purified[5] as reported in Chapter 3. 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] which are 358.15 K and 0.8612 g cm^{-3}, respectively.

The salts were of Fluka purum or puriss grade and they were prepared and purified as described in Chapter 3.

7.1.2 Apparatus and Procedures

Conductance, viscosity and ultrasonic measurements were carried out at 298.15 K, using the instruments and procedures as explained in Chapter 3. 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.

FT Raman spectra were excited at 1064 nm using a Nd:YAG laser and a Brucker IFS 66. V optical bench with an FRA 106 Raman module attached to it. Laser power was set at 200mW, and 250 (averaged) scans were accumulated with a resolution 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 (ϵ = 7.075 at 298.15 K) was taken from the literature.[6]

7.2   RESULTS AND DISCUSSION

7.2.1 Electrical Conductance

The equivalent conductance (Λ) versus 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 1 a-c.

The conductance data have been analyzed by the Fuoss-Krauss' theory[7] of triple ion formation in the form

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

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

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

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 $\Lambda = \Lambda_0 - S (c \Lambda/ \Lambda_0)^{1/2}$. Also Λ_0 is the sum of the limiting

equivalent conductances of the simple ions Li^+ and B^- (B = ClO_4, BF_4 and BPh_4) and Λ_0

the sum of the values for the two possible triple ions, LiB_2^- and Li_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,

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

For the present data, it was found that equation 3 was inadequate, the data showing

a downward curvature when plotted as $\Lambda c^{1/2}$ vs. c. On the contrary, equation 1 gives

reasonably straight lines, the curvature having almost disappeared.

To apply equation 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 eqv^{-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 dimethyl formamide[8]). 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:

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

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 solution have been calculated using the following relations:

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

$$\alpha \;= (K_P\, c)^{-1/2} \qquad (6)$$

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

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

and are reported in Table 2. Also included in this Table are the Λ_0, K$_P$, K$_T$, r^2 , c$_P$ and c$_T$ values for LiClO$_4$ and LiBF$_4$ for comparison from our previous study. 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^- ion than 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 pairs (SSIP) in greater amount. $NaBPh_4$ is the least associated among the three. The behaviour of this salt gives some important insight into its solution properties when its conductivity parameters are analyzed in conjunction with its spectral information (see later).

7.2.2 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,[9] 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.[10] For the solutions of $NaClO_4$, $NaBF_4$ and $NABPh_4$ in DME we have:

for $NaBF_4$,

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

for $NaClO_4$,

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

and for $NaBPh_4$,

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

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.

7.2.3 Compressibility

The isentropic compressibility coefficients (κ_s) were derived from the relation,

$$\kappa_s = 1/(u^2\rho) \tag{12}$$

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

The apparent molal isentropic compressibility (κ_ϕ) of liquid solutions was calculated from the relation

$$\kappa_\phi = (1000/m\rho\rho_0)\ (\kappa_s\rho_0 - \kappa_s{}^\circ\ \rho) + \kappa_s\ (M/\rho_0) \tag{13}$$

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

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

The limiting apparent molar isentropic compressibilities ($\kappa_\phi{}^\circ$) were obtained by extrapolating the plots of κ_ϕ versus the square root of the solute molarity to zero concentration:

$$\kappa_\phi = \kappa_\phi{}^\circ + S_K\ c^{1/2} \tag{14}$$

where S_K is the experimental slope.

The limiting apparent molar isentropic compressibilities (κ_ϕ°) of $NaClO_4$ and $NaBF_4$ are found to be negative. The κ_ϕ° values at 298.15 K for $NaClO_4$ and $NaBF_4$ are -116.96×10^{-4} and -123.99×10^{-4} $cm^3 mol^{-1} bar^{-1}$, respectively. These negative κ_ϕ° 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 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, the Na^+ ion being common, the anions are evidently making the difference. Since a BF_4^- ion is smaller in size (r = 2.02 Å) than a ClO_4^- ion (r = 2.40 Å), the former will have higher surface charge density.

7.2.4   Raman Spectra

The Raman spectrum of pure 1,2-dimethoxyethane together with those of the solutions of $NaClO_4$ (at three different molarities, e.g., 0.05 M, 1 M 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 through 7. 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. 1,2-Dimethoxyethane (DME) shows ν_s (C-O) and

v_{as} (C-O) in the range of 1150-1100 cm^{-1} and 950-800 cm^{-1}, respectively. The v_{as} (C-H) stretching mode of the solvent appears in the wave number range of 1150-1100 cm^{-1}, and the v_s (C-H) mode in the range of 3000-2700 cm^{-1}. It can be seen from Table 5 and Figures 2 through 7 that the spectra of the salt solutions show several remarkable changes from that of the pure solvent.
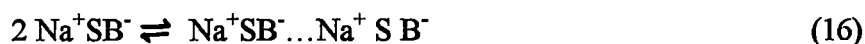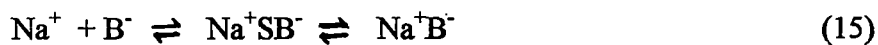
For all the salt solutions, a broad band near 370 cm^{-1} appears. This band has been assigned to the vibration primarily involving the sodium ion. This cation band frequency is found to be anion dependent. This observation is similar to those found in other weakly solvating non-polar solvents such as tetrahydrofuran,[11,12] and pyridine.[13] The variation of this band for Na$^+$ ion with different counter anions 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 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,[14] methyl acetate,[15] methyl formate,[15] pyridine,[13] tetrahydrofuran,[11,12] 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 which determine this band frequency.

For NaClO$_4$, a new non-degenerate band appearing at ~933 cm^{-1} is attributed to the infrared forbidden totally symmetric stretching vibration of the perchlorate ion.[14,16] Raman spectrum of NaBF$_4$ solution shows two very weak new bands peaking around 1025 and 991 cm^{-1} due to an internal vibration of the anion.[12] NaBPh$_4$ solution exhibits a band of medium intensity centering at 1582 cm^{-1} presumably due to the 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$_4$ and ~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$^+$ S B$^-$ (S is solvent molecule) and /or to the solvent-separated dimer, Li$^+$ S B$^-$ ... Li$^+$ S B$^-$, spectroscopically indistinguishable from each other.

No contact ion pairs are detectable for 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 towards the higher wave number 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 multi-step mechanism:

$$Na^+ + B^- \rightleftharpoons Na^+SB^- \rightleftharpoons Na^+B^- \qquad (15)$$

$$2\,Na^+SB^- \rightleftharpoons Na^+SB^-...Na^+\,S\,B^- \qquad (16)$$

$$2\,NaB \rightleftharpoons (NaB)_2 \qquad (17)$$

For NaClO$_4$, one would therefore expect only the presence of an equilibrium between the solvent-separated and contact ion-pairs represented by equation 15 that is strongly shifted toward the left. The equilibrium represented by equation 16 to form the solvent-separated dimer may also exist since Na^+SB^- and $Na^+SB^-...Na^+SB^-$ are indistinguishable by Raman spectra. However, no contact quadrupole is expected to form through equation 17 for NaClO$_4$. For both NaBF$_4$ and NaBPh$_4$, where contact ion-pair are also found to be present, the formation of contact quadrupoles or dimers via equation 17 is possible.

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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$_4$	
10^4 c	Λ	10^4 c	Λ	10^4 c	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

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

Electrolyte	Λ_0	K_P	K_T	r^2	$10^4 c_P$	$10^6 c_T$
$NaClO_4$	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

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

c	ρ	u	$\kappa_s \times 10^6$	$\kappa_\phi \times 10^4$
		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

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

DME	NaClO$_4$ (0.05 M)	NaClO$_4$ (1 M)	NaClO$_4$ (2 M)	NaBPh$_4$ (~ 0.1 M)	NaBF$_4$ (~0.02M)
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.

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$_4$)
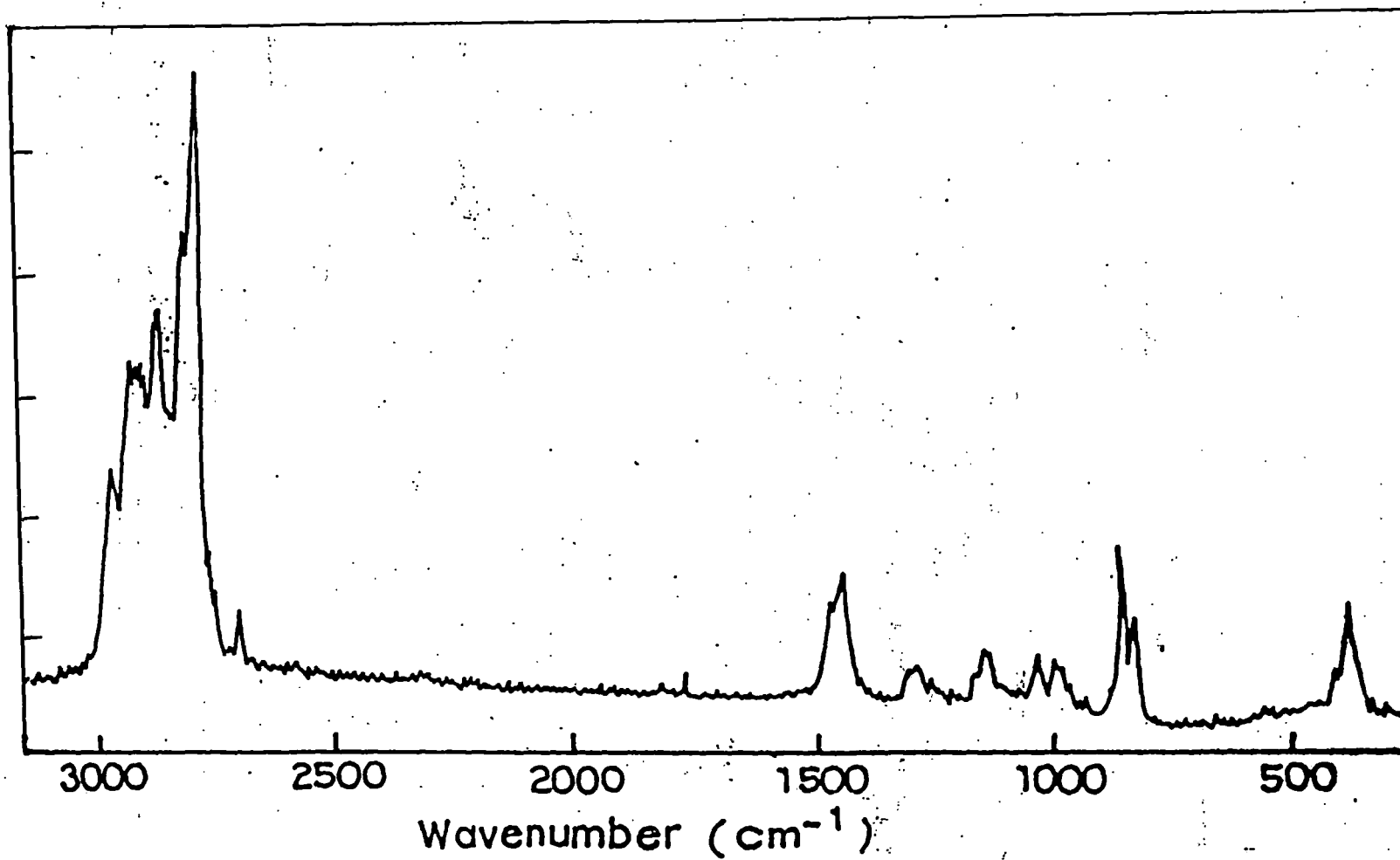
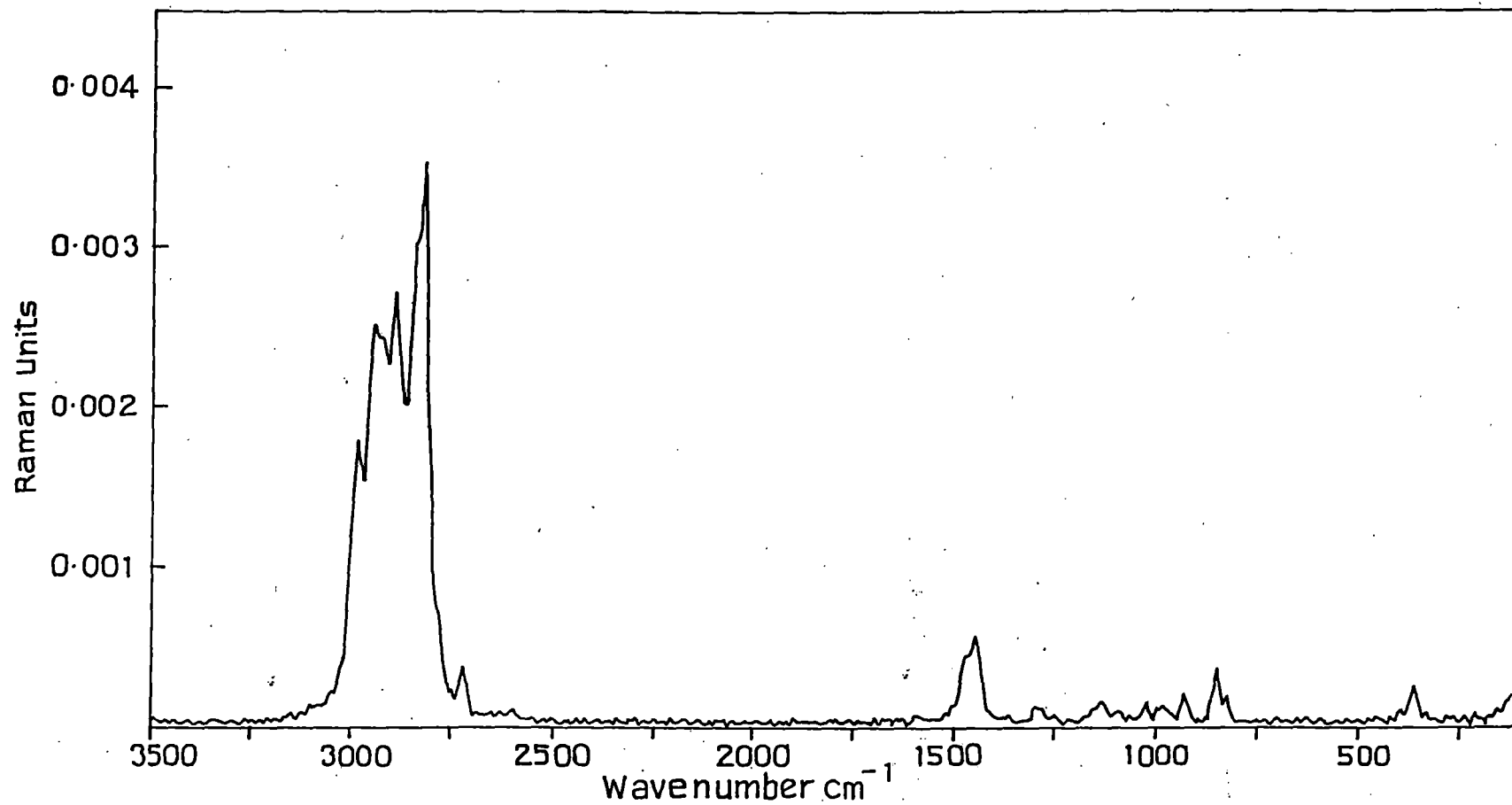Figure 2: FT-Raman spectrum of 1,2- dimethoxyethane.

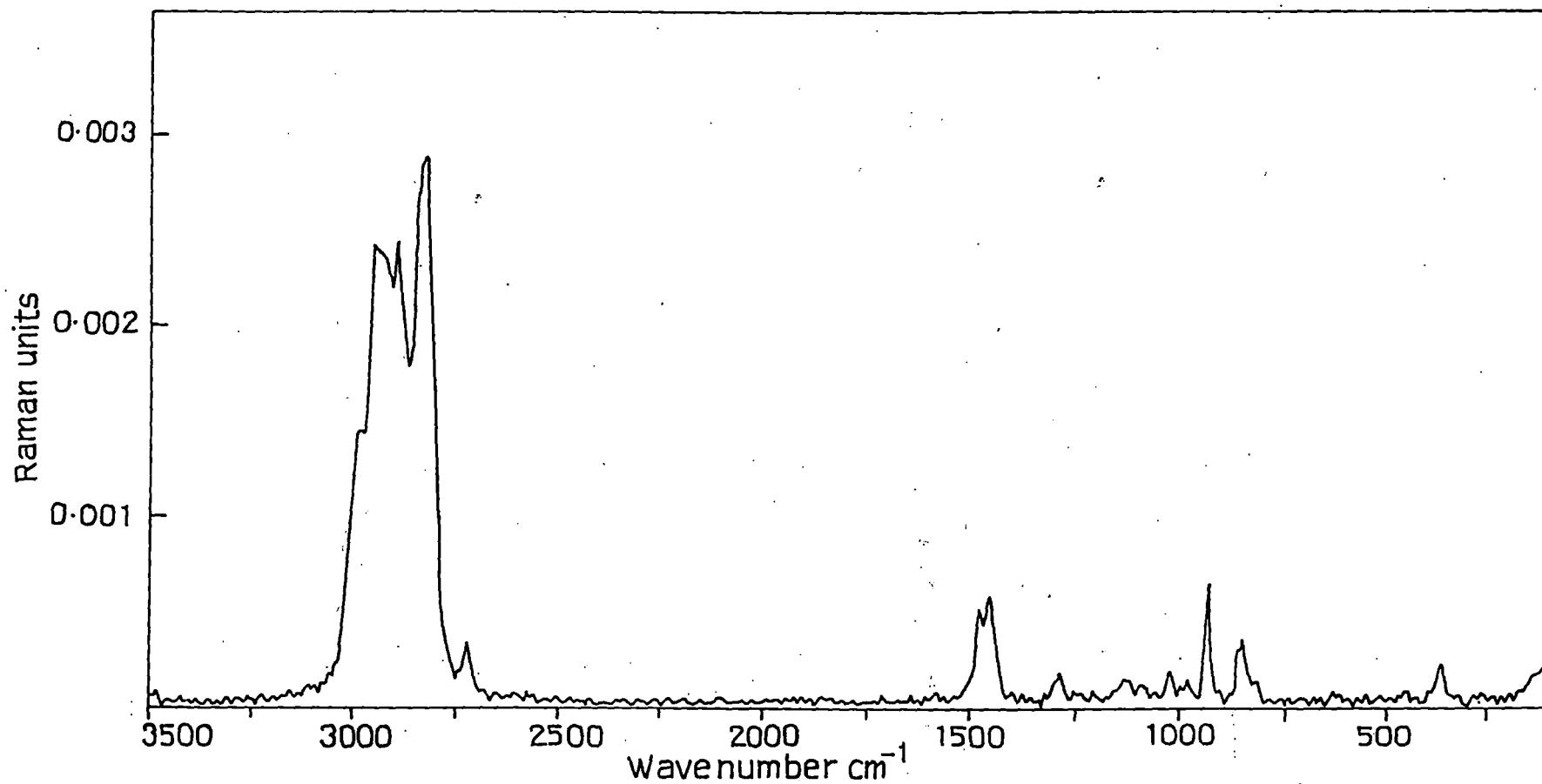Figure 3: FT-Raman spectrum of 0.05 M NaClO$_4$ in 1,2- dimethoxyethane

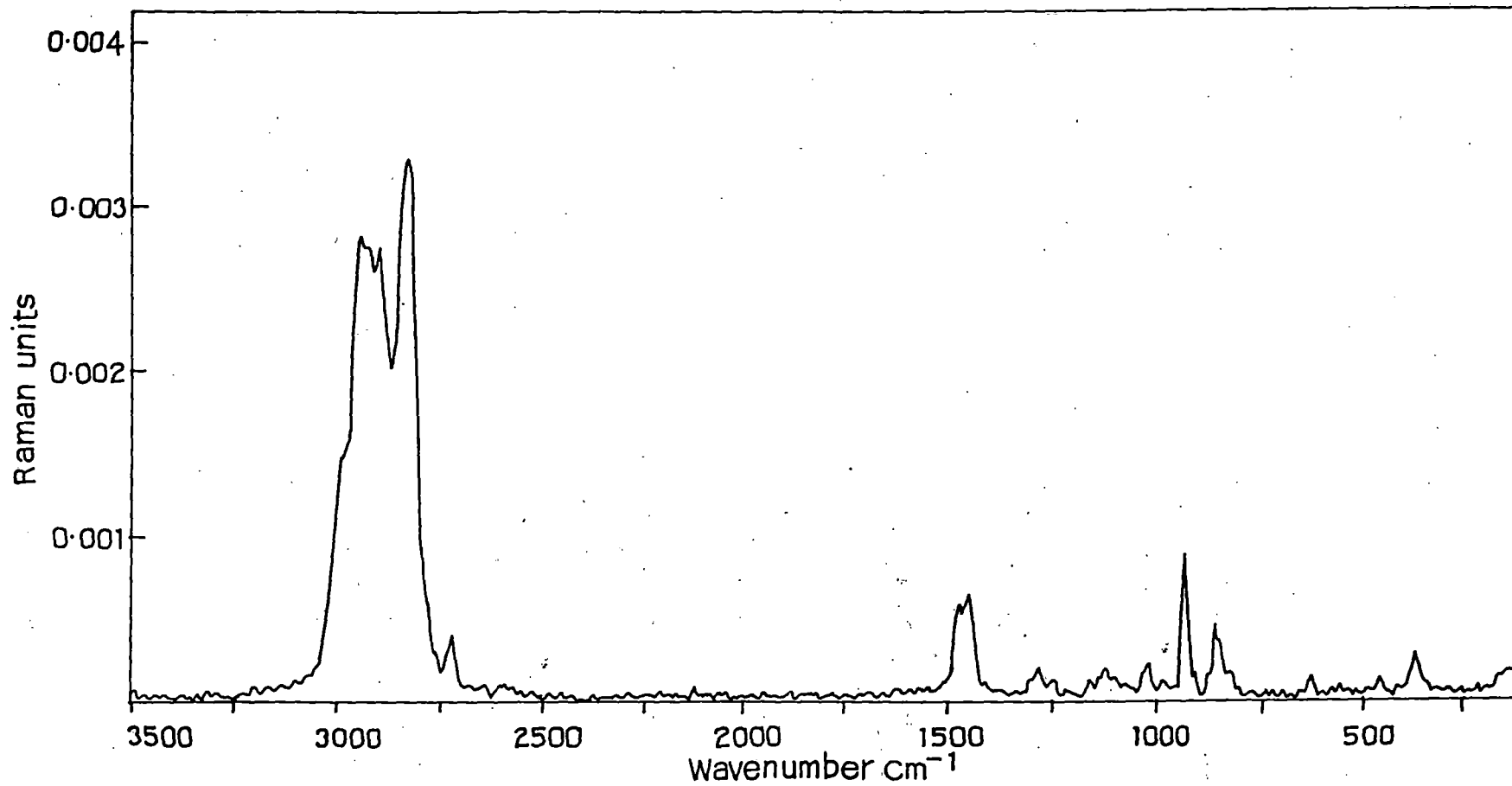Figure 4: FT-Raman spectrum of 1 M NaClO₄ in 1,2- dimethoxyethane

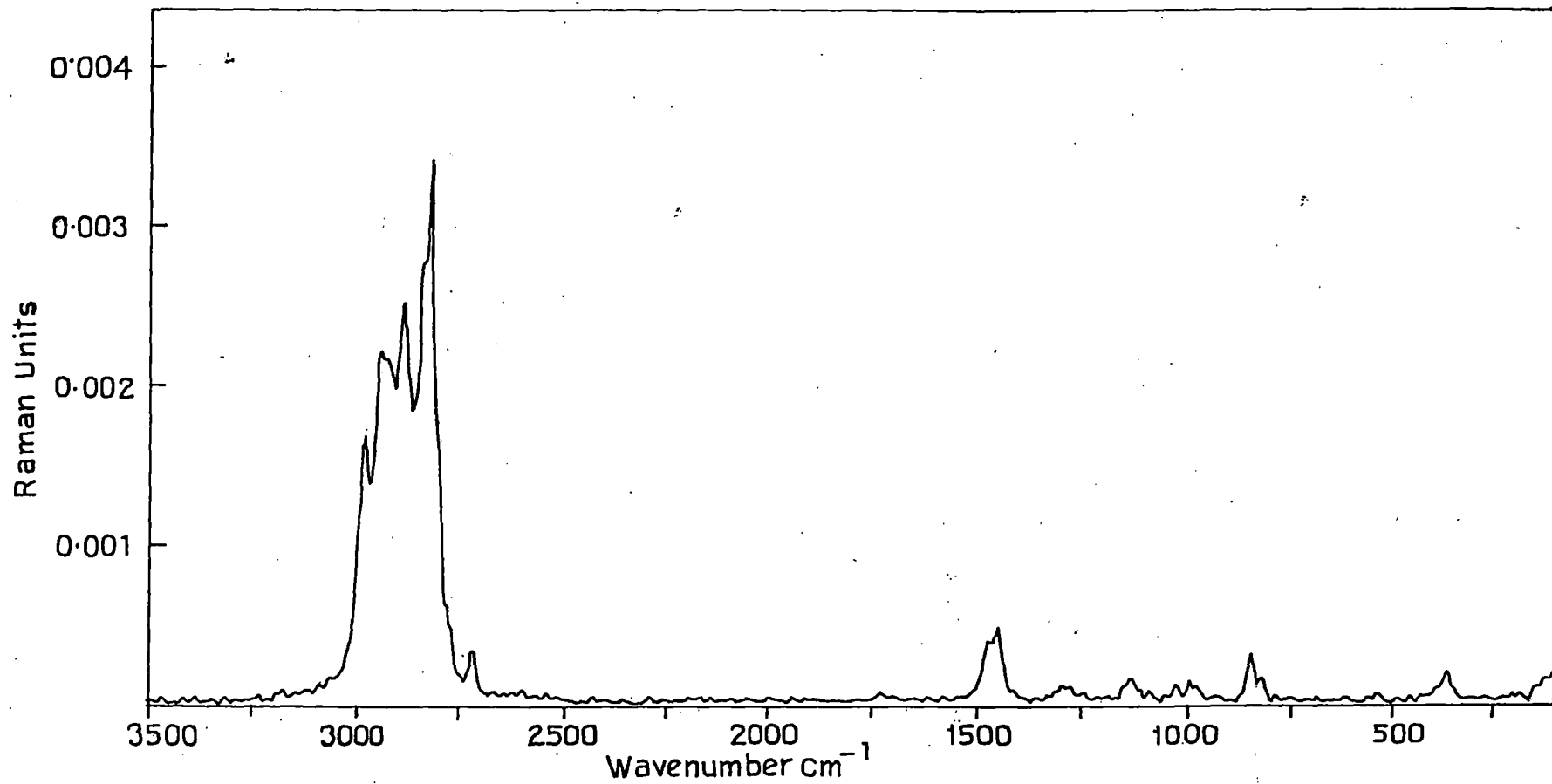**Figure 5:** FT-Raman spectrum of 2 M NaClO₄ in 1,2- dimethoxyethane

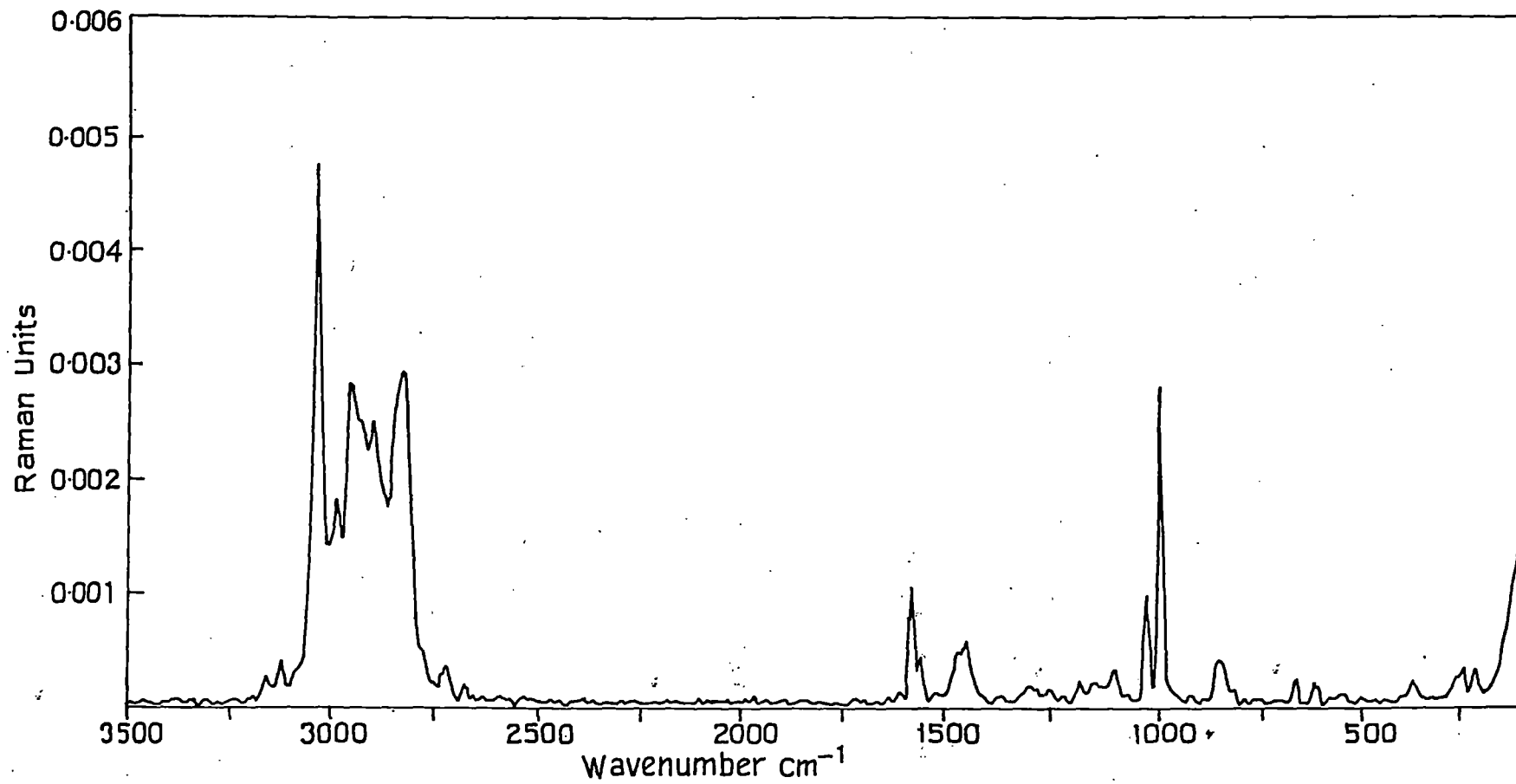Figure 6: FT-Raman spectrum of ~ 0.02 M NaBF₄ in 1,2- dimethoxyethane

Figure 7: FT-Raman spectrum of ~ 0.10 M NaBPh₄ in 1,2- dimethoxyethane