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Raman Study of Aqueous Solutions of Tetraalkylammonium and Bis(tetraalkylammonio) Electrolytes

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The Raman and infrared spectra of 1,4-bis(triethylammonio)butane dibromide (J4), 1,10-bis(triethylammonio)decane dibromide (J10), and tetraethylammonium bromide (TEABr) were measured in the solid and dissolved states. The Raman spectra of these salts in the solid and solution states were roughly similar to those of normal paraffins having the same number of skeletal atoms, but some minor differences were found. It was confirmed that molecular conformations of these ions in the solid and solution states are somewhat similar and take the all-trans form, but in main chain of J4 and J10, the gauche form is also observed. In addition, the effects of hydrophobic interaction of these salts in aqueous solution are discussed by comparison of the Raman spectra of OH stretching vibration region of water.

A number of nonspectroscopic studies of aqueous solutions of bolaform type electrolytes[1—4] have been reported with the object of investigating their effect on water structure and the ability of the bolaform cation to act as a model for cation-cation pairing in R_4NX systems. Unlike thermodynamic properties, spectroscopic investigations of aqueous solutions of these salts can provide additional information on the conformation of the hydrocarbon chains of these cations in solution.

In a previous paper,[5] it was confirmed by means of Raman spectroscopy that the molecular structure of the tetraalkylammonium ion in aqueous solution is an extended one, *i.e.*, the $-CH_2-$ groups assume an all-trans conformation, much the same as the lower members of the normal paraffin series of molecules.

In this study the Raman and infrared spectra of several bis(tetraalkylammonio) electrolytes and tetraethylammonium bromide were measured in the solid and dissolved states. In this paper emphasis is placed on obtaining information about molecular conformations of the hydrocarbon chains in aqueous solutions from a comparison of the analysis of the Raman spectra in both the solid and solution states. In addition, the effects of hydrophobic interaction of these salts in aqueous solution are discussed by comparison of the Raman spectra of the OH stretching vibration region of water with that for the pure solvent.

Experimental

Materials. Tetraethylammonium bromide, hereafter abbreviated as TEABr was of extra-pure reagent grade supplied by Nakarai Chemical Co., Ltd. The Bis(tetraalkylammonio)salts, 1,4-bis(triethylammonio)butane dibromide and 1,10-bis(triethylammonio)decane dibromide, abbreviated J4 and J10, respectively, were prepared and purified as described elsewhere.[4] Water used was deionized by ion-exchange-regin and distilled by means of usual laboratory techniques.

Apparatus. The apparatus used for Raman spectroscopy measurements consisted of an argon ion laser source manufactured by Coherent Radiation Co., Ltd. and the scattered light was analyzed with a JRS-Ul Laser Raman spectrometer from Japan Electron Optics Laboratory Co., Ltd. An A-2 IR spectrometer manufactured by Japan Spectroscopic Co., Ltd. was used to obtaine IR spectra.

Procedures. Solutions used for Raman measurements were prepared so as to contain 2 M** of bromide ion and $^+NEt_4$ unit, ($^+NEt_3-(CH_2)_2$ for the case of the bolaform cation). All measurements were carried out at room temperature.

The experiments were done using 90° scattering. The horizontal ($I_{\parallel}$) and vertical ($I_{\perp}$) components of the scattered light were measured with a polaroid analyzer.

The Raman spectra of water in the OH stretching region were obtained in aqueous solutions of TEABr, J4, and J10. The intensities were corrected for photomultiplier sensitivity. In the case of J10 it was impossible to correct the spectra owing to the existence of luminescence and consequently this salt was excluded from the analysis of salt effect on the OH vibrational spectra. The observed spectra were divided into their isotropic ($I_{\rm isot}$) and anisotropic ($I_{\rm anis}$) components.

$$I_{\rm isot} = I_{\parallel} - 4/3\, I_{\perp}$$

$$I_{\rm anis} = 4/3\, I_{\perp}$$

In the case of the infrared measurements, the solid sample was mixed with Nujol and measured at room temperature.

Results and Band Assignments

The Raman and infrared bands observed in the solid state and aqueous solutions are summarized in Table 1. The vibrational assignment of these bands was carried out on the basis of previous assignments made for normal paraffins,[6—9] and tetramethylammonium halides,[10—12] in the solid state.

At low frequencies (below 300 cm^{-1}), lattice modes, which are not observed in aqueous solutions, are found in the solid state for all compounds investigated. Commonly, the $C-N^+$ symmetric and asymmetric stretching bands are observed at about 700 cm^{-1} and 800 cm^{-1}, respectively. These bands are assigned on the basis of the following criteria: (1) The $C-N^+$ symmetric and asymmetric bands must be observed below 752 cm^{-1} and 955 cm^{-1}, respectively, since the corresponding bands for $(CH_3)_4N^+$ are centered at 752 cm^{-1} and 955 cm^{-1}, respectively and, for all compounds investigated in this work the mass of the substitutional groups on the N atom is heavier than that of $(CH_3)_4N^+$.

** 1M=1 mol dm^{-1}.

TABLE 1. OBSERVED RAMAN AND IR FREQUENCIES (cm^{-1}) OF Et_4NBr, $Et_3N(CH_2)_4NEt_3Br_2$, $Et_3N(CH_2)_{10}NEt_3Br_2$

Et_4NBr				$Et_3N(CH_2)_4NEt_3Br_2$				$Et_3N(CH_2)_{10}NEt_3Br_2$				
Solid		Solution		Solid		Solution		Solid		Solution		
IR	Raman	Raman	ρ	IR	Raman	Raman	ρ	IR	Raman	Raman	ρ	Assignments
					60 vw							
	66 m											
					72 m							
									81 w			Lattice
									88 w			
					105 m							
	112 w											
									122 vw			LA(J10)
	128 m											
					138 m							
					201 m	195 w	0.23					LA(J4)
		200 w	0.75									
	217 w								216 w	200 vw		CH_2-CH_3 torsion
										222 vw		
					265 vw				271 w			
		312 vw								300 vw	0.3	
	372 m	360 vw	0.75		369 m	360 w	0.7		360 w	361 vw	0.7	
		391 m	0.11			395 m	0.14		396 w	391 m	0.11	N-C-C bend
418 w	424 vs	418 vs	0.21		418 s	423 s	0.17		420 s	420 vs	0.18	LA(Et_4N^+)
		467 w	0.75		458 m	466 w	0.75		467 vw	456 vw	0.75	
515 vw						504 vw	0.75	488 vw	485 vw	494 vw	0.55	
		559 vw	0.54	560 vw	542 vw	552 w	0.36		532 w	552 w	0.15	
									572 w	572 w	0.29	
						582 vw	0.75					
	663 vs											
673 vw	683 vs	673 vs		700 vs	704 s	708 vs	0.01	700 w	702 s	702 vs	0.01	C-N sym. stretch
								742 m				C-H_2 rock-twist
				746 m								C-H_2 rock-twist
785 s				785 m	782 w			785 s	788 w			
		790 m	0.71			792 vw	0.75			800 w	0.65	C-N^+ asym. stretch
798 s	792 w			798 m	792 w			800 s	804 w			
				815 m	810 w	810 w	0.56	817 w	820 w			C-H rock-twist
	838 w											
								850 vw	851 w	847 vw	0.43	
						871 vw	0.75			874 vw	0.5	
895 m	900 w	900 w	0.75	893 vw	893 m			894 w	897 m	893 w	0.6	
						900 m	0.72					C-H rock
	913 s	905 m	0.75		899 m				909 w	908 vw	0.75	
948 w				942 m	948 m	951 m	0.72	938 w	942 w	938 w	0.63	
								954 m	954 m	954 w	0.67	
				968 w								C-C stretch
									983 w			C-C stretch

1006 s	1007 s	1005 m	0.75	1009 m	1007 s	1010 m	0.75	1003 s	1004 m	1006 w	0.74	C-H_3 rock
						1017 m	0.75	1017 m	1014 m	1011 m	0.74	
	1028 sh	1033 sh	0.75									C-C stretch
								1036 w	1033 w	1030 w		C-C stretch
				1040 vw	1040 w	1047 w	0.59					C-C stretch
1052 m				1054 w				1055 m				C-C stretch
1070 w	1073 s	1073 s	0.16	1075 w	1068 w	1077 m	0.23	1075 w	1088 w	1078 w	0.31	C-C stretch
	1107 sh			1105 w				1097 vw	1103 vw	1093 w	0.75	
				1115 vw		1116 m	0.08	1113 m	1116 m	1114 m	0.03	C-C stretch
	1120 s	1120 s	0.06		1120 s	1119 s	0.08	1128 vw	1129 m	1124 m	0.11	C-C stretch
	1157 vw	1154 vw	0.33	1158 m	1159 m	1155 vw	0.4	1142 vw	1153 vw	1154 vw		C-C stretch
1173 s								1163 s				
	1182 m	1177 w	0.75		1173 m	1172 m	0.75		1166 m	1165 w	0.75	C-H_2 twist-rock
1188 m		1187 vw	0.5	1193 w				1192 m		1187 vw	0.75	
									1234 w			
				1235 vw								
								1261 vw				
	1269 m			1267 w	1269 w			1277 w	1280 m			C-H_2 wag
									1295 m			
	1308 s	1304 m	0.75	1302 w	1292 s	1306 m	0.75		1303 m	1307 m	0.72	C-H_2 twist-rock
								1320 vw	1317 w			
					1323 w							
1334 m	1335 vw			1334 w	1338 w	1336 w	0.72	1336 vw				C-H_2 wag
		1355 vw	0.75		1353 w	1363 vw	0.64	1347 m		1355 vw	0.53	
1377 s	1379 vw	1379 vw	0.75	1376 s	1379 w			1378 m	1376 vw			C-H_2 sym. bend
								1386 m	1385 vw			
1398 m	1397 m	1393 m	0.5	1397 m	1398 m	1399 w	0.45	1400 s	1400 w	1394 w	0.38	C-H_2 wag
1407 m	1408 vw	1408 vw	0.75									
				1418 w					1417 w			
1442 s	1445 m	1449 m	0.75	1449 m	1443 m	1455 m	0.75	1443 s	1448 s	1448 m	0.72	C-H_3 asym. bend
1475 m	1472 s	1466 s	0.75	1467 s	1471 m	1471 s	0.75	1456 m	1456 s	1466 s	0.75	C-H_3 asym. bend
1495 s	1499 w	1494 w	0.63	1488 m	1492 w	1495 w	0.32	1496 s	1496 m	1488 m	0.67	C-H_2 bend
				2728 vw					2731 w			
	2744 w	2754 w			2747 w				2755 vw	2751 vw		
2760 w						2767 vw						combination
	2774 w	2774 w			2777 w	2788 vw				2778 vw		
									2792 vw			
2852 s	2852 w			2860 s				2860 s	2852 s	2861 m	0.06	C-H_2 sym. stretch
2900 w	2905 m	2900 m		2904 w	2887 m	2905 m			2892 s	2900 s	0.17	C-H_3 sym. stretch
2920 s	2928 w			2930 w	2925 m			2920 s	2918 w			C-H_2 asym. stretch
	2946 s	2951 s	0.03		2937 s	2960 s	0.06		2933 vs	2950 s	0.07	
2952 m	2970 s				2946 s							
									2963 w			
					2960 s	2972 s			2979 s			
2988 m	2997 s	2997 s	0.34		2986 s	3001 s	0.27	2980 s	2985 s	2994 s	0.32	C-H_3 asym. stretch
	3003 w				3005 m				2996 w			

ρ: Depolarization ratio

(2) The C–N$^+$ symmetric stretching mode gives rise to the strong, polarized, Raman bands usually observed. (3) The asymmetric stretching mode gives rise to the depolarized Raman line and strong infrared band commonly observed. Above 900 cm^{-1}, the Raman and infrared spectra of all compounds investigated are roughly similar to those of normal paraffins having the same number of skeletal atoms.

The band assignments were made from consideration of those criteria and are summarized in the last column of Table 1. A careful comparison of the Raman spectra of solid state and aqueous solution shows that some minor differences exist for the compounds investigated. Therefore it appears that the molecular conformations in the solid and solution states are somewhat similar.

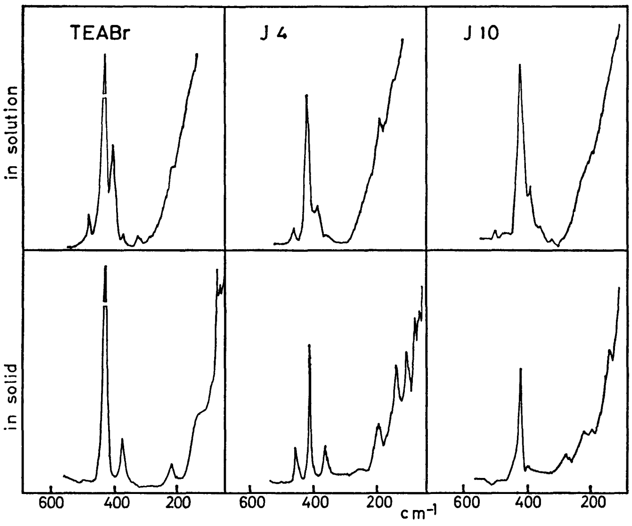

Fig. 1. Raman spectra for TEABr, J4, and J10 in the frequency range below 500 cm^{-1} in the solid and solution states.

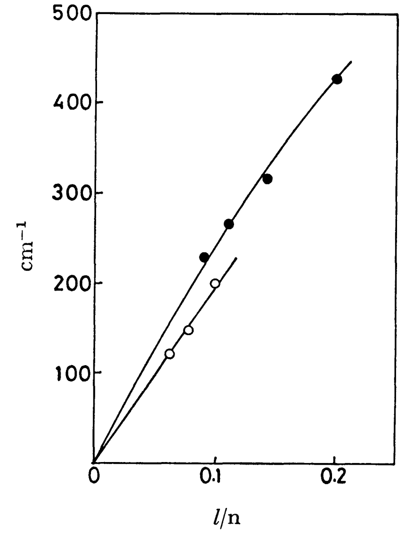

Fig. 2. Relationship between the frequencies of the LA mode and the reciprocal carbon number (involving nitrogen atom); (○) bolaform ions, (●) tetraalkylammonium ions.

Discussion

Low Frequency Regions (below 500 cm^{-1}). The Raman spectra for each compound in the frequency range below 500 cm^{-1} are shown in Fig. 1. In the solid state, several lattice modes are observed, but in aqueous solutions, these lattice modes disappear. Also, some longitudinal accoustic vibrational modes (LA mode) are observed in both the solid phase and aqueous solution, X-ray crystallographic studies have shown[13,14] that the chain conformation of $-CH_2-$ groups in normal paraffins and in tetraalkylammonium ions are in all-trans form. By analogy with these results, the chain conformations in the Bis(tetraalkylammonio) salts in the solid state can be considered to be in all-trans form.

The LA mode is regarded as a symmetric accordion-type longitudinal vibration of a string of beads with antinodes at the chain ends. Therefore, this band is ascribed to the molecules taking an all-trans form. In the previous paper,[5] studies were reported on the LA band of tetraalkylammonium ions. From the existence of the LA band, it was confirmed that the tetraalkylammonium ions in the solid and aqueous solution are in an extended form, such as the all-trans form of the $-CH_2-$ chain.

For TEA ion, the LA bands were observed at 424 cm^{-1} in the solid and 420 cm^{-1} in aqueous solution.[5] A strong peak is observed at about 420 cm^{-1} in the Raman spectra of J4 and J10 in both states. This band corresponds to the LA band of TEA ion and is ascribed to the LA band in the Et–N–Et structure of the bolaform ion. Therefore, the Et–N–Et structure is mostly in the all-trans form in both states.

In solid J4 and J10, the LA bands of the main chain were also observed, although they were weak. These were identified by the criterion that the frequency of the band decreases as the length of the carbon chain (involving nitrogen atom) increases. The relationship between the frequency of the LA band and the reciprocal carbon number shown in Fig. 2 along with the corresponding relationship for tetraalkylammonium ions.[5] The existence of this band indicates the molecules take an all-trans form in main chain in the solid state. This band is observed weakly in aqueous solution of J4, but not in aqueous solution of J10. Therefore, it appears that in aqueous solution the J4 ions assume an all-trans conformation to some extent but less in those of the J10 ion. This result may be rationalized on the basis that random conformation in the main chain increases as the distance between the two charged nitrogen atoms increases and hence the repulsive force decreases.

Intermediate Frequency Regions (500 cm^{-1}—1400 cm^{-1}). The solution and solid state Raman spectra of TEABr, J4, and J10 are shown in Figs. 3, 4, and 5, respectively. Some minor differences are observed between the two phases. In the case of TEABr, Raman lines observed in aqueous solution at 467 cm^{-1} and 559 cm^{-1} are not seen in the solid state. These lines are ascribed to the rotational conformations around the $-CH_2-CH_2-$ bonds.

In the Raman spectra of J4, the two bands at 466

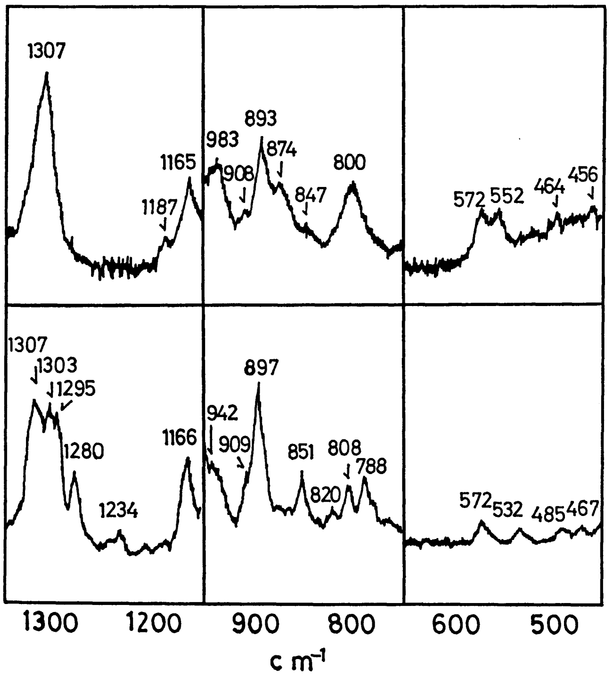

Fig. 3. Raman spectra of TEABr in the solid and solution states in the frequency range from 500 cm^{-1} to 1400 cm^{-1}.

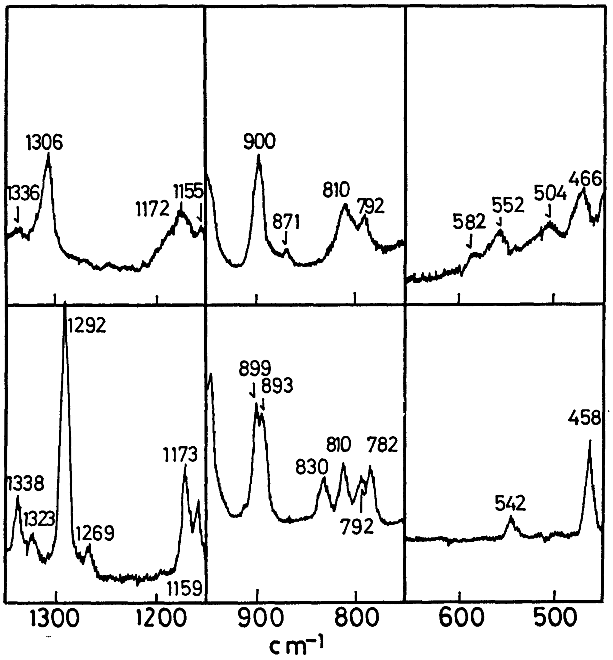

Fig. 4. Raman spectra of J4 in the solid and solution states in the frequency range from 500 cm^{-1} to 1400 cm^{-1}.

cm^{-1} and 552 cm^{-1} in aqueous solution are also observed in the solid state. These lines correspond closely to the Raman bands of TEABr at 467 cm^{-1} and 559 cm^{-1} in aqueous solution, which have been attributed to the *gauche* conformation around the $-\mathrm{CH_2}-\mathrm{CH_2}-$ bonds. Accordingly, the molecular structures taking a *gauche* conformation in the Et–N structure of J4 exist both in aqueous solution and in the solid state. Further, since the two Raman lines at 504 cm^{-1} and 582 cm^{-1} in aqueous solution are not observed in the solid state, these may indicate that they are the *gauche* isomers that relate to the main chain of the J4 ions.

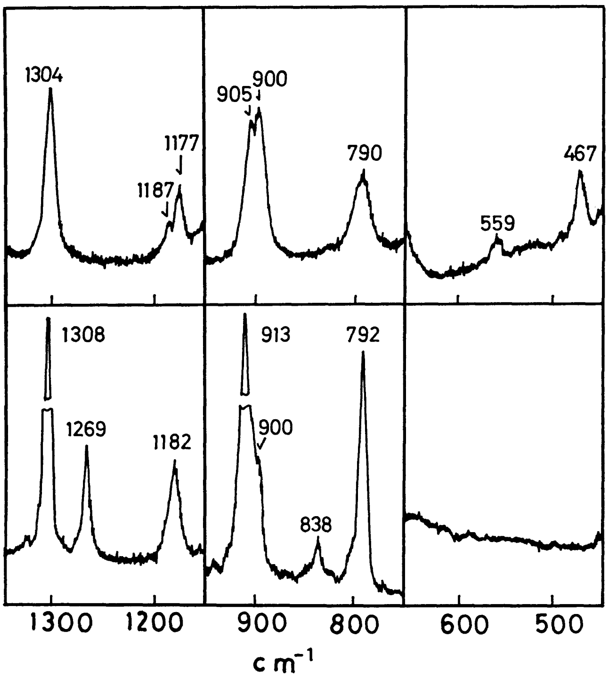

Fig. 5. Raman spectra of J10 in the solid and solution states in the frequency range from 500 cm^{-1} to 1400 cm^{-1}.

For the J10 salt, the two Raman lines observed in solution at 456 cm^{-1} and 552 cm^{-1} are also observed in the solid state. They correspond to those of TEABr at 467 cm^{-1} and 559 cm^{-1} in aqueous solution and have been ascribed to gauche conformation. Therefore, the molecular units taking a gauche conformation in the Et–N chain of J10 exist in both aqueous solution and solid phases. The two Raman lines at 494 cm^{-1} and 572 cm^{-1} in aqueous solution are also found in the solid state. These lines correspond to those of J4 at 504 cm^{-1} and 582 cm^{-1} in aqueous solution, which have been ascribed to the gauche isomers in the main chain. Accordingly, the molecules taking *gauche* form in main chain exist in both states.

The bands located at 1269 cm^{-1} for J4 and 1234 cm^{-1}, 1230 cm^{-1}, 1295 cm^{-1}, and 1303 cm^{-1} for J10 are observed only in the solid state. These bands can be assigned to the twisting-rocking mode of $-\mathrm{CH_2}-\mathrm{CH_2}-$ groups in the molecular chains. The fact that these bands are not observed in solution indicates that the motion of the $-\mathrm{CH_2}-\mathrm{CH_2}-$ groups in the main chains of the ions are less constrained. The bands located at 838 cm^{-1} for TEABr, 830 cm^{-1} for J4, and 820 cm^{-1} for J10 are observed in the solid state, but not in solution. Also, the bands located at 782 cm^{-1} for J4 and 788 cm^{-1} for J10 are not observed in solution. Although at this stage we can not assign these bands to the internal motions of these molecules, one may speculate that these bands are related to the terminal $-\mathrm{CH_2}-\mathrm{CH_3}$ rocking-twisting vibrational modes.

C–H Stretching Vibration Regions (2850 cm^{-1}*—3000*

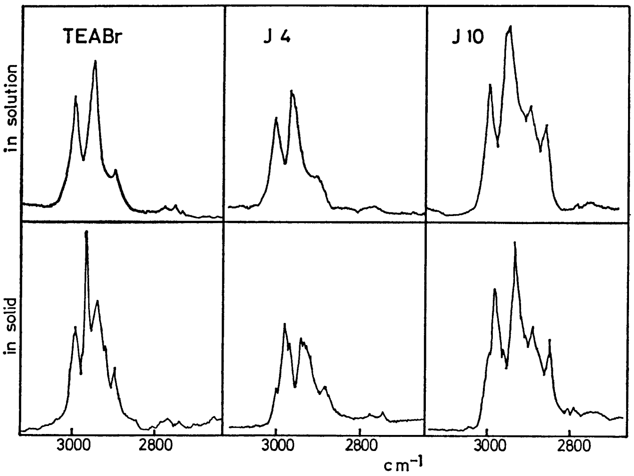

Fig. 6. Raman spectra for TEABr, J4, and J10 in the frequency range from 2850 cm^{-1} to 3000 cm^{-1} in the solid and solution states.

cm^{-1}). The vibrational C–H stretching modes can be classified into two groups; one from the methyl end group and the other arising from the methylene group vibrations. The symmetric and asymmetric methyl C–H stretching vibrations located at 2884 cm^{-1} and 2967 cm^{-1} are independent of the chain length in normal paraffins.[7] On the other hand, the methylene symmetric and asymmetric vibrations located at 2849 cm^{-1}—2861 cm^{-1} and 2912 cm^{-1}—2929 cm^{-1} are slightly dependent on the chain length.[7]

The Raman spectra for each compound in this frequency range are shown in Fig. 6. As can be seen, there are many bands which can be assigned to the methylene group vibration in the solid state. On the other hand in solution, only three bands are observed in each compound, located at about 2900 cm^{-1}, 2951 cm^{-1}, and 2997 cm^{-1} and these frequencies are almost independent of the chain length. In the case of the J10 ion in solution, one additional band at 2861 cm^{-1} is observed. This band can be assigned to the methylene symmetric stretching band. As J10 has 16 $-CH_2-$ units in an ion, this weak band is likely to be observed in the case of J10.[11] The reason that only three bands are observed in the solution state may be due to the fact that, since in the solution state the C–C bond of the main chain and branched chains are rotating or tumbling, then the C–H stretching vibration mode of the methylene groups will be strongly coupled to each other and leads to a reduction in the number of observed bands.

Raman Spectra of Water, OH Stretching Region. The isotropic (I_{isot}) and anisotropic (I_{anis}) Raman spectra of water and aqueous solutions of TEABr and J4 are shown in Fig. 7. The main effect of the salts on the water spectra is to change the spectral line shape. The opposing results are clearly evident for the I_{isot} and I_{anis} spectra; intensities in the lower frequency region (3000 cm^{-1}—3350 cm^{-1}) decrease while intensities in the higher frequency region (3350 cm^{-1}—3550 cm^{-1}) increase, in comparison with the spectrum of water. The effect of salt addition to water is similar to the effects produced by increasing temperature.[15–17] Therefore these salts, at least superficially seem to have a structure breaking effect on water at these high concentration and this is contrary to their structure-enforcing effect at dilute concentration. The influence of the TEA ion on the OH stretching region is greater than that of the J4 ion. The main effects of these salts on the water structure are of an electrostatic and hydrophobic nature.

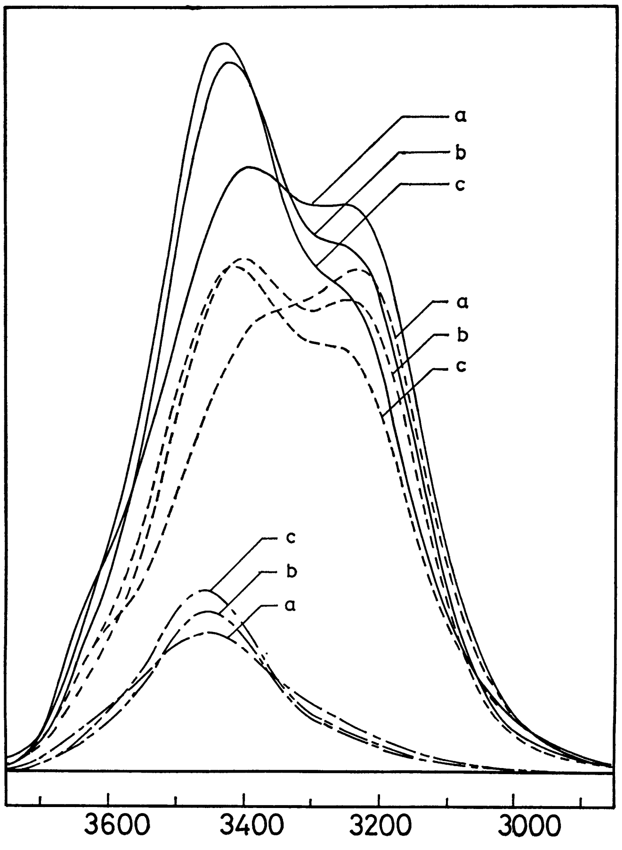

Fig. 7. Effects of added salts on the OH stretching vibration regions; —— observed, ---- isotropic parts, and —·— anisotropic ones.
(a) Water, (b) aqueous solution of TEABr, and (c) aqueous solution of J4.

Since the molecular conformations of the TEA and J4 ions are both observed to be of the extended form in aqueous solutions and the salt concentrations have been prepared so as to normalize the hydrophobic effect (approximately same hydrocarbon concentration for each ion in solution), it would appear that the difference in line shape for the OH stretching vibration in aqueous solutions of these salts is caused by the electrostatic atmosphere of the ion. The presence of two charged sites in a single ion and the incompatibility of several "type" of water around the solute to "interface" readily indicate the J4 ions are more complex in their influence on solvent interactions.

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