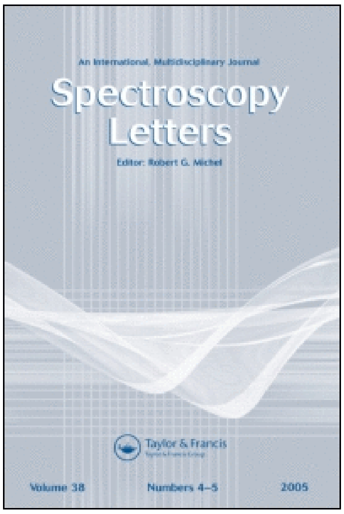

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Solvent Effects on Infrared Spectra of Methyl Methacrylate

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ABSTRACT

Infrared spectroscopy studies of methyl methacrylate (MMA) in 20 different organic solvents were undertaken to investigate the solute–solvent interactions. The frequencies of carbonyl stretching vibration $\nu_{C=O}$ of MMA were correlated with the solvent properties such as the KBM parameter, the solvent acceptor number (AN), and the linear solvation energy relationships (LSER). The solvent-induced stretching vibration frequency shifts showed a better correlation with LSER than AN while the correlation with the KBM parameter was not good.

Key Words: Solvent effects; Infrared spectroscopy; Methyl methacrylate; Hydrogen bonding.

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INTRODUCTION

Solvent effects play an important role in organic reactivity phenomena such as the chemical equilibrium, the rate of chemical reactions, the conversion of the polymerization, and so on. Many organic chemists usually try to explain the solvent effects by some physical properties of the solvents. In previous work, the research on solvent effects on infrared spectra of 5-methyl-7-methoxy-iso-flavone (MMIF) in single solvent systems has been reported.[1] In this paper, the frequency shifts of the carbonyl stretching vibration ($\nu_{C=O}$) of methyl methacrylate (MMA), in different solvents, are observed by the method of infrared spectroscopy and correlated with the KBM parameter, the solvent acceptor number (AN), and the linear solvation energy relationship (LSER). MMA has a variety of commercial applications. It is the monomer of poly(methyl methacrylate) (PMMA), a common thermoplastic that is widely used in industry and dentistry.[2] The polymerization behavior of MMA is not only influenced by the polymerization conditions such as the reaction temperature, time, and catalyst, but also by the properties of the solvent used in the reaction.[3] In order to explore the mechanism of the solute–solvent interaction, the study of MMA in 20 different organic solvents, both polar and nonpolar, was undertaken with infrared spectrometry. A number of attempts to develop a quantitatively accurate and physically meaningful explanation of solvent-induced stretching vibration frequency shifts are described.

EXPERIMENTAL

Infrared spectra were recorded on a Nicolet Nexus 670 FTIR spectrometer with a Ge/KBr beamsplitter and a DTGS detector. For all spectra, 40 scans recorded at 1 cm^{-1} resolution were averaged. Solution spectra were measured using 0.1 mm pathlength NaCl cells. The spectra of pure solvents were recorded under the same condition as the background spectra and were stored in the computer. All solvents were either of analytical or spectroscopic purity. The concentrations of the solute in the pure solvents were between 1.0×10^{-5} and $5.0 \times 10^{-5}\,\mathrm{mol/L^{-1}}$.

In order to eliminate the disturbance of water vapor from the solution spectra, interactive spectral subtraction was performed with a reference of water vapor. Nicolet Omnic software, version 5.2, was used for all data manipulation. The data files were transferred to a computer for analysis using Origin version 6.0.

RESULTS AND DISCUSSIONS

The $\nu_{\mathrm{C=O}}$ of MMA in 20 different pure solvents and the solvent parameters are presented in Table 1. The frequency of $\nu_{\mathrm{C=O}}$ appears in the range 1740–1700 cm^{-1}. The Kirkwood–Bauer–Magat relationship was the first theoretical equation of solvent-induced stretching vibrational frequency shifts and was presented in 1937[4,5]:

$$\frac{\nu_{\mathrm{gas}} - \nu_{\mathrm{sol}}}{\nu_{\mathrm{gas}}} = \frac{A(\varepsilon - 1)}{2\varepsilon + 1} = Af(\varepsilon) \qquad (1)$$

Here ν_{gas} is the vibrational frequency of a solute in the gas phase, ν_{sol} is the frequency of a solute in the solvent, ε is the dielectric constant of the solvent, and A is a constant, that is dependent on the dimensions and electrical properties of the vibrational solute dipole.

Figure 1 shows plots of $\nu_{\mathrm{C=O}}$ of MMA vs. the KBM parameter $f(\varepsilon)$. It is evident that there is almost no linear correlation between $\nu_{\mathrm{C=O}}$ and the KBM parameter. The solvent-induced frequency shifts of the solute depend on both the solvent dielectric constants and other solvent–solute interactions such as the hydrogen bonding and the steric effects. These interactions are not taken into account by the KBM parameter. Therefore, the correlation between $\nu_{\mathrm{C=O}}$ and the KBM parameter is poor.

The solvent acceptor number (AN) is one of the empirical parameters developed by Gutmann from the ^{31}P-NMR chemical shifts of triethylphosphane oxide in different solvents[6] and also, it is a measure of the electrophilicity of the solvent.

Figure 2 is a plot of the frequencies of $\nu_{\mathrm{C=O}}$ for MMA vs. AN. There is a good correlation between the two variables:

$$\begin{aligned} &\nu_{\mathrm{C=O}} = 1729.33 - 0.47\mathrm{AN} \\ &R^2 = 0.97, \quad \mathrm{SD} = 1.20\,\mathrm{cm}^{-1}, \quad N = 19 \end{aligned} \qquad (2)$$

The negative slope demonstrates that the $\nu_{\mathrm{C=O}}$ of MMA is shifted to lower frequencies as the AN of the solvent increases.[7] The frequencies of $\nu_{\mathrm{C=O}}$ for MMA in alcohols appear in the region 1716–1709 cm^{-1}. Since the alcohols are good electron acceptors, the intermolecular hydrogen bonding between the C=O of MMA and the hydroxyl of alcohols is stronger. Thus, the frequencies of $\nu_{\mathrm{C=O}}$ for MMA in alcohols are correspondingly lower than that in other solvents.

The good correlation indicates that the solvent AN is applicable not only to NMR chemical shifts, but also to the solvent-induced stretching frequency shifts in the infrared spectrum.

Table 1. The $\nu_{c=o}$ of MMA and solvent parameters.

Solvent	$\nu_{c=o}$[a] cm^{-1} Band I	Band II	AN[b]	$f(\varepsilon)$[c]	α[d]	β[d]	π^{*}[d]	δ[d]	ν_{cal} for band I[e]
N-hexane	1,731.27		0	0.186	0	0	−0.08	0	1,730.65
Cyclohexane	1,730.12		0	0.203	0	0	0	0	1,729.99
Diethyl ether	1,728.54		3.9	0.345	0	0.47	0.27	0	1,727.14
Tetrachloromethane	1,726.16		8.6	0.226	0	0	0.28	0.5	1,727.31
Tetrahydrofuran	1,725.22		8.0	0.405	0	0.55	0.58	0	1,724.48
Toulene	1,725.16		4.5	0.245	0	0.11	0.54	1.0	1,724.65
Benzene	1,724.04		8.2	0.231	0	0.1	0.59	1.0	1,724.25
1,4-Dixone	1,723.85		10.8	0.223	0	0.37	0.55	0	1,724.96
Acetonitrile	1,721.96		18.9	0.479	0.19	0.31	0.75	0	1,720.59
1,2-Dichloroethane	1,720.93		16.7	0.431	0	0	0.81	0.5	1,722.94
Dichloromethane	1,719.34		20.4	0.422	0.3	0	0.82	0.5	1,718.42
Chloroform	1,718.14		23.1	0.359	0.44	0	0.58	0.5	1,717.60
Methanol	1,710.60	1,726.12	41.5	0.478	0.93	0.62	0.60	0	1,710.49
Ethanol	1,712.00	1,727.40	37.9	0.471	0.83	0.77	0.54	0	1,712.26
n-Propanol	1,712.38	1,727.85	37.3	0.465	0.78	—	0.52	0	—
n-butanol	1,713.51	1,727.83	36.8	0.459	0.79	0.88	0.47	0	1,713.28
2-Propanol	1,713.32	1,728.59	33.6	0.46	0.76	0.95	0.48	0	1,713.55
2-Butanol	1,713.36	1,728.84	32.0	0.454	0.76	0.95	0.48	0	1,713.55
tert-Butanol	1,714.48	1,729.14	27.1	0.442	0.68	1.01	0.41	0	1,715.23
2-Methyl-2-butanol	1,715.92	1,729.27	—	0.381	—	—	—	—	—

[a] The frequencies of C═O for MMA.
[b] The solvent acceptor number.
[c] $(\varepsilon - 1)/(2\,\varepsilon + 1)$.
[d] LSER solvent parameters.
[e] Calculated by **Eq. (4).

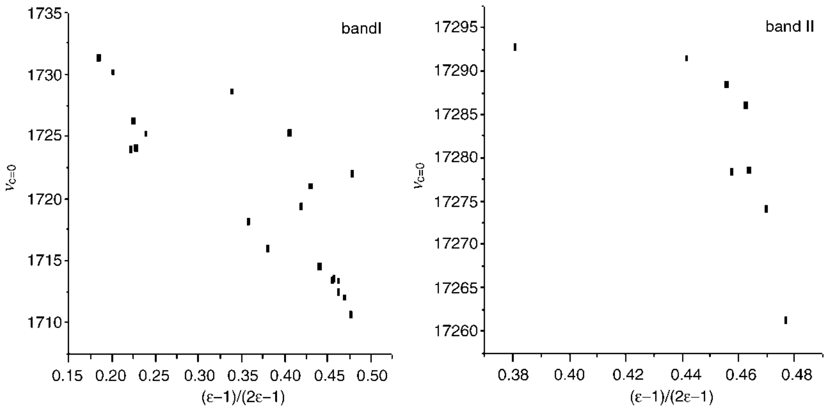

Figure 1. $\nu_{C=O}$ vs. KBM parameter $(\varepsilon - 1)/(2\varepsilon + 1)$.

The LSER proposed by Koppel and Palm is a multiparameter treatment used to describe the solvent effects.[8] The model equation of LSER is shown in Eq. (3)

$$A = A_0 + (s\pi^* + d\delta) + (a\alpha + b\beta) \tag{3}$$

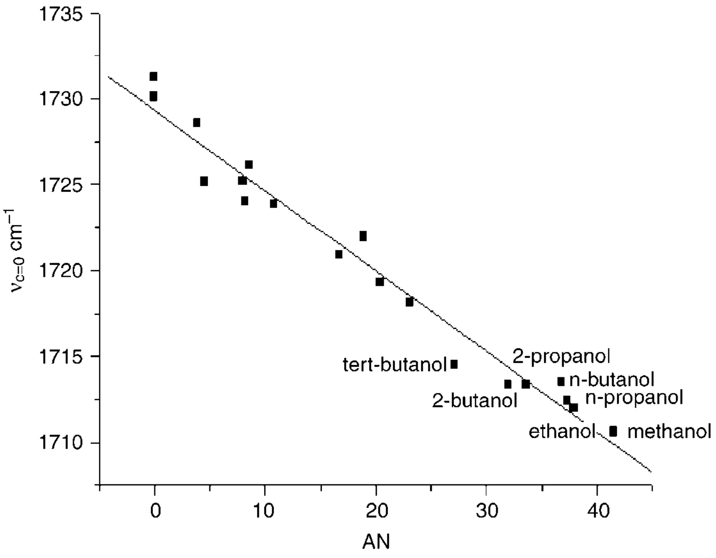

Figure 2. The frequencies of $\nu_{C=O}$ vs. AN.

A is a solute property, such as the rate constant and equilibrium constant, the position of maximal absorption in an UV/VIS, IR, NMR, or ESR spectrum, and so on. A_0 is the regression value of this solute property in cyclohexane as a reference solvent. In this paper, A is the carbonyl vibrational frequency of MMA ($\nu_{C=O}$) in the solution, A_0 is the regression value of the $\nu_{C=O}$ in cyclohexane as a reference solvent, π^* is a measurement of the solvent dipolarity/polarizability, δ stands for the rectification of poly-chlorine substituted aliphatic and aromatic solvents, α and β are measures of the solvent hydrogen-bond donor acidity (HBD) and hydrogen-bond acceptor basicity (HBA), respectively. The regression coefficients a, b, d, and s measure the relative susceptibilities of the solvent-dependent vibration frequency of the solute to the corresponding solvent parameters. The equation for band I is shown in Eq. (4):

$$\begin{aligned}\nu_{C=O(I)} = {} & (1729.99 \pm 0.88) \\ & - [(8.25 \pm 1.37)\pi^* + (0.74 \pm 0.80)\delta] \\ & - [(14.77 \pm 1.16)\alpha + (1.32 \pm 1.37)\beta] \\ R^2 = 0.97, \quad & \mathrm{SD} = 1.05\,\mathrm{cm}^{-1} \end{aligned} \tag{4}$$

There is very little deviation between the frequencies from the experiment and the frequencies calculated from Eq. (4) (Table 1). Judging from the coefficients of the equation, the solvent dipolarity/polarizability (measured by π^*) plays an important role in interactions between the aprotic solvents and the C═O of MMA since $\alpha = 0$ and $s/b = 6.25$ [s/b is the ratio of the regression coefficients of π^* and β in Eq. (4)]. While in protic solvents, the solvent acidity, measured by α, is the most sensitive factor since $a/b = 11.19$ [a/b is the ratio of the regression coefficients of α and β in Eq. (4)]. The lower value of b (1.32) indicates a rather weak influence of the solvent basicity, measured by β, on the solvent-induced frequency shifts. The LSER applied for band II is shown in Eq. (5) with a correlation coefficient of 0.99 and estimated standard deviation of 0.13 cm^{-1}:

$$\begin{aligned}\nu_{C=O(I)} = {} & (1723.72 \pm 4.02) + (10.24 \pm 4.16)\pi^* - (8.79 \pm 4.29)\alpha \\ & + (7.11 \pm 1.82)\beta \end{aligned} \tag{5}$$

It shows that the contribution of α in band II decreases compared to that in band I because the value of a/b in Eq. (5) ($a/b = 1.24$) is smaller than that in Eq. (4) ($a/b = 5.82$). This is the result of the alcohol-association, which makes it difficult for the solvent to donate hydrogen protons. On the other hand, the deviations of the LSER parameters in this equation are relatively large. Probably the influence of the alcohol-association is not considered by

Koppel and Palm when they proposed the LSER parameters. The good relationship between the frequencies of $\nu_{C=O}$ for MMA and the LSER parameters demonstrates that the multiparameter equation is applicable for describing the solute–solvent effects accurately since the specific and non-specific solute–solvent interactions are all considered in it.

Interestingly, two well-resolved C=O absorption bands are observed in alcohols (Fig. 3) instead of one peak in the above 12 non-alcoholic solvents, which means two species of carbonyl stretching vibrational bands of MMA coexist in alcohols.[9,10]

The alcohol molecules can associate to become a big molecule, because the hydroxyl group of the alcohol is a hydrogen bond acceptor, as well as a hydrogen bonding donor. So, there are two types of alcohol molecules in the alcohol solvent system. One of these is the associated alcohol molecule, and the other is the non-associated. The steric hindrance of the former is more than that of the latter. Therefore, the hydrogen bonding between the C=O of MMA and the associated alcohols is weaker than the one between C=O and the non-associated. As a result, the corresponding band induced by the associated alcohols (band II) appears at a higher wavenumber, and the band I induced by the non-associated alcohols appears at a lower

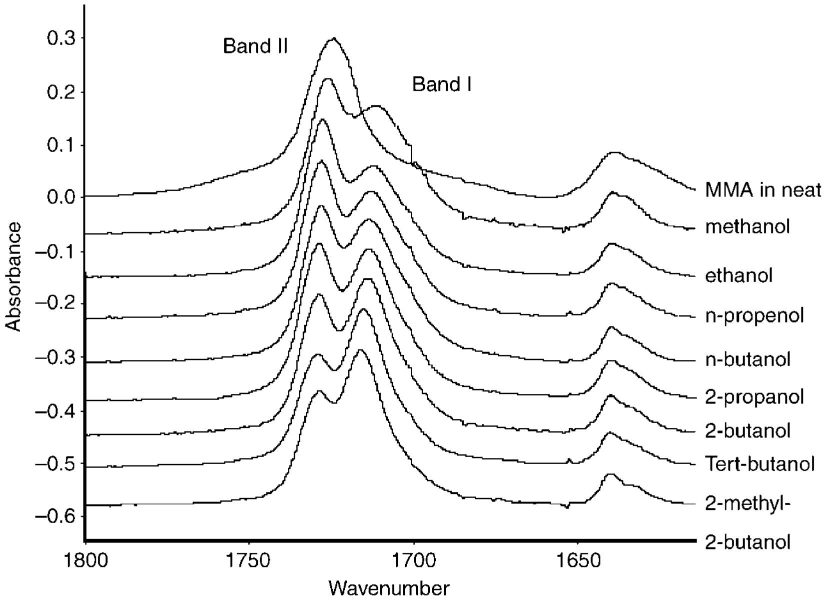

Figure 3. The bands of $\nu_{C=O}$ for MMA in alcohols.

wavenumber. In simple alcohols, such as methanol, ethanol, *n*-propanol, *n*-butanol, and 2-propanol, the associated alcohol molecule is in the majority, as band II is more intense than band I. As the structure of the alcohols becomes more complicated, such as 2-butanol, *tert*-butanol, and 2-methyl-2-butanol, the steric hindrance of the mono-alcohol molecule increases gradually and it is difficult for alcohols to associate by themselves. The majority of the solvent molecules exist in the form of non-associated, so that band II is less intense than band I.

CONCLUSIONS

The frequencies of $\nu_{C=O}$ for MMA were correlated with the solvent properties such as the KBM parameter, the solvent AN and the LSER. The results showed that the correlation between KBM and the frequencies of $\nu_{C=O}$ for MMA was not good while there was a better correlation with LSER than the correlation with acceptor number (AN). Two types of C=O stretching vibrational bands for MMA were found in alcohols. The higher wavenumber band (band II) corresponded to the hydrogen bonding between the associated alcohols and MMA. The lower one (band I) was assigned to the interaction between the non-associated alcohols and MMA.

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