Infrared Spectral Studies of Propanoic Acid in Various Solvents

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Summary: Effects of various solvents on the infrared spectra of propanoic acid were studied. Fundamental vibrations v (O-H), δ (O-H) and v (C-O) were investigated with respect to solvent change. The v (C=O) vibration was also studied in a binary mixture of carbon tetrachloride and acetonitrile. Results were interpreted in terms of solute-solvent interactions.

Introduction

The vibrational spectrum of a molecule depends not only on the strength of the bond but is also markedly affected by the environment. These changes generally arise from a change in the polarity, which can have a pronounced effect upon the spectrum characteristics like intensity, position of peak and its shape, and can be easily related to various types of solute-solvent interactions. Many such examples are well documented in the literature [1-7]. In continuation of our earlier work on solute-solvent interactions [8], the present study is aimed to investigate the interactions of propanoic acid in various solvents. The study is done by IR technique with a focus on functional groups.

Carboxylic acids exist normally in dimeric form with strong hydrogen bonding between the carbonyl and hydroxyl group of the two molecules. This association even persists to some extent in the vapour state and in dilute solutions of these acids in various solvents. A number of aliphatic acids have been studied as vapours at various temperatures, and as solutions in carbon tetrachloride and other solvents. Intensity observations relating to the monomeric and dimeric forms of these acids by various workers have been reported in the literature [9].

Results and Discussion

The dimeric OH peak in organic acids is observed between 3000 and 2500 cm⁻¹ [9], which in the present work appears at 3016 cm⁻¹ in neat propanoic acid. The environmental effect shifts this peak appreciably in various solvents. In the present case, solvents of various natures were picked up to study this change. Table 1 summarizes the effect of various solvents on propanoic acid in terms of its dimeric OH peak position. It can be seen from this

table that the shift occurs to lower wavenumbers in all cases, and is maximum in the case of dimethyl sulphoxide (Δv=594 cm⁻¹). This indicates a very strong type of interaction between DMSO and the solute under investigation. This interaction is highly likely because of the strong polar nature of DMSO and the polar sites in organic acid. The strong interaction between the two requires extra energy for the bond to vibrate, which in turn causes the frequency shift.
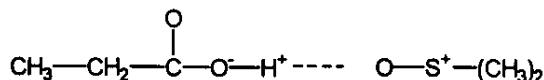
$$CH_3\!-\!CH_2\!-\!\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\!-\!O^-\!-\!H^+ \text{----} \quad O\!-\!S^+\!-\!(CH_3)_2$$

Table 1: Observed frequencies in (cm⁻¹) of propanoic acid in various solvents

Solvents	v(O-H)	v(C=O)	δ(O-H)
Propanoic acid (neat)	3016	1712	936
Carbon tetrachloride	2848	1682	903
Chloroform	2818	1677	891
Dichloroethane	2632	1677	843
Dichloromethane	2632	1677	891
Dimethylsulphoxide	2422	1692	—
Acetonitrile	2854	1692	951

On the other hand, a minimum frequency change of 162 cm⁻¹ is observed when the organic acid is present in acetonitrile. Acetonitrile is an aprotic solvent and does not act as a hydrogen bond donor and therefore minimum interaction with the organic acid. Other solvents showed intermediate frequency changes.

Investigations on frequency changes of v(C=O) were also carried out in the same solvents. These changes are also listed in Table 1. In neat propanoic acid, v(C=O) appears at 1712 cm⁻¹ in the liquid state. This peak is shifted to lower wavenumbers in the presence of different solvents.

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The shift is minimum in the case of acetonitrile and DMSO (Δv in both these cases is 20 cm^{-1}). Maximum change is observed in the case of chloroform, dichloroethane and dichloromethane (Δv in these solvents is 35 cm^{-1}). Since both acetonitrile and DMSO have high dipole moments, the shift is maximum in both these solvents.
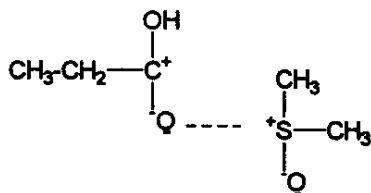
The electron donating tendency of CH$_3$ and CH$_2$ groups in propanoic acid causes the electron density to increase at C=O group, which in turn becomes less polar in nature thereby causing lesser interactions with the polar solvent. Thus the overall effect of shift becomes smaller. A similar explanation for C=O interaction in ketones with different solvents is given elsewhere [10].

The OH deformation frequency in propanoic acid appears at 936 cm^{-1} and is also affected in the presence of solvents. The frequency change observed in this case is also included in Table 1. The absorption band shows a maximum shift of 93 cm^{-1} in chloroform. A very likely cause of this is due to the strong hydrogen bonding between the solute and the solvent.

On the basis of above IR spectral changes observed in various solvents, it was decided to study these effects in a mixture of solvents. The two solvents chosen to form the mixture was the one, which caused a maximum frequency shift, whereas the other chosen showed a minimum frequency shift. The solvents were acetonitrile and chloroform. Both these solvents can be mixed in any proportion without any formation of separate phases. Mixtures of acetonitrile and chloroform in varying mole fractions of 0-1 were prepared. Propanoic acid in an amount of 5% v/v was added to each of these mixtures. The mixtures were then subjected to IR analysis. The study was mainly focused on v(C=O) stretching frequency. The results of such investigations are reported in Table 2. The data seems to show a slightly rising pattern in terms frequency value, in the early stages where the acetronitrile

concentration is low in the mixture. As the concentration of acetonitrile increases beyond a certain value (0.28 mole fraction value of acetonitrile in this case), the frequency change becomes constant in all the remaining mixtures. This probably can be reasoned on the basis that in mixtures where a change is being seen and is not yet constant, propanoic acid is still interacting with the acetonitrile. In such mixtures, the concentration of acetonitrile is low. However, beyond a certain concentration of acetonitrile, this interaction has achieved a maximum value, and there is no more propanoic acid left in solution to interact with any excess amounts of acetonitrile. Thus at that point the change in terms of v(C=O) flattens out. In this particular case the phenomenon tends to happen at when 0.28 mole fraction of acetonitrile is present in acetonitrile and chloroform mixture.

Table-2: Observed frequency (in cm^{-1}) of propanoic acid (5%) in acetonitrile + chloroform mixture

Mole fraction of acetonitrile in mixture	v(C=O)
0.0	1677
0.15	1681
0.28	1683
0.51	1683
0.70	1683
0.78	1683
0.86	1683
0.93	1683
1.0	1683

Experimental

All chemicals used in the present work were obtained from E.Merck and were of analytical grade with a certified purity of >99.9%. Solution of propanoic acid (5%) was prepared volumetrically. The IR spectra were recorded on a Hitachi IR spectrophotometer (model 270-50). The cells used were of NaCl and pure solvent was used as a reference in all measurements. For mixture analysis, acetonitrile and chloroform were mixed in varying mole fractions ranging from 0-1. All such mixtures also contained 5% (v/v) of propanoic acid. The mixtures were then subjected to IR investigations with a suitable blank as a reference.

Conclusions

Infrared spectra of propanoic acid in various solvents show different behaviour. The predominantly occurring bands of v(O-H), v(C=O) and δ(O-H) in propanoic acid are influenced by the solvent properties. The v(O-H) is shifted to lower

wave numbers in highly polar solvents. On the other hand, $v(C=O)$ is shifted by a least value m highly polar solvents. This is because of the greater affinity of O-H with a polar solvent, whereas, this interaction is less in terms of C=O interaction with the polar solvent.

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