

# Effects of Various Solvents on the Infrared Spectra of Benzyl Alcohol

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**Summary:** Effects of various solvents on the infrared spectra of benzyl alcohol were studied. Fundamental vibrations  $\nu_{\text{O-H}}$ ,  $\delta_{\text{O-H}}$  and  $\nu_{\text{C-O}}$  were investigated with respect to solvent change. The  $\nu_{\text{O-H}}$  mode was also investigated in a binary mixture of carbon tetrachloride and acetonitrile. Results were interpreted in terms of solvent-solute interactions.

## Introduction

The application of IR spectroscopy is a simple and convenient method for understanding the phenomenon of hydrogen bonding. The O-H bond length is increased due to intermolecular bonding [1] as a result of which the absorption band of the original molecule is shifted to a lower frequency [2]. The magnitude of the shift of O-H fundamentals could be used as a measure of the strength of the hydrogen bond.

Change in polarity of the solvent may have a profound effect on the spectrum of a molecule [3]. The shift in position, intensity and shape of absorption bands of a solute due to the effect of solvents can be correlated to the intermolecular solute-solvent interactions [4-7]. The aim of the

present study was to investigate the effects of solvents such as carbon tetrachloride, chloroform, 1,2-dichloromethane, 1,2-dichloroethane, acetonitrile and dimethyl sulphoxide on the IR spectra of benzyl alcohol.

## Results and Discussion

The important group frequency of benzyl alcohol is associated with the O-H stretching vibration, which falls in the range of 3500-3000  $\text{cm}^{-1}$  [8]. In addition to this, the  $\nu_{\text{C-O}}$  stretching vibration in alcohols is also of importance and lies between 1080-1010  $\text{cm}^{-1}$ . The  $\delta_{\text{O-H}}$  for alcohol is also characteristic and lies between 1350-1250  $\text{cm}^{-1}$ . For pure benzyl alcohol,  $\nu_{\text{O-H}}$  occurs at 3262  $\text{cm}^{-1}$  in the

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liquid state. On addition to a given solvent, this peak position is shifted and Table-1 shows the shift in frequencies in various solvents. In the case of non-polar solvents like  $\text{CCl}_4$ , the shift is quite pronounced. This may be explained on the basis that when a polar solute is present in a non-polar solvent, a temporary induced polarization occurs which causes the non polar molecule to assume a polar character. This causes the resultant interaction between the solvent and the solute and thus results in the shift of the spectra. The effect of solvent on  $\nu_{\text{C-O}}$  is also remarkable and the effect is listed in Table-1. The  $\nu_{\text{C-O}}$  in pure benzyl alcohol occurs at  $1194 \text{ cm}^{-1}$  and is shifted by a maximum value in dichloromethane since benzyl alcohol is a hydrogen bonded solvent, the shift towards lower wavenumber suggests that the intermolecular bonding in benzyl alcohol is increasing.

Table-1: Frequency shift in  $\text{cm}^{-1}$  of  $\nu_{\text{O-H}}$ ,  $\nu_{\text{C-O}}$  and  $\delta_{\text{O-H}}$  of benzyl alcohol in various solvents.

Type of vibrations	Solvents					
	$\text{CCl}_4$	$\text{CHCl}_3$	$\text{CH}_2\text{Cl}_2$	$\text{C}_2\text{H}_4$	DMSO	$\text{CH}_3\text{CN}$
$\nu_{\text{O-H}}$	3220	3316	3274	--	3190	3370
$\nu_{\text{C-O}}$	1185	--	1179	--	1188	1185
$\delta_{\text{O-H}}$	1320	1374	1365	1338	1356	--

Concentration of benzyl alcohol was 5% v/v in each solvent.

Table-2: Frequency shift of  $\nu_{\text{O-H}}$  absorption band of benzyl alcohol in carbon-tetrachloride-acetonitrile mixture.

Mole fraction of $\text{CCl}_4$ in $\text{CCl}_4$ -acetonitrile mixture	$\nu_{\text{O-H}} \text{ cm}^{-1}$
0.0	3370
0.057	3340
0.119	3310
0.189	3300
0.267	3300
0.353	3274
0.449	3258
0.586	3250
0.691	3240
0.830	3240
1.0	3240

Concentration of benzyl alcohol in each solvent mixture was kept at 5% v/v.

The shift due to  $\delta_{\text{O-H}}$  is also listed in Table-1. The effect on this band is also associated due to hydrogen bonding effects. For pure benzyl alcohol,  $\delta_{\text{O-H}}$  occurs at  $1368 \text{ cm}^{-1}$  and is shifted by a

maximum value towards lower wavenumber in the case of  $\text{CCl}_4$ . The explanation is the same as suggested earlier in the case of  $\nu_{\text{O-H}}$ . Figure 1 represents the frequency shifts of  $\nu_{\text{O-H}}$ ,  $\delta_{\text{C-O}}$  and  $\nu_{\text{C-O}}$  of benzyl alcohol in various solvents.

On the basis of IR spectral studies of benzyl alcohol in various solvents, it is observed that the two solvents in which the peak shift for a given group had the maximum difference are  $\text{CCl}_4$  and acetonitrile. Thus various compositions of these two solvents were prepared in varying mole fraction with a fixed concentration of benzyl alcohol in order to see the trend in peak position. For this purpose,  $\nu_{\text{O-H}}$  was selected and the IR data is shown in Table-1 and shown diagrammatically in Fig. 2. With increasing concentration of acetonitrile in carbon tetrachloride+acetonitrile mixture, the  $\nu_{\text{O-H}}$  starts shifting which is indicative of the fact that the benzyl alcohol is preferentially interacting with acetonitrile. This increase is more gradual in the earlier stages of acetonitrile addition and becomes more pronounced at higher concentration of acetonitrile. At lower concentration of acetonitrile; benzyl alcohol molecular competes for interaction with both partners of the mixture but probably showing more affinity with acetonitrile because of its polar nature. When the concentration of acetonitrile is increased beyond 0.8-mole fraction value, this interaction becomes predominant and is reflected as an increased value in the data.

### Experimental

All chemicals used in the present work were supplied by Merck and were of analytical grade, with the exception of  $\text{CCl}_4$ ,  $\text{CHCl}_3$  and DMSO, which were further, purified by distillation. The purified solvents were stored in airtight bottles and kept in the dark. The purity of all the compounds used in these studies was checked by taking their IR spectra and their refractive indices, which were compared with the literature values [9].

The solutions of benzyl alcohol (5% v/v) in different solvents were prepared. The IR spectra were recorded using a Hitachi IR spectrophotometer (model 270-50). The cells used were of NaCl and pure solvent was used as a reference for each solution.

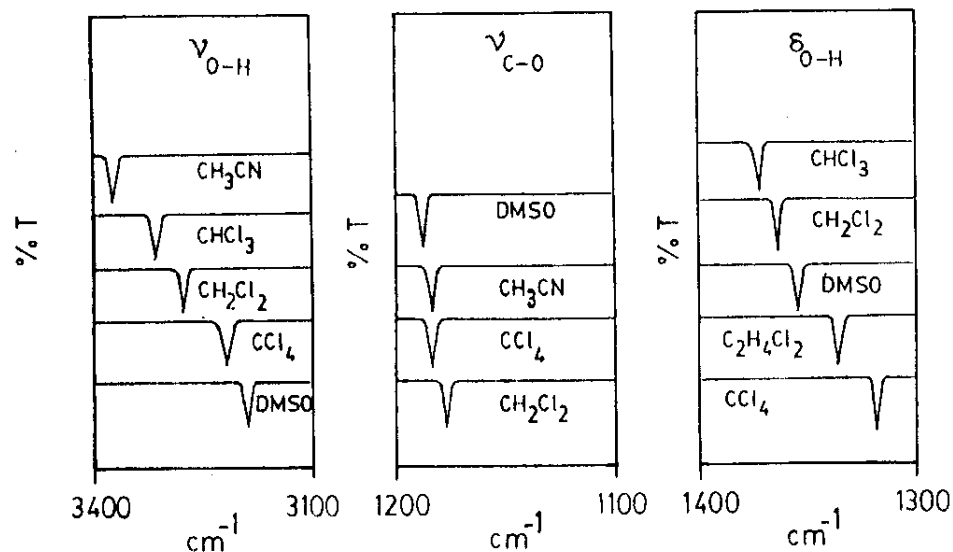


Fig. 1: Peak positions of  $\nu_{O-H}$ ,  $\nu_{C-O}$  and  $\delta_{O-H}$  of benzyl alcohol in various solvents.

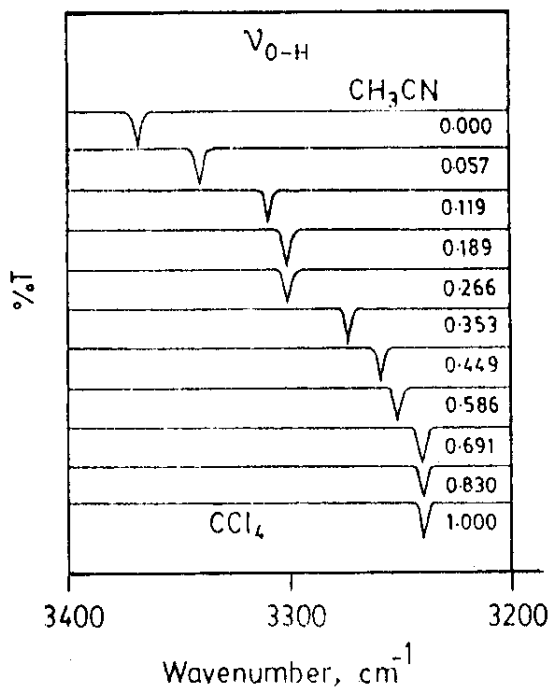


Fig. 2: Peak position of  $\nu_{O-H}$  absorption band of benzyl alcohol in varying mole fractions of carbon tetrachloride in carbon tetrachloride + acetonitrile mixtures.

Benzyl alcohol solution in CCl<sub>4</sub> and acetonitrile showed a maximum peak shift from that

of the pure benzyl alcohol. It was therefore decided to prepare mixed (binary) solvents comprising of carbon tetrachloride and acetonitrile in various mole fractions (from 0-1) for benzyl alcohol. The mixtures were prepared in such a way that the compound concentration was kept at 5% v/v in all the solvent mixtures.

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