

## IR study of ethyl lactate in $3\mu$ region

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### Abstract

Spectra of ethyl lactate were recorded in  $3\mu$  region using different solvents of varying dielectric constants and ionization energies. Band assignments were made on the basis of the behaviour of the bands in different solvents. The relative stabilities of the two types of chelation in ethyl lactate were determined making use of solvent influence on the bands. By calculating formation constants the strength of chelation in ethyl lactate as well as the relative proton accepting abilities of the solvents were assessed.

**Key words:**  $3\mu$  region, band assignments, proton acceptor solvents, binary solvent mixtures, formation constants, strength of chelation, relative stabilities of two types of chelation.

### 1. Introduction

Chelation in ethyl lactate has been reported by a number of workers<sup>1-6</sup>. Tsuzuki *et al*<sup>1</sup> reported three bands for ethyl lactate at  $3450\text{ cm}^{-1}$ ,  $3543\text{ cm}^{-1}$  and  $3613\text{ cm}^{-1}$ . The first and the third bands were found to be weak and the second one to be strong. The first band was assigned by them to the overtone of  $\text{C}=\text{O}$  stretching vibration, the second and the third to the OH group intramolecularly bonded to the carbonyl and ether oxygen atoms respectively.

Flett<sup>3</sup> also observed three bands for ethyl lactate, but the frequencies of the bands reported are slightly different from those reported by earlier workers.

In the papers published subsequently no mention, however, was made of the weak band at  $3450\text{ cm}^{-1}$  which was reported as overtone of the carbonyl stretching frequency.

Mori *et al*<sup>4</sup> felt that the exact assignment of the  $3613\text{ cm}^{-1}$  band was uncertain as it could either be due to the OH intramolecularly bonded to ether oxygen (as its frequency was close to that of OH found in diols where intramolecular hydrogen bonds of the same type exist) or to free OH although it was a little lower in frequency than the free OH of ethanol. The lowering of frequency in ethyl lactate may be due to the presence of electron withdrawing carboxylate group in the  $\alpha$  position. But Bolard<sup>5</sup> assigned this band to the free OH. The band at  $3550\text{ cm}^{-1}$  was assigned to OH intramolecularly bonded to the carbonyl oxygen by all the authors. Thus, there is a controversy regarding the number of bands in this compound in the  $3\mu$  region and their assignment. It should, however, be mentioned here that spectra of ethyl lactate were not recorded in any other solvent except in carbon tetrachloride and the influence of solvents on the shapes and intensities of bands in  $3\mu$  region were not reported earlier. Hence it is proposed in this paper to make a close and detailed study of ethyl lactate in

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the  $3\mu$  region in solvents of varying dielectric constants and proton accepting abilities so as to get an idea of the relative stabilities of the two types of chelates in these solvents.

## 2. Experimental

**Materials:** Ethyl lactate, carbon tetrachloride, acetone, dichloromethane, anisole, acetophenone, acetonitrile, chloroform, diethyl ether and dioxane used were all purified using standard procedures<sup>7</sup>. A saturated solution of benzophenone in  $\text{CCl}_4$  is used as a solvent.

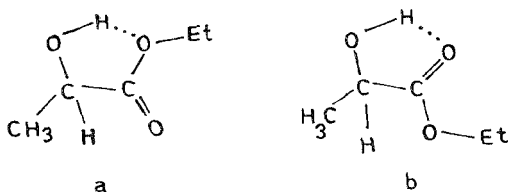
## 3. Instrumentation

The infrared spectra were recorded on Perkin-Elmer 337 grating spectrophotometer (wave number linear) at a temperature of  $28 \pm 2^\circ\text{C}$  at slow speed. NaCl matched cells of path lengths 0.1 and 1 mm were used to record the spectra. For obtaining the formation constant data the spectra were recorded using quartz cells of path length 0.5 cm. The method adopted by Barrow<sup>8</sup> was used for calculation of formation constants.

## 4. Results and discussion

The IR spectra of ethyl lactate in different solvents are presented in fig. 1 and the frequencies of OH and  $\text{C}=\text{O}$  bands and other data in Tables I and II.

A dilute solution of ethyl lactate in carbon tetrachloride exhibited three bands at 3610, 3550 and  $3450\text{ cm}^{-1}$ . The medium intensity band at  $3610\text{ cm}^{-1}$  is similar to the chelated OH band found in methoxyethanol. Hence, it is assigned to the OH intramolecularly bonded to the ether oxygen atom of the carboxylate group. The strong band at  $3550\text{ cm}^{-1}$  is similar to that of the chelated OH bond of methylmandelate and it is therefore attributed to the OH intramolecularly bonded to the oxygen of the carbonyl group (I).

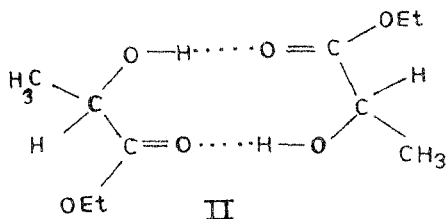


## I

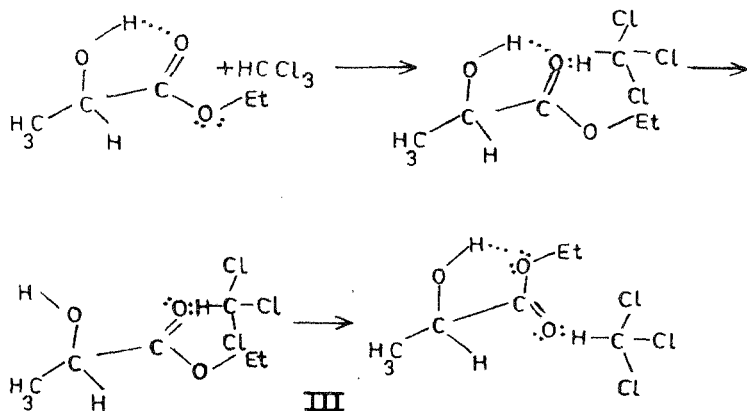
These two bands are hereafter called bands due to chelates *a* and *b* respectively. The insensitivity of the two bands to dilution shows that the bands are due to intramolecularly bonded OH groups and the band assignments are in agreement with the assignments of earlier workers.

The relative intensities of the two bands remained the same at all dilutions showing that in a non-interacting solvent the relative proportions of the two chelates (*a* and *b*) remain constant.

The band at  $3450\text{ cm}^{-1}$  cannot be assigned to the overtone of carbonyl frequency as reported by some earlier workers, since this band did not suffer any reasonable shift in  $\text{CHCl}_3$  relative to that in  $\text{CCl}_4$  which is normally expected of a  $\text{c}=\text{o}$  overtone when the  $\text{c}=\text{o}$  group is involved in hydrogen bonding. As the frequency of this band is closer to that of a dimeric OH and is insensitive to dilution it is assigned to a ring dimer involving OH and  $\text{c}=\text{o}$  (II)



In chloroform and dichloromethane the intensities of the band at  $3550\text{ cm}^{-1}$  decreased and that of the band at  $3610\text{ cm}^{-1}$  has significantly increased, indicating that in these solvents the proportion of chelate *b* decreased and that of chelate *a* increased. These observations are explicable if it is assumed that in these two solvents chelate *b* is partially broken as a result of formation of intramolecular hydrogen bond between  $\text{CHCl}_3$  and  $\text{c}=\text{o}$  group of ethyl lactate, which weakens chelation *b* and the molecules undergo re-orientation to form chelate *a* (III).



**Table I**  
 $\gamma$  OH &  $\gamma$  OO of ethyl lactate in different solvents

Sl. no.	Solvent	$\gamma$ OH (cm <sup>-1</sup> )	$\gamma$ CO (cm <sup>-1</sup> )
1.	Carbon tetrachloride	3610	1735
		3550	
		3430	
2.	Chloroform	3600	1733
		3545	
		3450	
3.	Dichloromethane	3600	1732
		3540	
		3450	
4.	Acetonitrile	3600 (sh)	1736
		3505	
5.	Benzophenone	3595 (sh)	—
		3525	
6.	Acetophenone	3500	—
7.	Acetone	3500	—
8.	Anisole	3535	1737
		3495 (sh)	
9.	Ether	3525 (sh)	1740
		3440	
10.	Dioxane	3440	1740

#### *Effect of proton acceptors*

In dioxane a broad band with absorption maximum at 3440 cm<sup>-1</sup> and small inflexions at 3550 and 3610 cm<sup>-1</sup> were observed (fig. 1.6). The former is assigned to OH bonded to the solvent and inflexions to OH of *b* and *a* respectively. When the spectra were recorded in CH<sub>2</sub>Cl<sub>2</sub> containing a small quantity of dioxane, as the proportion of dioxane increased the intensities of the latter two have further decreased, the former to a smaller extent than the latter and that of the first increased. Hence, the band 3440 cm<sup>-1</sup> is obviously due to the associated OH. These observations suggest that in the presence of dioxane chelation in *a* as well as *b* are broken, the former to a larger extent than the latter (fig. 2).

In ether also a broad band is observed at 3440 cm<sup>-1</sup> along with a very weak band at 3525 cm<sup>-1</sup>. An inflexion was found at 3610 cm<sup>-1</sup>. The band at 3440 cm<sup>-1</sup> is due to the associated species, the band at 3525 cm<sup>-1</sup> is OH of chelate *b* and the inflexion at 3610 is OH of chelate *a*.

Anisole solution exhibits a strong band at 3535 cm<sup>-1</sup> which is asymmetric on the lower frequency side and carried a shoulder at 3495 cm<sup>-1</sup>. The former corresponds to the chelate *b* and the shoulder to the associated species, the band due to chelate *a* is not observed as it is hidden under the high frequency wing of the principal band.

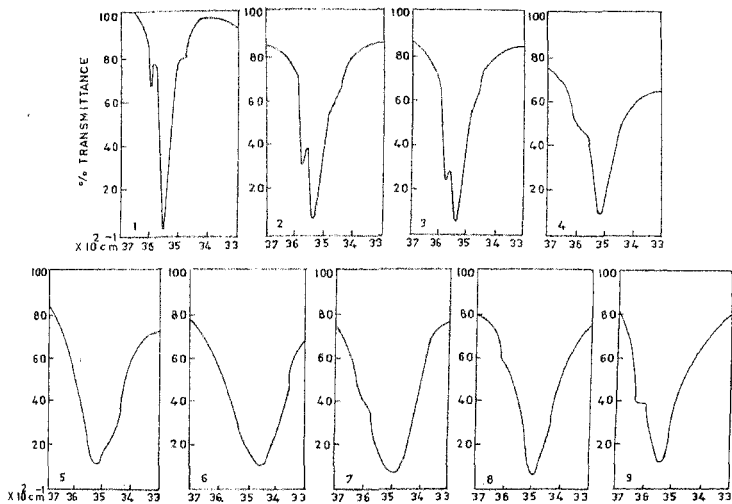


FIG. 1. OH stretching bands of Ethyl lactate in different solvents.

(1) Carbon tetrachloride, (2) Chloroform, (3) Dichloromethane, (4) Acetonitrile, (5) Anisole, (6) Dioxane, (7) Acetone, (8) Acetophenone, (9) Benzophenone.

In acetone a broad band at  $3500\text{ cm}^{-1}$  was observed with an inflexion at  $3610\text{ cm}^{-1}$ . On the basis of binary solvent mixture study, it has been shown that this new band is formed due to the overlap of OH band of chelate *b* and the band due to the associated species. Similar observations were made in acetophenone.

In acetonitrile, a broad band was found at  $3505\text{ cm}^{-1}$  with a significant shoulder at  $3610\text{ cm}^{-1}$ . Binary solvent mixture study revealed interesting and useful information. Addition of a small quantity of acetonitrile of  $\text{CH}_2\text{Cl}_2$  solution of the compound caused decrease in the intensity of the bands at  $3610\text{ cm}^{-1}$  (OH of chelate *a*) and  $3550\text{ cm}^{-1}$  (OH of chelate *b*) with simultaneous broadening of the second band on the lower frequency side. This may be due to the overlap of two bands due to chelate *b* and that due to the new band corresponding to the OH bonded to the solvent molecules. When the addition of the acetonitrile continued, the intensity of  $3610\text{ cm}^{-1}$  became still broad. In pure acetonitrile the band due to chelate *a* appeared only as a small shoulder and a broad band at  $3550\text{ cm}^{-1}$  was observed. The latter is due to the overlap of the band due to chelate *b* and the associated species.

**Table II**  
**Formation constants of complex of chelated OH of ethyl lactate with different solvents**

Sl. no.	Solvent	Eqb. const. (k)	$\Delta \nu$ OH (cm <sup>-1</sup> )
1.	Carbontetrachloride	—	—
2.	Anisole	0.09322	115a 55b
3.	Acetonitrile	0.2479	105a 45b
4.	Acetophenone	0.2687	110a 50b
5.	Acetone	0.3343	110a 50b
6.	Ether	0.5055	170a 110b
7.	Dioxane	0.5250	170a 110b

These observations indicate that both chelates *a* and *b* are broken in CH<sub>3</sub>CN and associated species are formed between solute and solvent through intermolecular hydrogen bonding.

As has been observed earlier in dioxane, the decrease in intensity of the band due to chelate *a* is much larger than that due to chelate *b* indicating that the former is ruptured to a larger extent than the latter.

The H-NMR of ethyl lactate has been examined to find out further evidence complementing the IR data. The NMR spectrum has been recorded in CDCl<sub>3</sub> on JEOD F 90 spectrometer using TMS as internal standard. In the spectrum, the ethyl group of ester showed the characteristic pattern of quartet at 3.65 ppm followed by a triplet at 1.19 ppm. The C-CH<sub>3</sub> protons appeared as doublet at 1.40 (J = 7 HZ). The methin ( $-\dot{\text{C}}\text{H}-$ ) proton and the hydroxyl proton appeared together as a broad peak at 4.70 ppm. Recording the spectrum in d<sub>6</sub> DMSO or d<sub>6</sub> acetone has not given any additional information except the solvent-induced shifts of the signals.

As the NMR data shows only one set of proton signals, it does not give any indication for the presence of different species. Hence this data could not serve the purpose of providing positive evidence for the different hydrogen-bonded species. This is perhaps due to the averaging of the signals caused by the fast equilibrium between the two species found in IR.

## 5. Conclusion

The following conclusions are made regarding the relative stabilities of the two chelates.

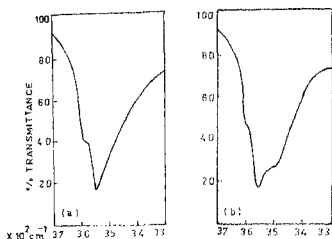


FIG. 2 OH-stretching bands of ethyl lactate.

(a) 0.7 ml ethyl lactate (0.5 M) + 0.3 ml  $\text{CH}_2\text{Cl}_2$ .

(b) 0.7 ml ethyl lactate (0.5 M) + 0.2 ml dioxane (1:4) + 0.1 ml  $\text{CH}_2\text{Cl}_2$ .

In most of the proton-acceptor solvents chelation in *a* is broken almost completely, but chelation in *b* is broken partially in acetonitrile, anisole, acetophenone and benzophenone, and to a very large extent in acetone, ether and dioxane. It may be recalled here that binary solvent mixture study (in  $\text{CH}_2\text{Cl}_2$  + dioxane and  $\text{CH}_2\text{Cl}_2$  +  $\text{CH}_3\text{CN}$ ) also indicated that chelate *a* is less stable than chelate *b*.

The extent of interaction of the solvents with chelate *b* is assessed by determining the formation constants through measurement of the intensities of the band, due to chelate *b*.

Comparison of the formation constants of the complex in different proton-acceptor solvents of equimolecular concentrations (Table II) reveals that the interacting abilities of the proton acceptors are in the order dioxane > ether > acetone > acetophenone > acetonitrile > anisole.

Similar conclusions could not be made with the band due to chelate *a* as its intensity is very little, often masked by the wider principal bands.

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