Solvents effect on infrared spectra of 1,3-indanedione in organic solvents

Nalan Tekin *, Hilmi Namli, Onur Turhan
Department of Chemistry, Balıkesir University, 10100 Balıkesir, Turkey

Received 23 December 2004; received in revised form 21 March 2005; accepted 30 March 2005
Available online 26 April 2005

Abstract

Infrared spectroscopy studies of 1,3-indanedione (ID) in 16 different pure organic solvents were undertaken to investigate the solvent–solute interactions and to correlate solvent properties, such as the Kirkwood–Bauer–Magat (KBM) equation, the solvent acceptor number (AN) and the linear solvation energy relationships (LSER), using the infrared band shift. The correlations were performed both symmetric and asymmetric band stretching. Poor correlation between dielectric constants and the frequencies in both symmetric and asymmetric C–O stretching showed that the KBM relationship was unsuitable for the molecule studied in this work. These frequencies exhibited a better correlation with the LSER than the solvent AN. The asymmetric C–O stretching was found in better correlation than symmetric.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Infrared spectroscopy; 1,3-Indanedione; Solvent effects; Linear solvation energy relationships

1. Introduction

Solvent-induced vibrational frequency shifts (SFS) have attracted interest for many years, since they provide important information on chemical bonding and solute–solvent interactions. Intramolecular frequency shifts are determined by the normal coordinate dependent parts of the attractive and repulsive interactions between solute and solvent molecules [1]. A number of attempts to develop a quantitatively accurate and physically meaningful explanation of solvent-induced stretching vibration frequency shifts have been presented [2–10]. The studied compounds were mainly simple molecules [7–10].

The solvent acceptor numbers (AN) have been found to be useful in the prediction of ν(C=O) vibrational band shifts for different molecules [11–15]. The acceptor number (AN) of a solvent was developed by Gutmann [14], and is reportedly a measure of the electrophilicity of the solvent.

The linear solvation energy relationships (LSER) is a multiparameter (that is, the Kamlet–Taft solvent parameters α, β, π* and δ) treatment used to describe the solvent effects [16–18]. The model equation of LSER applied in infrared spectroscopy is shown as Eq. (1):

$$\nu = \nu_0 + (s\pi^* + d\delta) + a\alpha + b\beta$$

(1)

ν is the vibrational frequency of solute (such as ν(C=O)) in pure solvent and ν0 is the regression value of the ν(C=O) in cyclohexane as a reference solvent, π* is an index of solvent dipolarity/polarizability, δ is a discontinuous polarizability correction term for poly-chlorine substituted aliphatic and aromatic solvents, α is a measure of the solvent hydrogen-bond donor acidity and β is a measure of the solvent hydrogen-bond acceptor basicity. The regression coefficients s, d, a, and b in Eq. (1) measure the relative susceptibilities of the solvent-dependent vibration frequency of the solute to indicate solvent parameters.

Solvent effect on the C=O stretching band was already investigated to verify the influence of various solvent parameters [18–26]. Most of these studied compounds have only one carbonyl affected from solvents and they do not have the acidic hydrogens.

A few works have been done with the compounds which have two carbonyls. Bruni et al. had analyzed the solvent
effect on compounds bearing both amide and ester carbonyl groups in order to evidence vibrational differences between the isomers of [2-oxo-pyrrolidin-4yl] carboxylate [6].

In an earlier study, Perjessy and Hrnčiar [27] studied CO stretching of many 1,3-indandione derivatives in three different solvents. They observed double absorption bands in the C=O region. This doubling is attributed to mechanical coupling between the in-phase (Scheme 1 (a)) and out-of-phase (Scheme 1(b)) vibration of two C=O groups. They assigned the band with lower frequency to the asymmetric (out-of-phase) and that with higher frequency to the symmetric (in-phase) stretching mode of two C=O groups.

In a previous publication [28], we discussed the solvent effect on infrared spectra of trimethyl phosphate in single solvent systems. The wavenumbers of \( \nu (P=O) \) of trimethyl phosphate in different solvents were obtained and correlated with the Kirkwood–Bauer–Magat (KBM) equation, the solvent acceptor numbers (AN) and the LSER. In this work we used infrared spectroscopy to study if and how two carbonyls of the ID molecule can affect solute–solvent interactions. The present study was performed to investigate the solvent-induced effects of a wide variety of different solvents on the spectra of ID and to correlate solvent properties, such as the acceptor number and dielectric constant with the infrared band shifts of \( \nu (C=O) \). The asymmetric and symmetric wave numbers of \( \nu (C=O) \) of ID in different solvents were obtained and correlated with KBM equation [15], the solvent AN, and the LSER [29–33].

ID molecule, shown in Scheme 2 (a), is worth studying as it has two carbonyls which are forced to be planar due to the W-form structure. Well known enol structure of acyclic 1,3-dicarbonyl (Scheme 2 (d)) is not preferable thus both carboxyls are in keto form and available for intermolecular interactions with solvents.

Scheme 2 illustrates the expected interactions between the ID and alcohols. As seen in Scheme 2 (b) two types of interactions can occur: (i) acidic \( \alpha \)-hydrogens of ID can interact with the oxygen electron pair of alcohol, (ii) the hydrogen of alcohol can interact with the oxygen electron pair of the carbonyl. These interactions may also be expected in both sides of the molecule (c).

2. Experimental

All solvents were either of analytical or spectroscopic purity and were distilled prior to use. ID was synthesized according to the literature [34]. Ethyl acetate and diethyl phthalate in ethyl alcohol reacts with metallic sodium powders to give 1,3-indanedione-2-ethylester as yellow solid. 1,3-Indanedione-2-ethylester was heated to 80 °C in water and solution was decarboxilated with the addition of concentrated H\textsubscript{2}SO\textsubscript{4}. Yellow ID powders were recrystallized into pure form in benzene/dioxane mixture. All spectral data agreed with the literature.

In all FT-IR measurements, the concentrations of the ID in the pure solvents were between 0.06 and 0.065 mol l\textsuperscript{-1}. The vibrational (1500–2000 cm\textsuperscript{-1}) absorption spectra of the solutions were measured using a Perkin Elmer 1600 BX 2 FT-IR spectrophotometer. Sixty-four scans were recorded and then averaged with a resolution of 1 cm\textsuperscript{-1} for each spectrum. Solution spectra were measured using 0.015 mm path length CaF\textsubscript{2} cell. The spectra of pure solvents were recorded as a background under the same conditions and were stored on the computer. The Spectrum v2.00 software was used for all data manipulation. The data files were transferred to a computer for analysis using a multivariate regression analysis program.

3. Results and discussion

The observed frequencies for the C=O stretching vibration mode of ID in 16 different pure solvents along
with the solvent parameters are presented in Table 1. The C=O stretching bands of ID were observed in the range of 1748–1757 cm\(^{-1}\) (weak intensity) and 1715–1726 cm\(^{-1}\) (strong intensity) in solvents. All calculations were performed for both stretchings and compared.

The first theoretical treatment of solvent-induced stretching frequency shifts was given by KBM, which is shown in Eq. (2):

\[
\frac{\nu_0 - \nu_s}{\nu_0} = \frac{\Delta \nu}{\nu_0} = \frac{C(\epsilon - 1)}{2\epsilon + 1}
\]

where \(\nu_0\) is the vibrational frequency of a solute in the gas phase, \(\nu_s\) the frequency of a solute in the solvent, \(\epsilon\) the dielectric constant of solvent and \(C\) is a constant depending upon the dimensions and electrical properties of the vibrating solute dipole.

Fig. 1 is a plot of (a) symmetric and (b) asymmetric \(\nu(C=O)\) stretching bands of ID versus \((\epsilon - 1)/(2\epsilon + 1)\) of the KBM equation. Since the KBM equation only takes into account the solvent dielectric constant, the correlation between \(\nu(C=O)\) and the KBM parameters are very poor, indicating that the frequency shifts depend not only on the solvent dielectric constant, but also on other solvent–solute interactions, such as the hydrogen bonding and the steric effects.

Fig. 2 shows (a) symmetric and (b) asymmetric \(\nu(C=O)\) stretching bands of ID as a function of the acceptor number. Two different slopes are observed for the \(\nu(C=O)\) stretching of symmetric and asymmetric bands. The second slope may be explained by the double interaction of alcohols, as discussed in Scheme 1. These results suggest that the OH protons are intermolecularly hydrogen bonded to the C=O group and methylene hydrogens to the alcohols oxygen, causing a large shift for the C=O asymmetric stretching, whereas relatively small shift for the C=O symmetric stretching bands are observed. Additionally, steric factors contribute to the strength of an intermolecular hydrogen bond, since the distance between the OH proton and the basic C=O site is a determining factor. When two or more equal alcohol molecules associate in the solution, so-called homo-intermolecular hydrogen bonds are formed. The associated alcohol molecules act as a large molecule. When

<table>
<thead>
<tr>
<th>No.</th>
<th>Solvent</th>
<th>(\nu(C=O))I</th>
<th>(\nu(C=O))II</th>
<th>(\epsilon)</th>
<th>(f(\epsilon))</th>
<th>AN</th>
<th>(\beta)</th>
<th>(\alpha)</th>
<th>(\pi^*)</th>
<th>(\delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methanol</td>
<td>1750.01</td>
<td>1716.46</td>
<td>32.7</td>
<td>0.477</td>
<td>41.5</td>
<td>0.62</td>
<td>0.93</td>
<td>0.6</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Ethanol</td>
<td>1748.93</td>
<td>1715.62</td>
<td>24.55</td>
<td>0.464</td>
<td>37.9</td>
<td>0.77</td>
<td>0.83</td>
<td>0.54</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>n-Propanol</td>
<td>1749.69</td>
<td>1716.13</td>
<td>20.33</td>
<td>0.464</td>
<td>37.83</td>
<td>–</td>
<td>0.78</td>
<td>0.52</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>i-Propanol</td>
<td>1749.64</td>
<td>1716.27</td>
<td>19.92</td>
<td>0.465</td>
<td>33.6</td>
<td>0.95</td>
<td>0.76</td>
<td>0.48</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>n-Butanol</td>
<td>1749.64</td>
<td>1716.62</td>
<td>17.8</td>
<td>0.459</td>
<td>36.8</td>
<td>0.88</td>
<td>0.79</td>
<td>0.47</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>i-Butanol</td>
<td>1749.93</td>
<td>1716.92</td>
<td>12.5</td>
<td>0.442</td>
<td>27.1</td>
<td>1.01</td>
<td>0.68</td>
<td>0.41</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Dichloromethane</td>
<td>1748.92</td>
<td>1717.23</td>
<td>8.9</td>
<td>0.420</td>
<td>20.4</td>
<td>0</td>
<td>0.3</td>
<td>0.82</td>
<td>0.5</td>
</tr>
<tr>
<td>8</td>
<td>Acetonitrile</td>
<td>1749.67</td>
<td>1717.84</td>
<td>35.9</td>
<td>0.479</td>
<td>18.9</td>
<td>0.31</td>
<td>0.19</td>
<td>0.75</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>1,4-Dioxane</td>
<td>1749.68</td>
<td>1717.86</td>
<td>2.25</td>
<td>0.227</td>
<td>10.8</td>
<td>0.37</td>
<td>0</td>
<td>0.55</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>Tetrahydrofuran</td>
<td>1750.14</td>
<td>1718.94</td>
<td>7.6</td>
<td>0.407</td>
<td>8.8</td>
<td>0.55</td>
<td>0</td>
<td>0.58</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>Carbon tetrachloride</td>
<td>1752.32</td>
<td>1720.15</td>
<td>2.24</td>
<td>0.226</td>
<td>8.6</td>
<td>0</td>
<td>0</td>
<td>0.28</td>
<td>0.5</td>
</tr>
<tr>
<td>12</td>
<td>Benzene</td>
<td>1750.76</td>
<td>1718.61</td>
<td>2.28</td>
<td>0.230</td>
<td>8.2</td>
<td>0.1</td>
<td>0</td>
<td>0.59</td>
<td>0.8</td>
</tr>
<tr>
<td>13</td>
<td>Toluene</td>
<td>1751.34</td>
<td>1719.26</td>
<td>2.45</td>
<td>0.246</td>
<td>4.5</td>
<td>0.11</td>
<td>0</td>
<td>0.54</td>
<td>0.7</td>
</tr>
<tr>
<td>14</td>
<td>Diethylether</td>
<td>1753.53</td>
<td>1721.86</td>
<td>4.2</td>
<td>0.340</td>
<td>3.9</td>
<td>0.47</td>
<td>0</td>
<td>0.27</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>Cyclohexane</td>
<td>1754.60</td>
<td>1724.25</td>
<td>2.02</td>
<td>0.202</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>n-Hexane</td>
<td>1755.31</td>
<td>1725.40</td>
<td>1.9</td>
<td>0.187</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>–0.08</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) The experimental \(\nu(C=O)\) stretching frequencies; (I) symmetric and (II) asymmetric.

\(^b\) \(f(\epsilon) = (\epsilon - 1)/(2\epsilon + 1)\).

\(^c\) Solvent acceptor number.
it interacts with solute molecule, the steric hindrance of the associated alcohol molecules is more than the one of the non-associated alcohol molecule (monomer) [7,18]. On the other hand, there are two hydrogen bondings between 1 mol of alcohol with an ID molecule. This brings a structural necessity to the approach of both side of the molecule (Scheme 2 (b)). These indicate that the steric factors for the association of alcohol molecules hinder the formation of the intermolecular hydrogen bond between the alcohol and the C=O of ID. Though, the acidity of the OH proton of methanol is stronger than that of other alcohols, the associated methanol molecule approaches the C=O of 1,3-indanedione as difficult if not as associated alcohol molecules. As a result, the frequencies of $\nu$(C=O) of 1,3-indanedione in different alcohols are similar. So the $\nu$(C=O) values in alcohols are less sensitive to the solvent AN and higher than expected. In Fig. 2(b), the six alcohols (1 to 6) used as solvents exhibit a linear relationship between AN and $\nu$(C=O). It may be explained by solvents proton acceptability that play an important role by interaction with two position protons. One site interaction may be affecting the other carbonyls to have different shifting. This may be the reason why the slope of the region for alcoholic solvents is positive for the symmetric stretching mode and negative for the asymmetric mode in Fig. 2(a) and (b).

The results can be interpreted by considering the interactions between electrons on the C=O group of ID with the solvent acting as a Lewis acid [30]. The negative slopes indicate that the $\nu$(C=O) of ID is shifted to lower frequencies as the Lewis acidity of the solvent increases. The biggest shifting is observed in ethanol, in which the $\nu$(C=O) stretching bands of symmetric and asymmetric of ID are at 1748.93 and 1715.62 cm$^{-1}$, respectively. They are about $\Delta \nu = 6.38$ and 9.78 cm$^{-1}$ lower than that in n-hexane for symmetric and asymmetric bands, respectively due to intermolecular hydrogen-bonds between the ID and alcohols.

LSER developed by Kamlet, Taft and co-workers [25–30] has been used to better understand and identify the different solvent–solute and solvent–solvent intermolecular interactions. LSER is a powerful tool for the study of the principal intermolecular interactions that control a specific physico-chemical process in solution, such as intermolecular electron transfer associated with a free-energy change. LSER assumes that the different solvent/solute interactions are additive and can be categorized in two groups: the exoergic and endoergic interactions. The exoergic interactions have their origins in attractive solute/solvent interactions and can be quantified by the solvatochromic parameters $\pi^*$, $\alpha$ and $\beta$. These parameters can be classified in non-specific ($\pi^*$) and specific ($\alpha$ and $\beta$). The $\pi^*$ parameter measures the exoergic effects of dipole/dipole and dipole/induced dipole interactions between the solute and the solvent molecules. A discontinuous polarizability correction term, $\delta$ must be added to $\pi^*$ parameter when polichlorinesubstituted aliphatics and aromatic solvents are used. The solvatochromic parameter $\alpha$ is a quantitative empirical measure of the ability of a bulk solvent to act as hydrogen-bond donor towards a solute. By contrast, the empirical parameter $\beta$ measures quantitatively the ability of a bulk solvent to act as a hydrogen-bond acceptor or electron-pair donor towards a given standard solute [29–33].

LSER is a multiparameter equation used to describe the solvent effects. LSER regression coefficients are produced and shown in Eqs. (3) and (4) for symmetric and asymmetric C=O stretching bands of ID, respectively, using the data for 16 solvents systems given in Table 1. The asymmetric C=O stretching band of ID exhibits a good correlation (correlation coefficients are 0.925 for symmetric stretching band of ID and 0.972 for asymmetric, standard deviations are 0.692 cm$^{-1}$ for symmetric C=O stretching band, while 0.609 cm$^{-1}$ for asymmetric):

$$
\nu(\text{C}=\text{O})_{\text{symmetric}} = (1754.90 \pm 0.45) - [(6.46 \pm 0.79) \pi^* + (0.52 \pm 0.45) \delta] - (0.58 \pm 0.80) \alpha - (2.05 \pm 0.88) \beta \tag{3}
$$

and

$$
\nu(\text{C}=\text{O})_{\text{asymmetric}} = (1724.58 \pm 0.40) - [(7.62 \pm 0.69) \pi^* + (1.33 \pm 0.40) \delta] - (2.21 \pm 0.71) \alpha - (3.06 \pm 0.78) \beta \tag{4}
$$

The major contribution to the solvent-induced stretching frequency shifts is the coefficient of $\pi^*$. From Eq. (3) or (4), it can be found that the coefficient of $\pi^*$ is the biggest. It means that the solvent dipolarity polarizability ($\pi^*$) plays an
important role in the solvent effects. Besides the dielectric effects (measured by \( \pi^* \)), solvent molecules interact directly with the C=O by two kinds of attractive forces. The first one is that the solvent molecule acting as Lewis acid (measured by \( \alpha \)) forms a hydrogen bond with the oxygen atom of the C=O. The second is that the solvent molecule which has electronegative atoms O, N, S, or X (F, Cl, Br, I) interacts as if Lewis base (measured by \( \beta \)) with partially positive hydrogen atoms of the solute.

The interactions mechanism of symmetric and asymmetric stretching bands of ID with solvents can be deduced from the coefficients of Eqs. (3) and (4). In aprotic solvents the solvent dipolarity/polarizability (\( \pi^* \)) also plays a significant role in interactions between solvent and the symmetric and asymmetric C=O stretching bands of ID since \( \alpha = 0 \) and \( (s/b) = 3.15 \) for symmetric and \( (s/b) = 2.49 \) for asymmetric \( (s/b) \) is the ratio of the regression coefficients of \( \pi^* \) and \( \beta \) in Eqs. (3) and (4), respectively. In protic solvents, the solvent basicity (\( \beta \)) is the most effective factor, since \( (b/a) = 3.57 \) and \( (b/a) = 1.39 \), which are the ratio of the regression coefficients of \( \beta \) and \( \alpha \) in Eqs. (3) and (4)), respectively. In the case of alcohols the role of \( \beta \) seems to be more important than \( \alpha \) because of large \( (b/a) = 3.57 \).

As mentioned above, solvent parameters \( \alpha \) and \( \beta \) are the measure of solvent hydrogen-bond donor acidity and acceptor basicity, respectively. The good correlations between \( \nu(C=O) \) and each of these parameters reveal that alcohols behave not only as a Lewis acid (by hydroxyl hydrogen) but also as a Lewis base (by hydroxyl oxygen). As proposed in Scheme 1 (b) and (c), which implies the presence of two hydrogen bonds. The first one is between the oxygen atom of alcohol and hydrogen atom of ID (O···H–C) and the other one is between the carbonyl oxygen and the alcohol hydrogen atom (C=O···H–O). Han and Kim [35] conducted a matrix isolation study of acetone and methanol in solid argon. They suggested that H–O···H–C and C=O···H–O hydrogen bonds coexist in the system. The theoretical calculations showed a planar six-membered ring-like structure possessing the above two kinds of hydrogen bonds. According to the discussions and experimental results, a similar structure (Scheme 1 (b) or (c)) is believed to exist at room temperature in the studied system. However, the interactions discussed above shown that asymmetric one is more affected than symmetric one.

4. Conclusions

As a summary, the solvent–solute interactions of ID in 16 different pure organic solvents were studied by using stretching band shift of infrared spectra for both symmetric and asymmetric bands. The results were correlated with solvent properties, such as the KBM equation, the solvent AN and LSER. No linear relationships were observed between the wave numbers of the asymmetric and symmetric C=O stretching bands of ID and KBM solvent-parameters indicating that the KBM relationship, which only takes into account the dielectric constants is inconvenient for the ID. It has been realized that beside dielectric contribution other solvent interaction effects, e.g., molecular geometry, basicity or acidity, dipolar interaction and steric factors are also operative in the determination of solvent-induced IR shifts. This is not a surprising result by considering the hydrogen bonding between alcohols oxygen and acidic methylene hydrogens.

A reasonable correlation was observed between the wave number of the asymmetric C=O stretching band of ID and the solvent AN. The solvent AN for the alcohols do not take into account the association of the alcohols and the steric factors which determine the strength of the intermolecular hydrogen bonding between solvent and solute. Therefore, parameters, such as AN values cannot be expected to exhibit universal linear relationships between IR group frequencies. However, they do help in predicting the direction of frequency shifts within a class of compound.

A deviation from the expected single linear correlation as the basicity of the solvent increases were attributed to the double interactions, as proposed in the model (Scheme 2). Compared to the previous two methods an excellent correlation between both C=O stretching frequencies and the LSER parameters of the solvents were obtained. These excellent correlations between \( \nu(C=O) \) and each of these parameters reveal that alcohols behave not only as a Lewis acid (by hydroxyl hydrogen) but also as a Lewis base (by hydroxyl hydrogen).
hydroxyl oxygen) in the ν(C=O) stretching bands of 1,3-indanodione. As is proposed in Scheme 2 (b) and (c), which implies the presence of two hydrogen bonds on both or one side of the ID molecule. Fig. 3(a) and (b) shows high concordance between the calculated and the experimental frequencies for the symmetric and asymmetric C=O stretching bands of ID. This fact allows the prediction of the wave number of the C=O stretching bands of ID in other solvents, if the LSER parameters of these solvents are obtained. Although, the KBM and AN methods can be applied to simple interactions, it seems better to use LSER for more complex interactions to obtain a quantitatively accurate and physically meaningful explanation of solvent-induced stretching frequency shifts.

References