Effect of Lithium Halides on the Characteristic Vibration Frequencies of 1 Propanol

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Summary: In the present work, emphasis is given to ν(O-H), δ(O-H) and ν(C-O) vibrations of 1-propanol and the effects of lithium chloride and bromide on frequencies of these vibrations. It has been found, in general, that solutions in lower concentration ranges departed to a greater extent from respective frequencies for pure 1-propanol, because of the fact that at lower concentration, there are large interactions between dipoles and the counter ions which result in decrease in energy of vibration. So, a fall in wavenumbers is of common occurrence with increasing salt concentration and tends to become constant at or near the saturation limit.

Introduction

Solvation of ions in a solution results in the formation of linkage between ions and the solvent molecules, which would have their characteristic vibrational frequencies. The vibrational frequencies may shift to lower or higher wavenumber by using different solvents. Such changes can be monitored by using I.R. technique.

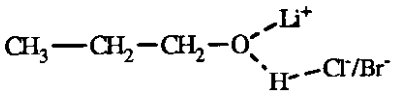
The aim of the present study has been to investigate the shift in vibrational frequencies of 1-propanol by interacting it with cations and anions of lithium halides. The I.R. spectral data of different salts solutions has been used to show the specific part of a solvent molecule which interacts with the ions [1-8]. For this purpose, lithium chloride and lithium bromide are used to investigate such interactions in 1-propanol.

Results and Discussion

The vibrations taken into consideration in this work were the fundamental frequencies of 1-propanol and are characterized as ν(C-O) (1047), νO-H (3244), δO-H (1383) cm^{-1}. The νO-H band at 3244 cm^{-1} in the case of pure 1-propanol suggests extensive hydrogen bonding.

Effect of LiCl and LiBr on νO-H

Lithium chloride solution in the concentration range of 0.01-2.0 M was scanned. The spectra reveals that at lower concentration (0.01-0.1 M), the shift in frequency of νO-H is quite significant and becomes smaller and smaller at higher concentrations. For example, the Δν at lower concentration (0.01 M) in 9 cm^{-1}, whereas this value reduces to 7 cm^{-1} at 1.0 M. This change in frequency shift may be of considerable interest as this is directly influenced by the concentration of the added salt. For example, in the former case the Δν value is only 0.01 whereas the latter corresponds to Δν value of 1.0. This shows that at lower concentration values, there is a strong interaction between the ions of the salt and the polar group of the solvent. Δν has a maximum value of 19 in the concentration range of 0.05-1.0 M and could possible arise due to strong interactions as shown below:



As we approach the saturation point (~ 2.0 M), the decrease in change in frequency shift per unit molar concentration (Δν/ΔM) becomes less and less for both LiCl and LiBr. This is because of the reason that at this point the number of furnished ions (both cations and anions) in solution becomes constant and can cause no further interaction with solvent. The change in vibrational frequencies are given in Table 1 and 2, the fig. 1 shows the plot between concentration and wavenumber.

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Table-1: ν(O-H) of LiCl solution in 1-Propanol

Conc. of LiCl in 1-propanol sol. (M)	ν(O-H)	ΔM(M)	Δν cm^{-1}	Δν/ΔM cm^{-1}/M
0.00	3244			
0.01	3235	0.01	9	900
0.05	3227	0.04	8	200
0.1	3208	0.05	19	380
0.5	3200	0.40	8	20
1.0	3193	0.50	7	14
1.5	3190	0.50	3	6
2.0	3182	0.50	8	16

Table-2: ν(O-H) of LiBr solution in 1-Propanol

Conc. of LiBr in 1-propanol sol. (M)	ν(O-H)	ΔM(M)	Δν cm^{-1}	Δν/ΔM cm^{-1}/M
0.00	3244			
0.01	3237	0.01	7	700
0.05	3233	0.04	4	100
0.1	3214	0.05	19	380
0.5	3204	0.40	10	25
1.0	3199	0.50	5	10
1.5	3194	0.50	5	10
2.0	3186	0.50	8	16

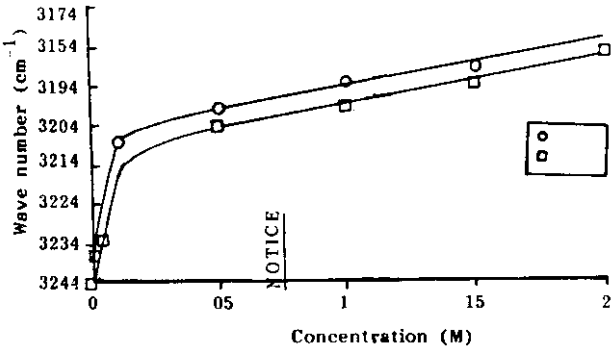

Fig. 1: Plot of Cone. Vs. Wave number of ν(O-H) in LiCl and LiBr Solution.

Effect of LiCl and LiBr on δO-H

The δO-H for 1-propanol appears at 1380 cm^{-1}. This peak value decreases with increasing amount of added salt. This may again be accounted due to the electronegative interactions between the polar sites of the solvent and the charged nature of the ions. The δO-H is basically the deformation vibrational motion of the molecule which is largely hindered by the presence of charged ions in its immediate vicinity thus requiring more energy for its motion. This is exactly reflected in the data, the shift of frequency from higher wavenumber to lower wavenumber on the addition of added amounts of salt. The changing concentration of lithium halide in 1-propanol also causes a different change in magnitude of frequency shift, for example, at lower concentration i.e. 0.01-0.05 M, the change in frequency towards lower side is between 1-4 cm^{-1} Whereas this difference increases to 8 cm^{-1} at 0.1 M salt concentration. The large change in frequency is because of the greater number of attractive interactions between the solvent and the ions which in turn require more energy for O-H bond to vibrate thus resulting the shift to lower wavenumbers. This trend of shift is flattened out at or near the saturation point. The frequency shift is more pronounced in case of LiCl than LiBr which may be explained due to large size of Br$^-$ ions than Cl$^-$ ion and also because of lesser charge density on Br- ion. Thus, the interactions become less in solution thereby causing lesser change in frequency shift on the addition of LiBr. The results are shown in Tables 3 and 4, the Fig. 2 represents the plot between concentration and wavenumber.

Table-3: δ(O-H) of LiCl solution in 1-Propanol

Conc. of LiCl in 1-propanol sol. (M)	δ(O-H)	ΔM(M)	Δν cm^{-1}	Δν/ΔM cm^{-1}/M
0.00	1383			
0.01	1382	0.01	1	100
0.05	1378	0.04	4	100
0.1	1370	0.05	8	160
0.5	1363	0.40	7	17.5
1.0	1361	0.50	2	4
1.5	1362	0.50	1	2
2.0	1360	0.50	2	4

Table-4: δ(O-H) of LiBr solution in 1-Propanol

Conc. of LiBr in 1-propanol sol. (M)	δ(O-H)	ΔM(M)	Δν cm^{-1}	Δν/ΔM cm^{-1}/M
0.00	1383			
0.01	1380	0.01	3	300
0.05	1382	0.04	2	50
0.1	1381	0.05	1	20
0.5	1378	0.40	3	7.5
1.0	1381	0.50	3	6
1.5	1378	0.50	3	6
2.0	1380	0.50	2	4

Effect of LiCl and LiBr on νC-O

In 1-propanol, νC-O appears at 1047 cm^{-1} in the form of a sharp peak. Added amounts of both LiCl and LiBr cause a decrease in this frequency which is more pronounced in the salt concentration range of 0.01-0.5 M and then becomes nearly constant at more higher concentrations. The interaction in this case is the one where oxygen having negative charge in the C-O dipole interacts

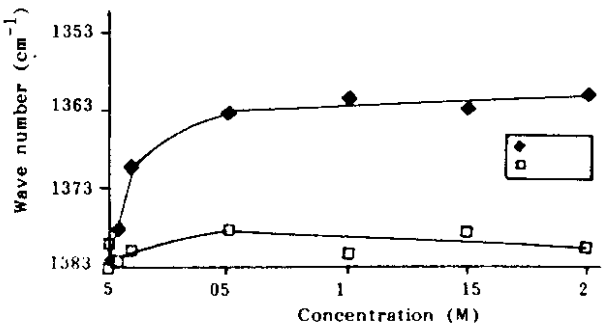

Fig. 2: Plot of Cone. Vs. Wave number of ν(O-H) in LiCl and LiBr Solution.

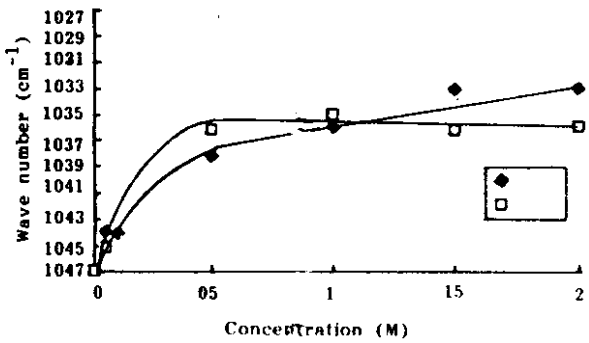

Fig. 3: Plot of Cone. Vs. Wave number of ν(C-O) in LiCl and LiBr Solution.

strongly with the Li^+ ions. The Cl^- and Br ions are not able to interact with C-O dipole as carbon atom is sterically hindered by four other atoms in a tetrahedral environment and Cl^- or Br^- ions because of their larger sizes instead of interacting with the carbon atom located deep in the molecule, interact with the H atoms of the C-H dipole on the periphery hence affecting νC-H which have been ignored in the present work. The vibrational frequencies are compared in Tables 5 and 6, the Fig. 3 shows the plot between the concentration and wavenumbers.

Table-5: ν(C-O) of LiCl solution in 1-Propanol

Conc. of LiCl in 1-propanol sol. (M)	ν(C-O)	ΔM(M)	Δν cm^{-1}	Δν/ΔM cm^{-1}/M
0.00	1047			
0.01	1046	0.01	1	100
0.05	1044	0.04	2	50
0.1	1044	0.05	0	0
0.5	1038	0.40	4	10
1.0	1036	0.50	2	4
1.5	1033	0.50	3	6
2.0	1033	0.50	0	0

Table-6: δ(O-H) of LiBr solution in 1-Propanol

Conc. of LiBr in 1-propanol sol. (M)	ν(C-O)	ΔM(M)	Δν cm^{-1}	Δν/ΔM cm^{-1}/M
0.00	1047			
0.01	1046	0.01	1	100
0.05	1045	0.04	1	25
0.1	1042	0.05	3	75
0.5	1036	0.40	6	15
1.0	1035	0.50	1	2
1.5	1036	0.50	1	2
2.0	1036	0.50	0	0

Experimental

Lithium chloride and lithium bromide were supplied E. Merck and had a purity of 99.0%. Due to the hygroscopic nature of these compounds they were dried at 110°C for about two hours before actual use. 1-propanol was supplied by BDH (GLC grade 99.5% purity). The purity was checked by taking refractive index (1.385) and I.R. spectra of 1-propanol and compared with the values already given in the literature [9].

The stock solution (2.0 M) of each of the lithium halide salts were prepared in 1-propanol. Necessary dilutions with the same solvent were made in order to prepare a range between 0.1-2.0 M. Ten ml of each of the above solutions was stored in well capped bottles to avoid contamination and evaporation. Solutions were made just prior to actual use.

The I.R. spectra were recorded at room temperature, on Hitachi 270-50 spectrophotometer. The KBr cell of 0.1 mm thickness was properly cleaned by pure CCl_4 and dried before spectral measurements. Blank correction was done with a KBr cell.

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