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Solvent effects on infrared spectra of 2-Methyl-4,5-dimethoxy-3-oxo-2H-pyridizine: Part 2. Binary Solvent Systems*

LIU Qing(刘清)†, SANG Wen-qiang(桑文强), Xu Xiao-min(徐小民)
(*Department of Chemistry, Zhejiang University, Hangzhou 310027, China*)
†E-mail: Lq2001@mail.hz.zj.cn

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Abstract: This research on the solvent effects of 2-methyl-4,5-dimethoxy-3-oxo-2H-pyridizine (MDOP) in binary solvent systems on the infrared spectra for MDOP in n-hexane/$CHCl_3$ mixture solvents showed that there were three forms of carbonyl stretching vibration band [$\upsilon(C=O)$] of MPOP as the mole fraction of $CHCl_3$ in the binary solvents changes. In pure n-hexane solvent, the $\upsilon(C=O)$ of MDOP appeared at a relatively high wavenumber. With $CHCl_3$ added, the $\upsilon(C=O)$ shifted to lower wavenumbers. Two new bands were observed over a certain range of mixture solvent compositions. The origin of the bands was discussed in the terms of two kinds of hydrogen bond together with their individual dependence on mixture composition. Comparisons were drawn for the solvent sensitivities of $\upsilon(C=O)$ for propanone.

Key words: Infrared spectra, 2-methyl-4,5-dimethoxy-3-oxo-2H-pyridizine, Binary solvent effects, Carbonyl stretching vibration
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INTRODUCTION

The solvent effects of 2-methyl-4, 5-dimethoxy-3-oxo-2H-pyridizine (MDOP) (Fig.1) in 12 various single solvent systems had been reported (Liu et al., 2002). It was observed recently that the wavenumbers of the carbonyl stretching vibration of MDOP are rather sensitive to the composition of the solvent mixtures. Investigations of solute-solvent interactions are best carried on employing binary solvent mixture (Engberts, 1992; 1993; Streck, 1999; Perjessy, 1995).

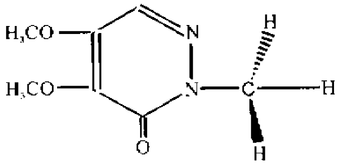

Fig.1 **The structure of 2-methyl-4,5-dimethoxy-3-oxo-2H-pyridizine**

The present study is aimed to research the solvent effects of MDOP in binary solvent systems and probe into the mechanism of the solute-solvent interactions; so that theoretical basis of solvent selection can be provided for production. Strong evidence for specific interactions was obtained from the spectra of MDOP in solvent mixtures. An interesting comparison emerges from the change trends of $\upsilon(C=O)$ for propanone in the same solvent systems.

EXPERIMENTAL DETAILS

1. Material

2-methyl-4, 5-dimethoxy-3-oxo-2H-pyridizine (MDOP) was twice crystallized. All solvents were of analytical purity and distilled prior to use. The binary mixture solvents of n-hexane/$CHCl_3$ were prepared by volume using microsyringes. The volume fractions of $CHCl_3$ in the co-solvents were 0.00, 0.05, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 0.95, and 1.00, respectively. The concentrations of MDOP in these binary solvent systems ranged from 1.0×10^{-4} to 1.5×10^{-4} mol/L.

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2. Spectroscopy

Infrared spectra were obtained by a Nicolet Nexus 670 FTIR spectrometer with a DTGS detector. The solutions were placed in 0.5 mm pathlength NaCl cells. Each sample was scanned 64 times and the spectral resolution obtained was 1 cm^{-1}. The subtraction spectra reported were obtained using corresponding mixture solvents as references.

RESULTS AND DISCUSSION

The wavenumbers of the carbonyl stretching vibrations of MDOP and propanone measured in mixtures of n-hexane/ $CHCl_3$ are listed in Table 1.

Table 1 Wavenumbers of the carbonyl stretching mode [υ(C=O)] of MDOP and propanone in n-hexane/$CHCl_3$ mixtures.

Mole fraction of $CHCl_3$ $x(CHCl_3)$	MDOP υ(C=O) cm^{-1}			Propanone υ(C=O) cm^{-1}	
	Band Ⅰ	Band Ⅱ	Band Ⅲ	Band Ⅰ	Band Ⅱ
0.00	1655.17			1722.91	
0.078	1653.89	1642.13			1719.25
0.152	1653.56	1641.84			1718.44
0.287		1641.42			1718.13
0.409		1640.73			1717.21
0.518		1639.83			1715.34
0.617		1638.61			1713.58
0.707		1637.93	1634.55		1713.05
0.79		1636.57	1634.35		1712.50
0.866		1636.51	1634.32		1711.91
0.936		1636.42	1634.22		1711.32
0.968		1636.34	1633.95		1710.80
1.00		1636.28	1633.80		1710.68

In pure n-hexane, MDOP exhibits one well-resolved carbonyl stretching vibration band (Band Ⅰ) at about 1655 cm^{-1}(Fig. 2a). Because n-hexane is an inert solvent, the interaction between MDOP and n-hexane is negligible. So Band Ⅰ belongs to the free monomeric carbonyl group of MDOP.

When $CHCl_3$ is added to the solution of MDOP in n-hexane, Band Ⅰ shifts gradually to lower wavenumbers; and a new band (Band Ⅱ) appears at about 1640 cm^{-1}(Fig. 2b). Band Ⅱ can be assigned to the hydrogen bond species between the carbonyl group of MDOP and $CHCl_3$. Band Ⅰ rapidly becomes less intensive with the increase of $CHCl_3$ concentration and disappears when the mole fraction of $CHCl_3$[x ($CHCl_3$)] is more than 0.152. This means that most of the carbonyl groups form hydrogen bonding with $CHCl_3$. Band Ⅱ is shifted to lower wavenumbers as the x ($CHCl_3$) continuously increases; its position is significantly dependent on the x ($CHCl_3$).

It is very interesting that another new band (Band Ⅲ) assigned to the carbonyl stretching mode emerges when the x ($CHCl_3$) is more than 0.707 (Fig. 2c). The new band (Band Ⅲ) gradually becomes more intensive as x ($CHCl_3$) increases until the solvent is pure $CHCl_3$(Fig. 2d). It is suggested that a new interaction occurs between MDOP molecules and $CHCl_3$ molecules when the concentration of $CHCl_3$ in the binary solvents is higher.

A series of infrared spectra for propanone in mixtures of n-hexane/ $CHCl_3$ were obtained (Table 1) as for comparison with MDOP. However, similar behavior was not observed from propanone. When $CHCl_3$ was added to the solution of propanone in n-hexane, the band assigned to carbonyl stretching vibration shifted gradually to lower wavenumbers until the solvent was pure $\mathrm{CHCl_3}$. Only one band was observed in the spectra. Evidently, there was one kind of hydrogen bond between propanone and $\mathrm{CHCl_3}$.

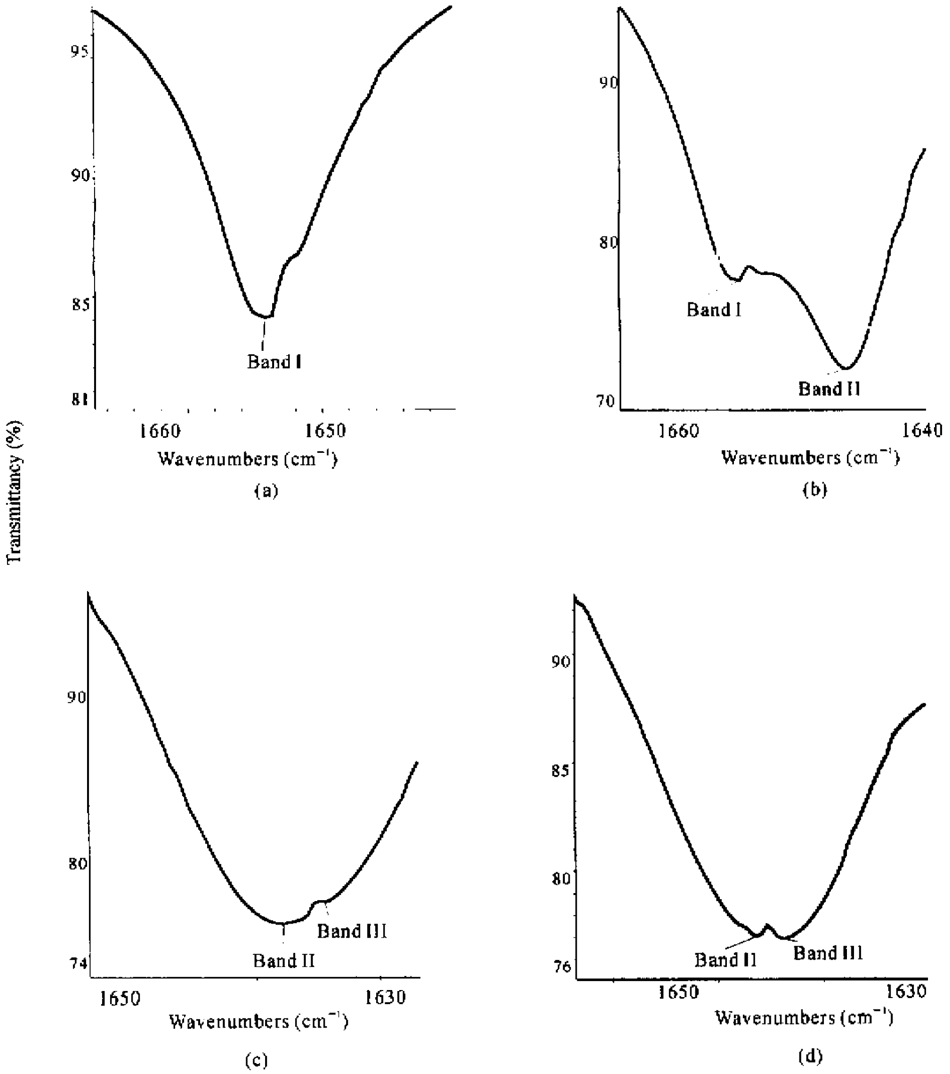

Fig. 2 Infrared spectra in the C=O stretching vibration region of MDOP dissolved in mixtures of n-hexane/$\mathrm{CHCl_3}$
(a) x ($\mathrm{CHCl_3}$)=0.00; (b) x ($\mathrm{CHCl_3}$)=0.078; (c) x ($\mathrm{CHCl_3}$)=0.707; (d) x ($\mathrm{CHCl_3}$)=1.00.

The result means that the interactions between MDOP and $\mathrm{CHCl_3}$ were more complex than those between propanone and $\mathrm{CHCl_3}$. The distinction of structure between MDOP and propanone is that the carbonyl group of MDOP is an amide group, which bears a nitrogen atom near the carbonyl group. Band Ⅲ can be assigned to the hydrogen bond species with coexisting of N···H-$\mathrm{CCl_3}$ and C=O···H-$\mathrm{CCl_3}$ (Fig. 3).

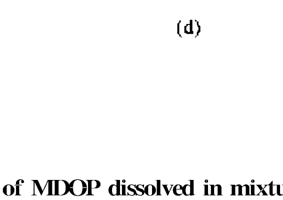

Fig. 3 The hydrogen bond structure of Band Ⅲ

The experimental data revealed that Band Ⅲ was observable only when the concentration of $CHCl_3$ was higher; and only partial nitrogen atoms of MDOP formed hydrogen bonding with $CHCl_3$ even in pure $CHCl_3$. This means that the hydrogen bond between $CHCl_3$ molecule and nitrogen atom is weak.

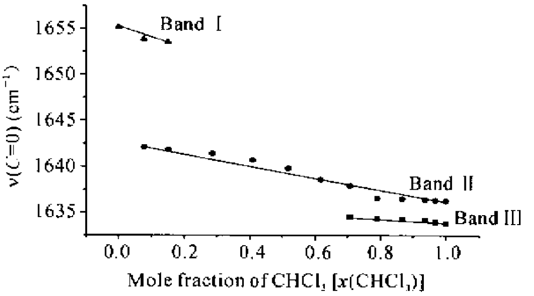

Fig. 4 **Dependence of υ（C=O）（cm^{-1}） for MDOP on the mole fraction of $CHCl_3$ in mixtures of n-hexane/$CHCl_3$.**

The dependence of the υ（C=O） for MDOP on the mole fraction of $CHCl_3$ is illustrated in Fig. 4. With x （$CHCl_3$） increases， Band Ⅰ， Band Ⅱ and Band Ⅲ shift to lower wavenumbers due to the influence of the reaction field. Linear correlation was found between υ（C=O） of each band of MDOP and x （$CHCl_3$）. The sensitivity to the influence of the reaction field for the carbonyl stretching vibration was in the following order: Band Ⅰ > Band Ⅱ > Band Ⅲ. It is most possible that the $CHCl_3$ molecules formed hydrogen bond with MDOP to hinder the interaction of van-der-Walls forces.

CONCLUSIONS

In the infrared spectra of 2-methyl-4，5-dimethoxy-3-oxo-2H-pyridizine （MDOP）， three forms of carbonyl stretching vibration band of MDOP are observable as the mole fraction of $CHCl_3$ in the n-hexane/ $CHCl_3$ binary solvents changes. In pure n-hexane， the carbonyl group of MDOP exists in free monomeric state. With $CHCl_3$ added， a hydrogen bond is formed between the carbonyl group of MDOP and $CHCl_3$. In $CHCl_3$-rich mixture solvents， a hydrogen bond species forms simultaneously between two $CHCl_3$ molecules and the amide group of MDOP. The υ（C = O） of the above three bands of MDOP decrease linearly along with x （$CHCl_3$） in n-hexane/ $CHCl_3$ mixture solvents increase.

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