Infrared study of vinyl acetate, methyl acrylate and methyl methacrylate in various solvents

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Abstract

Alkyl alcohols have two AN (solvent acceptor number) values. One AN value for the alkyl alcohol is for intermolecular hydrogen bonded species such as (C=O:OH), and the other AN value for the alcohols is for the (ROH:OHR)$_n$ species where the solute molecules are not hydrogen bonded with OH groups. The AN value for the latter species is similar to the AN values for dialkyl ethers. Steric factors of the solute and solvent are suggested to be the cause of the deviation from linearity of ν(C=O) vs. AN values of the solvents. Inductive and resonance effects are stated to be the cause of the ν(C=O) frequency differences exhibited by the three esters included in this study.

We have studied several classes of organic compounds in various solvent systems in an effort to understand solute–solvent interactions [1–30]. Vinyl acetate, methyl acrylate, and methyl methacrylate are important monomeric materials used in the manufacturing of polymers and copolymers. Therefore, we have undertaken a study of these monomers in order to further enlarge our understanding of solute–solvent interactions.

EXPERIMENTAL

Infrared (IR) spectra were recorded using a Nicolet 710 FT-IR spectrometer with 4 cm^{-1}

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resolution, which is smaller than the half-band widths of the carbonyl stretching absorption bands. IR spectra were recorded of 1% solutions placed in 0.1-mm KBr cells for each of the solvents listed in Tables 1–3.

The certified solvents were obtained from Fisher Scientific and the 99 + % monomers were obtained from Aldrich.

RESULTS AND DISCUSSION

Tables 1–3 contain IR data for vinyl acetate, methyl acrylate and methyl methacrylate in various solvents, respectively.

The carbonyl group

Figure 1 shows plots of the ν(C=O) frequency difference between the ν(C=O) frequency for each

TABLE 1

IR data for vinyl acetate in various solvents (1% solutions)

Solvent	ν(C=O) (cm^{-1})	ν(C=O:HO) (cm^{-1})	ν(C=O)(hexane) minus ν(C=O)(solvent) (cm^{-1})	ν(C=O)(hexane) minus ν(C=O:HO)(ROH) (cm^{-1})	ν(C=C) (cm^{-1})	CH=CH$_2$ twisting (cm^{-1})	CH=CH$_2$ wagging (cm^{-1})	AN
Hexane	1769.95		0.00		1648.49	950.40	869.81	
Diethyl ether	1766.16		3.79		1647.61			3.9
Methyl tert-butyl ether	1765.91		4.04		1647.56			
Carbon tetrachloride	1763.32		6.63		1646.96	950.05	872.97	8.6
Benzene	1761.32		8.63		1646.56	950.42	873.37	
1,2-Dichlorobenzene	1759.28		10.67		1646.75			
Nitrobenzene	1758.28		11.67		1646.19			14.8
Acetonitrile	1758.52		11.43		1647.28			19.3
Benzonitrile	1758.12		11.83		1646.57			15.5
Nitromethane	1756.97		12.98		1646.83			
Methylene chloride	1755.74		14.21		1646.81	949.62		20.4
Chloroform	1753.67		16.28		1646.87	947.20	878.38	23.1
tert-Butyl alcohol	1767.46	1748.05	2.49	21.90	1648.79			29.1
Isopropyl alcohol	1766.69	1747.38	3.26	22.57	1648.38		870.79	33.5
Ethyl alcohol	1765.01	1746.19	4.94	23.76	1647.98	950.72		37.1
Methyl alcohol	1763.39	1746.93	6.56	23.02	1647.86			41.3
Dimethyl sulfoxide	1754.26		15.69		1645.29			19.3

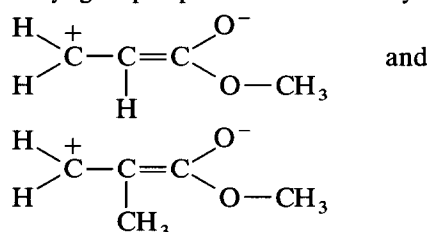compound in hexane solution and the ν(C=O) frequency for the same compound in each of the other solvents. These three 45° linear plots are parallel to each other and this is always the case when plotting data obtained in this manner [7]. An interesting feature of these plots is that the

TABLE 2

IR data for methyl acrylate in various solvents (1% solutions)

Solvent	ν(C=O) (cm^{-1})	ν(C=O:HO) (cm^{-1})	ν(C=O)(hexane) minus ν(C=O)(solvent) (cm^{-1})	ν(C=O)(hexane) minus ν(C=O:HO)(ROH) (cm^{-1})	ν(C=C) (cm^{-1})		CH=CH$_2$ twisting (cm^{-1})	CH=CH$_2$ wagging (cm^{-1})	AN
Hexane	1740.46		0.00		1636.06	1620.08	984.98	972.04	0.0
Diethylether	1736.53		3.93		1635.35	1622.39	987.25	965.26	3.9
Methyl tert-butyl ether	1736.41		4.05		1635.24				
Carbon tetrachloride	1734.12		6.34		1635.31	1620.40	984.91	968.08	8.6
Benzene	1731.26		9.20		1633.98	1617.78	988.59	970.28	
1,2-Dichlorobenzene	1728.88		11.58		1633.85		985.02		
Nitrobenzene	1727.39		13.07						14.8
Acetonitrile	1727.96		12.50						19.3
Benzonitrile	1727.03		13.43						15.5
Nitromethane	1726.52		13.94						
Methylene chloride	1725.40		15.06		1634.74	1619.99	986.34	971.40	20.4
Chloroform	1724.53		15.93		1635.05	1619.86	985.04	970.33	23.1
tert-Butyl alcohol	1736.58	1721.21	3.88	19.25	1635.83	1621.05	985.37	967.17	29.1
Isopropyl alcohol	1736.15	1718.81	4.31	21.65	1635.55	1620.84			33.5
Ethyl alcohol	1734.74	1716.83	5.72	23.63	1635.21	1619.77			37.1
Methyl alcohol	1732.73	1715.83	7.73	24.63	1634.95	1617.83			41.3
Dimethyl sulfoxide	1723.93		16.53		1634.48	1620.56			19.3
(Neat, no solvent)	1729.78				1634.85	1621.20	988.32	971.21	

ν(C=O) frequency decreases in the order vinyl acetate, methyl acrylate and methyl methacrylate in all of the solvents. The relatively higher ν(C=O) frequency for vinyl acetate compared to the ν(C=O) frequencies for methyl acrylate and methyl methacrylate is attributed to the increased inductive effect of the OCH=CH$_2$ group compared to the OCH$_3$ group, and/or the fact that the non-bonding electron pairs of the vinyloxy oxygen in CH$_2$=CH–O– are less likely to overlap with the carbonyl carbon π electron, as a result of their overlap with a C=C π electron, than are the non-bonding oxygen electron pairs in CH$_3$–O– [31]. The relatively low ν(C=O) frequencies exhibited by methyl acrylate and methyl methacrylate are attributed to the resonance of the carbon–carbon double bond with the carbonyl group represented classically as

$$\begin{array}{c} H \\ \diagdown \\ \\ H \diagup \end{array} \overset{+}{C} - C = C \begin{array}{c} O^- \\ \diagdown \\ O-CH_3 \end{array} \quad \text{and}$$
$$\qquad\qquad\; | \\ \qquad\qquad\; H$$

$$\begin{array}{c} H \\ \diagdown \\ \\ H \diagup \end{array} \overset{+}{C} - C = C \begin{array}{c} O^- \\ \diagdown \\ O-CH_3 \end{array}$$
$$\qquad\qquad\; | \\ \qquad\qquad CH_3$$

which weakens the C=O bond. The ν(C=O) frequency for methyl methacrylate is lower than the ν(C=O) frequency for methyl acrylate, and this we attribute to the negative inductive contribution of the CH$_3$ group of the methyl acrylate group which further weakens the C=O bond.

Another interesting feature of the three 45° linear plots shown in Fig. 1 is the fact that two bands are observed in the carbonyl stretching region of the spectrum for each ester in each of the four alkyl alcohols used as the solvent. In the case of these three compounds in alkyl alcohol solution the higher ν(C=O) frequency results from non-intermolecularly hydrogen bonded ester solute molecules surrounded by intermolecularly hydrogen bonded alkyl alcohol molecules. The lower-frequency carbonyl stretching band in each of the 45° linear plots is assigned as ν(C=O:HO), where the carbonyl group of the ester solute is intermolecular hydrogen bonded with the OH proton of the alkyl alcohol. In all three plots the ν(C=O:HO) frequency decreases in the order ν(C=O:H–OC(CH$_3$)$_3$) > ν(C=O:H–OCH(CH$_3$)$_2$) > ν(C=O:HOC$_2$H$_5$) > ν(C=O:H–OCH$_3$). The strongest ν(C=O:HO) bond is formed with methyl

TABLE 3

IR data for methyl methacrylate in various solvents (1% solutions)

Solvent	ν(C=O) (cm^{-1})	ν(C=O:HO)(ROH) (cm^{-1})	ν(C=O)(hexane) minus ν(C=O)(solvent) (cm^{-1})	ν(C=O)(hexane) minus ν(C=O:HO)(ROH) (cm^{-1})	ν(C=C) (cm^{-1})	=CH$_2$ wagging (cm^{-1})
Hexane	1731.49		0.00		1640.82	938.57
Diethyl ether	1728.75		2.74		1639.81	
Methyl *tert*-butyl ether	1728.54		2.95		1639.86	939.65
Carbon tetrachloride	1725.98		5.51		1638.46	940.96
Benzene	1724.32		7.17		1638.49	943.38
1,2-Dichlorobenzene	1722.40		9.09		1638.55	941.56
Nitrobenzene	1721.70		9.79			
Acetonitrile	1721.84		9.65		1637.19	948.61
Benzonitrile	1720.82		10.64		1636.92	
Nitromethane	1720.62		10.87			
Methylene chloride	1719.58		11.91		1638.27	945.43
Chloroform	1717.96		13.53		1636.58	946.48
tert-Butyl alcohol	1729.08	1714.70	2.41	16.79	1640.25	
Isopropyl alcohol	1728.45	1713.34	3.04	18.15	1639.27	
Ethyl alcohol	1727.40	1711.77	4.09	19.72	1638.79	943.53
Methyl alcohol	1725.94	1710.51	5.55	20.98	1635.71	
Dimethyl sulfoxide (Neat, no solvent)	1718.54		12.95		1635.58	

alcohol and the weakest ν(C=O:H–O) bond is formed with *tert*-butyl alcohol.

The *tert*-butyl group has a larger steric factor than a CH_3 group, and *tert*-butyl alcohol is more basic than methyl alcohol. Therefore, the strongest intermolecular hydrogen bond between C=O:HO is favored for methyl alcohol, since the CH_3 group has the least steric factor and the OH proton is the most acidic. The observed data support these theoretical factors.

The data in Table 1 and the plots in Fig. 1 show that the frequency differences between ν(C=O) (hexane) and ν(C=O:HO) (alkyl alcohols) are smaller for the methyl methacrylate than for the methyl acrylate. This difference, we suggest, results from two factors. First, the basicity of the C=O group for acrylates is less than the basicity of the C=O group for methacrylates. Second, the steric factor of the CH_3 group for methacrylates

is larger than the steric factor of the proton for acrylates, and the larger steric factor in the case of methyl methacrylate hinders the OH proton from coming as near in space to the C=O group as in the case of methyl acrylate. Thus, the ν(C=O:HO) intermolecular hydrogen bond formed in the case of methyl methacrylate is weaker than in the case of methyl acrylate.

Figure 2 shows plots of the ν(C=O) and ν(C=O:HO) frequencies for ν(C=O) of vinyl acetate, methyl acrylate and methyl methacrylate vs. the solvent acceptor number (AN). The AN values were developed by Gutmann using nuclear magnetic resonance (NMR) spectroscopy [32]. AN is reportedly a measure of the electrophilicity of the solvent. AN is defined as a dimensionless number related to the relative chemical shift of ^{31}P in $(C_2H_5)_3P$=O in that particular solvent with hexane as the reference solvent on the one hand,
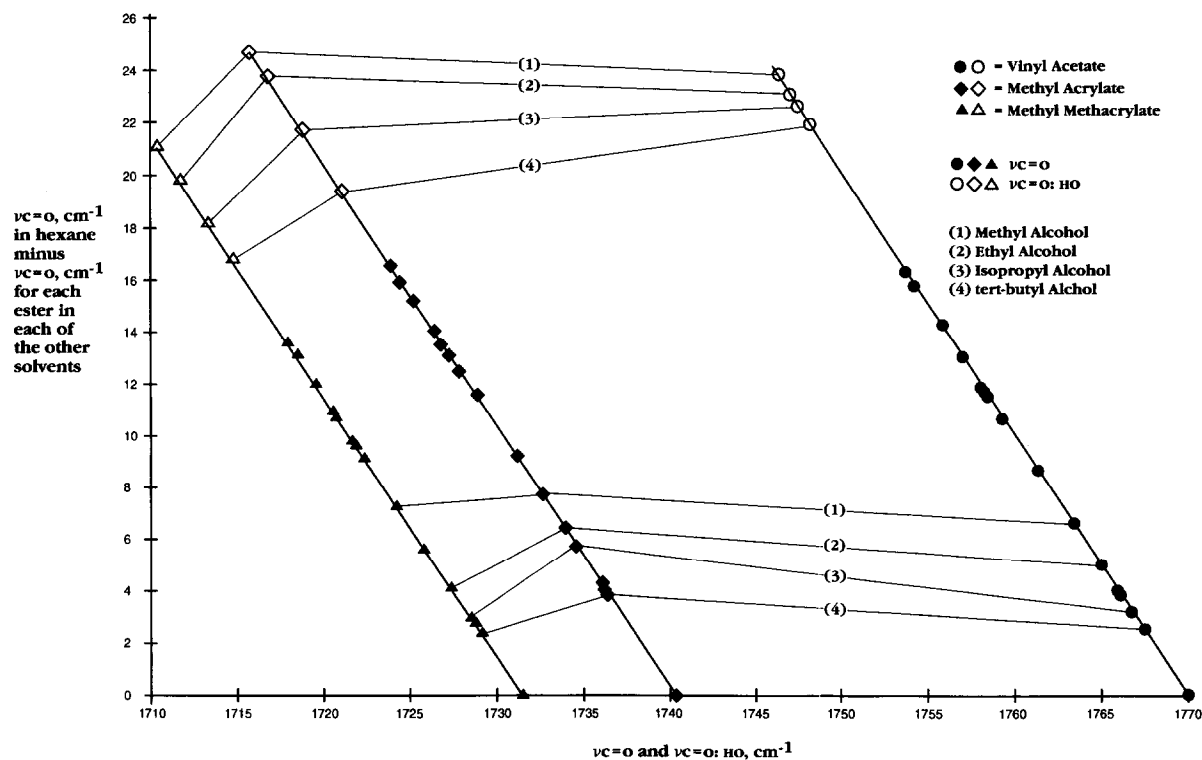

Fig. 1. Plot of ν(C=O) and ν(C=O:HO) for vinyl acetate, methyl acrylate and methyl methacrylate vs. the frequency difference between ν(C=O) in hexane solution and ν(C=O) or ν(C=O:HO) for each of the other solvents.
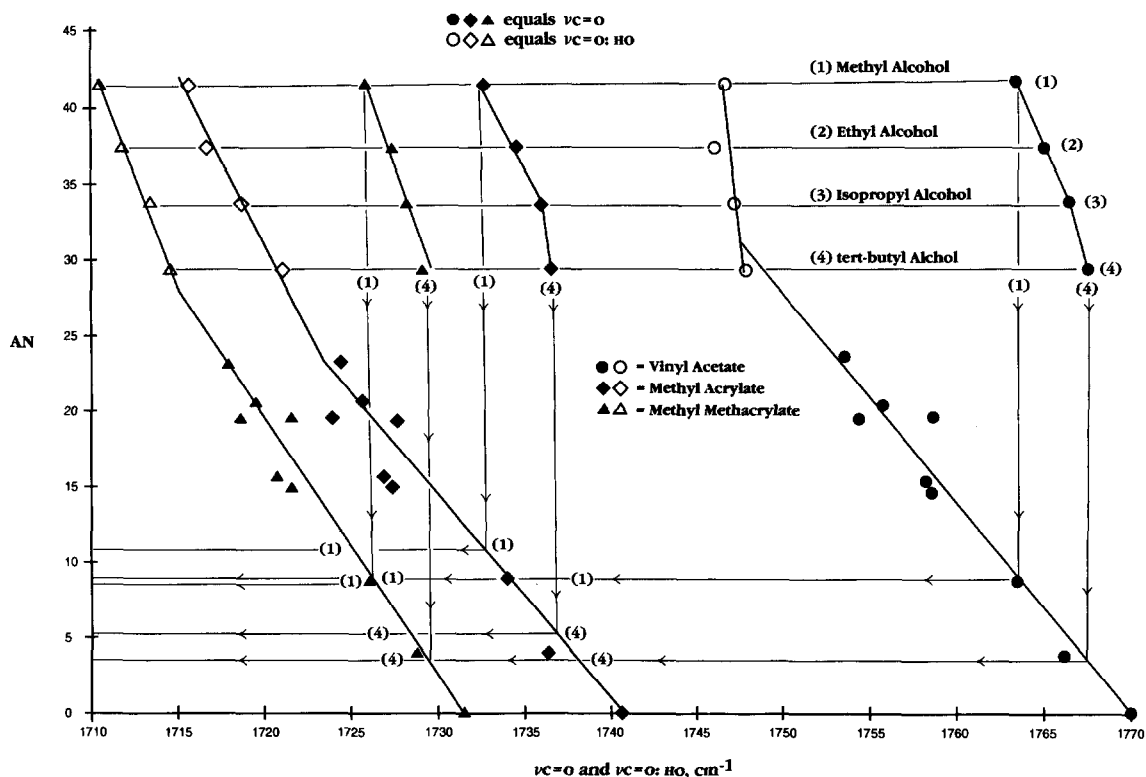
Fig. 2. Plot of ν(C=O) and ν(C=O:HO) for vinyl acetate, methyl acrylate and methyl methacrylate vs. the solvent acceptor number (AN) for each of the solvents.

and $(C_2H_5)_3P=O \cdot SbCl_5$ in 1,2-dichloroethane on the other, to which the acceptor number of 0 and 100 have been assigned, respectively

$$AN = \frac{\delta_{corr} - 100}{\delta_{corr}(C_2H_5)_3P=O \cdot SbCl_5} = corr - 2.348$$

Gutmann has stated that the acceptor number allows the interpretation of numerous solvent-dependent NMR, IR, Raman and UV spectroscopic and kinetic data.

The AN value for *tert*-butyl alcohol was estimated using IR data [6]. As stated previously the alkyl alcohol solutions exhibit both ν(C=O) and ν(C=O:HO) frequencies, but only one AN value has been given for each alkyl alcohol. The AN values for these alcohols plotted vs. the ν(C=O) and ν(C=O:HO) frequencies exhibit two separate curves. The plot of ν(C=O:HO) vs. the AN value for each alkyl alcohol correlates with the AN values for the ν(C=O) frequencies obtained

in the other solvents. In other words, the Gutmann AN values developed for the alcohols correspond to the intermolecularly hydrogen bonded P=O:HO or C=O:HO species. Projection of the ν(C=O) frequencies for the ester C=O groups not intermolecularly hydrogen bonded, but surrounded by intermolecularly hydrogen bonded alkyl alcohols, onto the three separate curves indicates that the AN values for the intermolecularly hydrogen bonded alcohols are comparable to the AN values for dialkyl ethers. The projected AN values (as shown by the arrowed lines) for the intermolecularly hydrogen bonded CH_3OH molecules surrounding each ester are not identical nor are the AN values identical for the intermolecularly hydrogen bonded $(CH_3)_3OH$ molecules surrounding each ester. However, the projected AN values for $(CH_3OH)_n$ are approximately twice that of the AN values for $[(CH_3)_3COH]_n$. We suggest that the steric factor

of the alcohol R group and the steric factor of each ester affects the AN value for $(ROH)_n$ surrounding non-hydrogen bonded ester carbonyl groups, since the AN values projected for each alcohol and ester are not identical. In other words, the AN values are not a precise measure of solute–solvent interactions, since steric factors for both the solute and solvent vary for each solute–solvent system.

The C=C group

Table 1 also contains IR data for ν(C=C) for vinyl acetate. There is a general trend that ν(C=C) decreases in frequency as ν(C=O) decreases in frequency in these various solvents, but the correlation is not linear. The ν(C=C) frequency shift is small (ca. 4 cm^{-1}) compared to the ν(C=O) frequency shift (ca. 16 cm^{-1}) with change in the solvent system.

Table 2 lists IR data for ν(C=C) for methyl acrylate in the same solvents. In this case ν(C=C) exists as a doublet, and this doublet is suggested to arise from S-trans and S-cis rotational alkyl acrylate isomers [33]. The one peak of the doublet for methyl acrylate occurs in the region

1633.85–1636.06 cm^{-1} and the other peak of the doublet occurs in the region 1617.78–1621.20 cm^{-1}.

Table 3 lists IR data for ν(C=C) for methyl methacrylate. In this case only one ν(C=C) frequency is observed, and it occurs in the region 1635.58–1640.82 cm^{-1} for the various solvent systems studied. The ν(C=C) frequency generally decreases as the ν(C=O) frequency decreases for methyl methacrylate for the solvents studied.

Table 4, column A, compares the frequency difference between ν(C=O) (hexane) and ν(C=O : HO) (ROH) for vinyl acetate, methyl acrylate and methyl methacrylate for each of the four alcohols. Table 4, column B, compares the frequency difference between ν(C=O) (ROH) and ν(C=O : HO) (ROH) for vinyl acetate, methyl acrylate and methyl methacrylate for each of the four alcohols. Table 4, column C, compares the percentage of the frequency difference between ν(C=O) (ROH) and ν(C=O : HO) (ROH) for vinyl acetate, methyl acrylate and methyl methacrylate attributed to intermolecular hydrogen bonding (C=O : HO) for each of the four alcohols.

The data in Table 4 show that the major shift

TABLE 4

Comparison of the effect of hydrogen bonding on the ν(C=O) frequencies for vinyl acetate, methyl acrylate, methyl methacrylate in alkyl alcohols

Alcohol	(A) ν(C=O) (hexane) minus ν(C=O : HO) (ROH) (cm^{-1})	(B) ν(C=O) (ROH) minus ν(C=O : HO) (ROH) (cm^{-1})	ν(C=O) shift from ν(C=O) (hexane) % due to C=O : HO (ROH) (cm^{-1})
Vinyl acetate			
tert-Butyl	21.90	19.41	88.60
Isopropyl	22.57	19.31	85.60
Ethyl	23.76	18.82	79.20
Methyl	23.02	16.46	71.50
Methyl acrylate			
tert-Butyl	19.25	15.37	79.80
Isopropyl	21.65	17.34	80.10
Ethyl	23.63	17.91	75.80
Methyl	24.63	16.90	68.60
Methyl methacrylate			
tert-Butyl	16.79	14.38	85.60
Isopropyl	18.15	15.11	83.30
Ethyl	19.72	15.63	79.30
Methyl	20.98	15.43	73.55

in the $\nu(C=O)$ frequency results from intermolecular hydrogen bonding between the C=O group and the OH group (C=O:HO). The remainder of the $\nu(C=O)$ frequency shift from $\nu(C=O)$ (hexane) is attributed to the AN contribution of the solvent. In other words, the published AN values for the alcohols are in error by approximately 68.6–88.6% because the NMR data do not distinguish between solute molecules which are intermolecularly hydrogen bonded with the R–OH proton and solute molecules which are not intermolecularly hydrogen bonded but surrounded by intermolecularly hydrogen bonded alkyl alcohol molecules, where the effect is a dipolar interaction between the solute and solvent.

What is surprising is that the percentage of the $\nu(C=O)$ shift in frequency due to intermolecular hydrogen bonding decreases in the order *tert*-butyl alcohol to methyl alcohol (the exception being for methyl acrylate in *tert*-butyl alcohol), since the strength of the intermolecular hydrogen bonding between C=O:HOR molecules increases in the order *tert*-butyl alcohol to methyl alcohol. A plausible explanation is that the steric factor for a *tert*-butyl group is larger than the steric factor for the methyl group, and a larger steric factor decreases the dipolar interaction between the alcohol oxygen atom and the carbonyl carbon atom (the dipolar interaction between carbonyl compounds lowers the C=O frequency).

Conclusions

The AN values are not a precise measure of the solute–solvent interaction. This is because steric factors of the solute and solvent are different for each solute–solvent pair. The behavior of the $\nu(C=O)$ frequencies are affected by steric, inductive and resonance factors.

The $\nu(C=O)$ frequency is affected more than the $\nu(C=C)$ frequency by changing the solvent system.

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