

# Effect of Lithium Halides on the Characteristic Vibrational Frequencies of Propanoic Acid

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**Summary:** Effect of Lithium Chloride and Bromide on  $\nu(\text{C}=\text{O})$  and  $\delta(\text{O}-\text{H})$  have been investigated. Ion solvent interactions are responsible for the shift of characteristic vibrational frequencies of pure propanoic acid in solution. As concentration of solution is increased the departure from respective frequencies for pure propanoic acid becomes less pronounced. A general decrease in vibrational frequencies is observed with rise in concentration, it is almost stabilized near saturation point.

## Introduction

Addition of ions to a solvent generate various types of forces responsible for shift of characteristic vibrational frequencies of the molecule of pure solvent. The linkages produced also have their own specific vibrational frequencies [1-3]. The shift of vibrational frequencies to lower or higher wave numbers as a consequence of changed environment in solution can be observed through I.R. Spectroscopy, the interpretation of change in vibrational spectrum of the solvent provide information from which specific characteristics of ion-solvent interaction can be inferred. The I.R. spectroscopic data of different salt solutions can help to suggest the particular portion of the solvent molecule where ions are interacting [4-6].

Present work deals with the study of ion-solvent interactions. Effects of lithium halides on vibrational modes of propanoic acid has been investigated, since the low dielectric constant [7] of solvent permits dissolution of a limited number of salts therefore the study is restricted to the effect of monoatomic ions on different stretching and bending modes.

## Results and Discussion

Selection of frequency range to be studied in the present work is governed by the probability of

interaction of ions with a particular portion of the solvent molecule, it is known that a cation prefers to interact with an electronegative atom and an anion shows its affiliation for hydrogen atom in the molecule of the solvent. The vibrational changes of  $\nu(\text{O}-\text{H})$ ,  $\nu(\text{C}=\text{O})$  and  $\delta(\text{O}-\text{H})$  have been investigated.

### a) $\nu\text{O}-\text{H}$ stretching frequency

Propanoic acid shows a strong band in the region  $3500-2500\text{ cm}^{-1}$  due to hydrogen bonded OH stretching vibration, a mean frequency of  $3016\text{ cm}^{-1}$  has been assigned to the OH vibration. Table-1 shows the wave number obtained for the dimeric OH stretching of various concentrations of LiCl and LiBr in propanoic acid. The decrease in  $\nu\text{O}-\text{H}$  can be explained on the basis of ion-solvent interaction. The carbonyl hydrogen is acidic and has a positive charge. The bonded electron pair of OH unit is shifted close to oxygen due to higher electronegativity. The electron density shift is also enhanced by the internal conjugation of  $\text{O}=\text{C}-\text{OH}$  system, so hydrogen of the carboxylic group is less electron dense and consequently the probability of interaction between OH and halide increases.

This strong interaction lengthens and weakens the OH bond resulting in lower vibrational frequency. The effect of electronegativity on the

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Table-1:  $\nu(\text{O-H})$  of LiCl/LiBr solution in propanoic acid

Conc. of LiCl/LiBr (M)	$\nu(\text{O-H})$ $\text{cm}^{-1}$ in LiCl solution	$\nu(\text{O-H})$ $\text{cm}^{-1}$ in LiBr solution
0.00	3010	3010
0.01	2912	2932
0.05	2950	2998
0.1	2962	2980
0.5	2952	2964
1.0	2948	2958
1.5	2944	2956
2.0	2968	2960

shift can be seen from the plot of concentration Vs.  $\text{cm}^{-1}$  given in Fig. 1. It is evident that larger charge density induces larger frequency shifts.

Increase in concentration also changes the absorption frequency. Since more and more halide ions are being introduced into the solution and the environment is constantly changing. However, when the number of ions become constant near the saturation point, then the frequency shift is less pronounced.

#### b) $\nu\text{C=O}$ stretching frequency

The  $\text{C=O}$  stretching frequency in acids is higher in comparison to aldehydes and ketones. The main reason for this shift is the substitution of hydrogen of alkyl group by oxygen. The inductive effect results in a larger rise in frequency. I.R. spectroscopic data of  $\text{C=O}$  stretching frequency of various solution is given in Table-2. The  $\text{C=O}$  is a

Table-2:  $\nu(\text{C=O})$  of LiCl/LiBr solution in propanoic acid

Conc. of LiCl/LiBr (M)	$\nu(\text{C=O})$ $\text{cm}^{-1}$ in LiCl solution	$\nu(\text{C=O})$ $\text{cm}^{-1}$ in LiBr solution
0.00	1692	1692
0.01	1686	1683
0.05	1680	1683
0.1	1671	1680
0.5	1677	1677
1.0	1674	1674
1.5	1644	1671
2.0	1662	1662

polar group and the electron density on oxygen is increased due to internal conjugation of  $\text{COOH}$  group.

The positively charged small lithium ions having large charge density interacts with the  $\text{C=O}$  stretching mode. The double bond becomes some what longer as compared to the original length and hence the vibrational frequency shifts towards lower wave numbers. The cation solvent vibration has been characterized in the far infrared region in solvents like pyridine, DMSO and pyridilone [8-10]. In the far region, weak bonds have been observed in the  $400\text{-}500\text{ cm}^{-1}$  range which were absent in the spectrum of pure propanoic acid which could be due to the cation-solvent vibrations.

A plot of concentration Vs.  $\text{cm}^{-1}$  is shown in Fig.2, the larger decrease in  $\text{C=O}$  stretching in both LiCl and LiBr solutions can only be attributed to

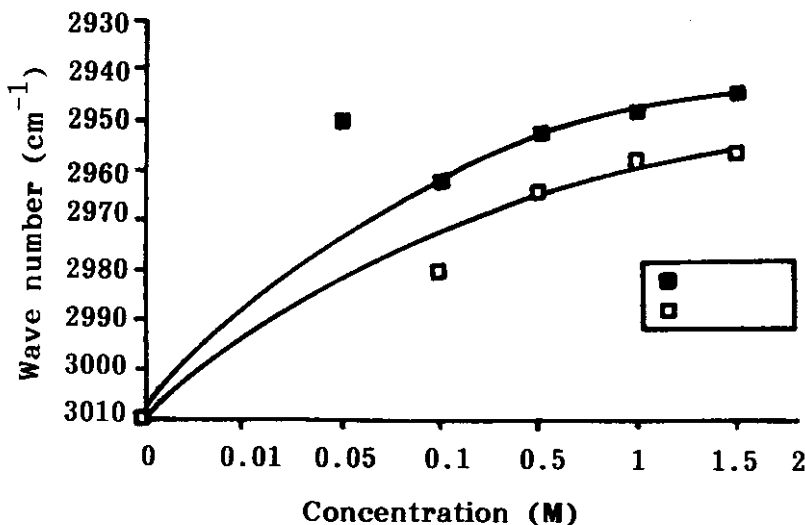


Fig. 1: Plot of  $\nu(\text{OH})$  Vs. Concentration for LiCl and LiBr solutions in propanoic acid.

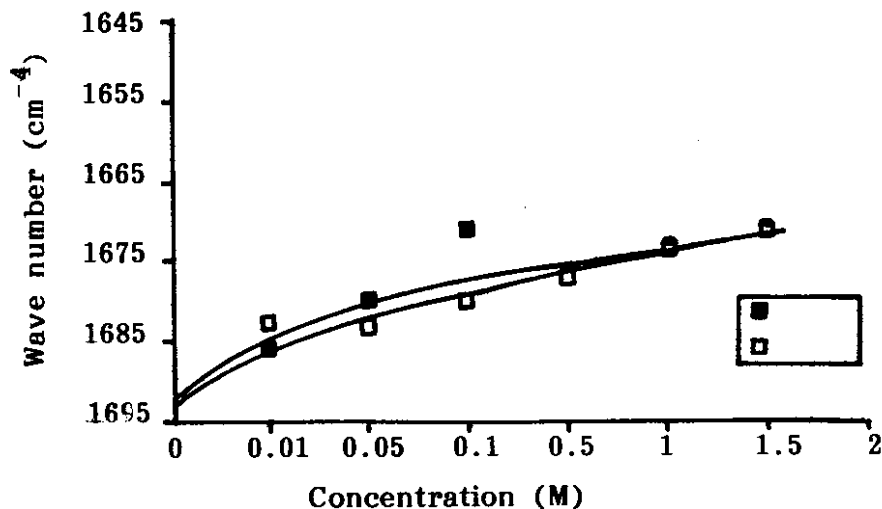
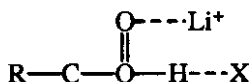


Fig. 2: Plot of  $\nu(\text{C-O})$  Vs. Concentration LiCl and LiBr solution in propanoic acid.

the cation since in both cases the curve pattern is almost the same. Alongwith a double bond  $\text{C}=\text{O}$  stretching there is also a  $\text{C}-\text{O}$  vibration in propanoic acid  $-\text{COOH}$ , it is logical to conclude that the change in  $\nu\text{C}-\text{O}$  cannot be due to direct interaction of ions with it. Vibrational frequency data is given in Table-3. There is a general trend towards decreased  $\nu\text{C}-\text{O}$  frequency, this can be attributed to the interaction of  $\text{Li}^+$  ion with doubly bonded oxygen and X with the hydrogen of  $\text{COOH}$  group as shown,



The weakening of  $\text{C}=\text{O}$  and  $\text{OH}$  bond also induce this process in the  $\text{C}-\text{O}$  bond, decreasing the  $\nu\text{C}-\text{O}$  absorption.

Table-3:  $\nu(\text{C}-\text{O})$  of LiCl/LiBr solution in propanoic acid

Conc. of LiCl/LiBr (M)	$\nu(\text{C}-\text{O})$ $\text{cm}^{-1}$ in LiCl solution	$\nu(\text{C}-\text{O})$ $\text{cm}^{-1}$ in LiBr solution
0.00	1221	1221
0.01	1218	1218
0.05	1212	1224
0.1	1215	1230
0.5	1206	1224
1.0	1206	1203
1.5	1203	1206
2.0	1200	1197

### c) Deformation of $\delta\text{O}-\text{H}$ group

Bending of  $\text{OH}$  group may be in plane occurring at  $1404 \text{ cm}^{-1}$  or out of plane at  $920 \text{ cm}^{-1}$ . Effect of ions on these bending modes is very complicated. We have to take into account the  $\text{H}\cdots\text{X}$  interaction as well as the presence of  $\text{Li}^+$  ions which also hinder the bending mode. The I.R. spectral data is provided in Table-4. The  $\text{X}^-$  interacts strongly with the hydrogen atom and decreases its extent of bending. The hindrance faced by the bending mode is also increased due to presence of  $\text{Li}^+$  ions in surroundings. The net effect is that bending mode vibrate to a smaller extent and absorption frequency is reduced.

Table-4:  $\delta(\text{O}-\text{H})$  of LiCl/LiBr solution in propanoic acid

Conc. of LiCl/LiBr (M)	$\delta(\text{O}-\text{H})$ $\text{cm}^{-1}$ in LiCl solution	$\delta(\text{O}-\text{H})$ $\text{cm}^{-1}$ in LiBr solution
0.00	1401	1404
0.01	1386	1386
0.05	1380	1398
0.1	1401	1404
0.5	1392	1401
1.0	1401	1407
1.5	1405	1407
2.0	1380	1383

### Experimental

Lithium chloride and lithium bromide were supplied by E. Merck with a 99% purity, Salts were oven dried at  $110^\circ\text{C}$  for 2 hours before use.

Propanoic acid was supplied by BDH (GLC grade 99.5% purity).

The purity of the acid was checked by taking I.R. spectrum and refractive index (1.404) and compared with the values given in the literature [7].

A 3.0 M stock solution of the halides were prepared in the acid. 0.01-2.0 M concentrations were prepared by dilution using the same solvent. All the solutions were stored in well capped bottles and scanned immediately.

Hitachi infrared spectrophotometer 270-50 was used with KBr cell of 0.1 mm thickness, at room temperature for recording I.R. spectra, KBr cells were cleaned with  $\text{CCl}_4$  before sample placement. Blank correction was also done with KBr cell.

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