

## **Correlation of IR and UV Studies for Solvent Solute Interactions; Carbonyl Compounds in Solution**

**Azhar M. Syed, M.A. Somali and M.A. Quddus**

*Quality Control Laboratory, Ministry of Commerce, Jeddah, Saudi Arabia and P.C.S.I.R. Laboratories, Karachi.*

IR and UV absorptions due to carbonyl group of different compounds have been studied in a wide range of solvents including water. IR absorptions have been measured by ATR Spectra. The changes occurring due to solvent effects in the electronic and vibrational transitions of carbonyl group have been discussed for a comparative study.

IR studies of solvent effect on individual group frequencies were first reported by Breit and Salant (1937) and later Kirkwood (1939), Bauer and Magat (1938) deduced the following expression known as KBM equation:

$$\frac{\frac{\Delta\gamma}{\gamma}}{\frac{\Delta\gamma}{\gamma}} = \frac{C(D-1)}{(2D+1)} \quad (i)$$

where  $\gamma$  is the relative frequency shift with respect to vapour,  $D$  is the dielectric constant of solvent and  $C$  is a constant.

Bayliss *et al.* (1955) observed that KBM equation could not be used to interpret, solvent induced frequency shifts for C-H, C = O and C-C vibrations. The equation (i) relates  $\Delta\gamma$  to the electrostatic polarization and in the case of non-polar solvents, where electronic polarization is important Bayliss modified the equation:

$$\frac{\Delta\gamma}{\gamma} = \frac{C(n^2-1)}{(2n^2+1)} \quad (ii)$$

where  $n$  is the refractive index of the solvent and  $C$  is another constant. In polar solvents, in addition to electronic polarization, the dipole reorientations are also considered and the equation (ii) fails to account for the later effect.

For the shifts of UV absorptions, Bayliss (1950) applied the same equation with some modifications and later McRae (1957) suggested the following improvement:

$$\Delta Y = \frac{A(n^2 - 1)}{(2n^2 + 1)} + B \left[ \frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad (\text{iii})$$

Where  $A$  and  $B$  are constants. The equation (iii) is not applicable in the hydrogen-bonding case Ito *et al.* (1960) observed that equation (iii) can also be applied to interpret the IR solvent shifts and therefore, appears likely that in both IR and UV spectra, the individual group frequencies are affected by solvent interaction to a similar extent.

Theories based on the generalization of results in an empirical manner have not been able to prove these effects. The previous work (Syed and Quddus 1961 and 1974) was an alternative approach to study the nature of solvent-solute interactions in the UV spectra by direct comparison of relative frequency shift of two different solutes in a wide range of solvents including hydrogen-bonding cases. This procedure eliminates all those properties of solvents which operate in a similar way for the two different solutes. In the present work, a similar type of study has been made on IR and UV absorptions of the carbonyl groups in a wide range of solvents, in order to study the comparative aspects of the solvent effects.

### Experimental

#### Materials

Acetone, acetaldehyde, cyclohexanone and acetyl acetone were of spectroscopic grade and used as such. Mesityl oxide (B.D.H.) was fractionated and the middle fraction (b.p. 127—128°) was used. Conductivity water was used as solvent. Other solvents were of analytical grade and the purity was checked before use by IR spectra.

#### Spectra

The absorptions in the UV spectra were measured on Beckman Model DK-2 spectrophotometer, using matched silica cells of 1m thickness. The IR absorptions were measured by Perkin-Elmer Model 577 spectrophotometer, using ATR unit (TR-3) of Research and Industrial Instruments Co.

### Results and Discussion

The shifts of the absorption maxima of  $n \rightarrow \pi^*$  transition of the carbonyl compounds are shown in Table 1. The shifts of the absorption maxima due to  $C = O$  vibrational transitions in the IR spectra of the same compounds are given in Table 2.

The IR absorptions have been measured by ATR spectra, in order to avoid cell thickness limitations for OH containing solvents. In both IR and UV transitions, red shifts have been observed.

A comparison of the behaviour of solvent effect in the IR and UV transitions has been made by an approach towards the plots of relative shift of the absorption maxima of more than one solute in a range of solvents, against that of a standard solute in the same range. Fig. 1 and 2 show such plots for the carbonyl group in the IR and UV transitions respectively, taking acetone as a standard solute in both the cases. For a particular solute, the plots are linear in all the range of solvents including hydrogen-bonding cases. This shows that in both vibrational and electronic transitions, the solvent shifts occur due to specific solvent-solute interactions. The only difference noticed is that slopes of different solutes in the UV transition ( $n \rightarrow \pi^*$ ), bear a better relationship with the polarity of the dipole than for the  $C = O$  vibrational transition in the IR spectra. This irregularity of slopes in the  $C = O$  group has also been observed by Bellamy and Williams (1959) and Bellamy and Hallam (1959) during the IR studies of solvent effects.

The relative shifts of the absorption maxima of  $C = O$  absorption in the IR spectra have been correlated with the similar shifts of  $n \rightarrow \pi^*$  absorption in the UV spectra of the same solute in a range of solvents by the plots shown in Fig. 3. The plots of  $\frac{\Delta\gamma}{\gamma}$  of  $n \rightarrow \pi^*$  transition against  $\frac{\Delta\gamma}{\gamma}$  of  $C = O$  transition of acetaldehyde and Mesityl oxide are linear Fig. 3, showing that the similar factors are involved for the observed solvent shifts in both UV and IR spectra.

The work has been extended to a more complex molecule such as acetyl acetone. Table 3 shows the absorption maxima shifts of the carbonyl group in the UV and IR spectra. It has been observed that in the IR spectra, the carbonyl frequency due to enol -group gives a broad band near  $1620 \text{ cm}^{-1}$  which is not solvent affected. The other carbonyl frequency due to keto -group near  $1712 \text{ cm}^{-1}$  is shifted by the solvents in a similar manner as in other carbonyl compounds discussed earlier. The  $n \rightarrow \pi^*$  absorption of acetyl acetone in the UV spectra shows a broad band unaffected by solvents, such as the enol -group in the IR spectra. Acetyl acetone is well known to be a mixture of keto and enolic tautomers and the intensity measurements by N.M.R. spectra (Shoolery 1960) have shown that keto and enol account for  $20.4 (\pm 0.4) \%$  and  $79.5 (\pm 0.7) \%$  respectively. In the UV spectra the broad absorption band near  $273 \text{ nm}$  is mostly formed by the enol group and is unaffected by solvents similar to the broad IR frequency at  $1620 \text{ cm}^{-1}$ .

*Acknowledgement:* We would like to thank Mr. Sulaiman Y. Farahidi, Director General, Department of Consumer Protection, Riyadh and Mr. Husain Shazli Farhoud Director, Quality Control Laboratory, Jeddah, for providing facilities and encouragement to carry out this work.

#### References

- Bauer, E. and Magat, M. (1938) *J. Phys. Radium*, **9**, 319.  
Bayliss, N.S. (1950) *J. Chem. Phys.*, **18**, 292.

- Bayliss, N.S., Cole, A.R.H. and Little, L.H.** (1955) *Australian J. Chem.*, **8**, 26.  
**Bellamy, L. H. and Hallam, H.E.** (1959) *Trans. Farad. Soc.*, **55**, 220.  
**Bellamy, L.J. and Williams, R.L.** (1959) *Trans. Farad. Soc.*, **55**, 14.  
**Breit, G. and Salant, E.O.** as quoted by **West and Edwards** in Ref. (13).  
**Ito, M., Inuzuka, K. and Imanishi, S.** (1960). *J. Am. Chem. Soc.*, **82**, 1317.  
**Kirkwood, J.G.** (1939) *J. Chem. Phys.* **7**, 911.  
**MC. Rae, E.G.** (1959) *J. Phys. Chem.*, **61**, 563.  
**Shoolery** (1960) *NMR and EPR Spectroscopy*, Pergamon Press, Oxford, Ch.7.  
**Syed, A.M. and Quddus, M.A.** (1961) *Pak. J. Sci. & Ind. Res.*, **13**, 467.  
**Syed, A.M. and Quddus, M.A.** (1974) *Proc. Pak. Acad. Sci.*, **11**, 19.  
**West, W. and Edwards, R.T.** (1937) *J. Chem. Phys.*, **5**, 14.

Table 1. The  $n \rightarrow \pi^*$  absorption bands of acetone, mesityl oxide, acetaldehyde and cyclohexanone in solvents.

| Solvents    | Acetone                                |  | Mesityl Oxide                          |  | Acetaldehyde                           |  | Cyclohexanone                          |  |
|-------------|--|--|--|--|--|--|--|--|
|             | Absorption maximum<br>$\text{cm}^{-1}$ | Shifts of absorption maximum<br>$\text{cm}^{-1}$ | Absorption maximum<br>$\text{cm}^{-1}$ | Shifts of absorption maximum<br>$\text{cm}^{-1}$ | Absorption maximum<br>$\text{cm}^{-1}$ | Shifts of absorption maximum<br>$\text{cm}^{-1}$ | Absorption maximum<br>$\text{cm}^{-1}$ | Shifts of absorption maximum<br>$\text{cm}^{-1}$ |
| n-Heptane   | 36100                                  |  | 30680                                  | —  | 34480                                  | —  | 34600                                  | —  |
| n-Hexane    | 36220                                  | 120  | 30870                                  | 190  | 34530                                  | 50   | 34720                                  | 120  |
| Dioxane     | 36370                                  | 270  | 31340                                  | 660  | 34960                                  | 490  | 34840                                  | 240  |
| Chloroform  | 36370                                  | 270  | 31750                                  | 1070   | 35210                                  | 730  | 34960                                  | 360  |
| Methanol    | 37030                                  | 930  | 32360                                  | 1680   | 35460                                  | 1080   | 35460                                  | 860  |
| Acetic Acid | 37450                                  | 1350   | 33220                                  | 2540   | 36000                                  | 1520   | 35840                                  | 1240   |
| Water       | 37750                                  | 1650   | 33560                                  | 2880   | 36100                                  | 1620   | 36100                                  | 1500   |

Table 2. The  $n \rightarrow \pi^*$  of acetone, mesityl oxide, acetaldehyde and cyclohexanone in solvents.

| Solvents   | Acetone                                |  | Mesityl Oxide                          |  | Acetaldehyde                           |  | Cyclohexanone                          |  |
|------------|--|--|--|--|--|--|--|--|
|            | Absorption maximum<br>$\text{cm}^{-1}$ | Shifts of absorption maximum<br>$\text{cm}^{-1}$ | Absorption maximum<br>$\text{cm}^{-1}$ | Shifts of absorption maximum<br>$\text{cm}^{-1}$ | Absorption maximum<br>$\text{cm}^{-1}$ | Shifts of absorption maximum<br>$\text{cm}^{-1}$ | Absorption maximum<br>$\text{cm}^{-1}$ | Shifts of absorption maximum<br>$\text{cm}^{-1}$ |
| n-Heptane  | 1727                                   |  | 1695                                   | —  | 1734                                   |  | 1720                                   | —  |
| n-Hexane   | 1725                                   | 2  | 1693                                   | 2  | 1732                                   | 2  | 1718                                   | 2  |
| Dioxane    | 1720                                   | 7  | 1688                                   | 7  | 1728                                   | 6  | 1712                                   | 8  |
| Chloroform | 1718                                   | 9  | 1688                                   | 7  | 1728                                   | 6  | 1708                                   | 12   |
| Methanol   | 1715                                   | 12   | 1682                                   | 13   | 1724                                   | 10   | 1705                                   | 15   |
| Water      | 1702                                   | 25   | —                                      | —  | 1720                                   | 14   | —                                      | —  |

**Table 3. U.V. and I.R. absorptions of C = O group of acetyl acetone in solvents.**

| Solvents   | U.V.                                   |  | I.R.                                   |  |  |  |
|------------|--|--|--|--|--|--|
|            | Absorption maximum<br>cm <sup>-1</sup> | Shifts of absorption maximum<br>cm <sup>-1</sup> | Enol - group                           |  | Keto - group                           |  |
|            |  |  | Absorption maximum<br>cm <sup>-1</sup> | Shifts of absorption maximum<br>cm <sup>-1</sup> | Absorption maximum<br>cm <sup>-1</sup> | Shifts of absorption maximum<br>cm <sup>-1</sup> |
| n-Heptane  | 26630 (b)                              | —  | 1620 (b)                               | —  | 1712                                   | —  |
| n-Hexane   | 36630 (b)                              | —  | 1620 (b)                               | —  | 1712                                   | 8  |
| Dioxane    | 36630 (b)                              | —  | 1620 (b)                               | —  | 1710                                   | 2  |
| Chloroform | 36630 (b)                              | —  | 1620 (b)                               | —  | 1707                                   | 5  |
| Methanol   | 36630 (b)                              | —  | 1620 (b)                               | —  | 1705                                   | 7  |
| Water      | 36630 (b)                              | —  | 1620 (b)                               | —  | 1705                                   | 7  |

(b) broad

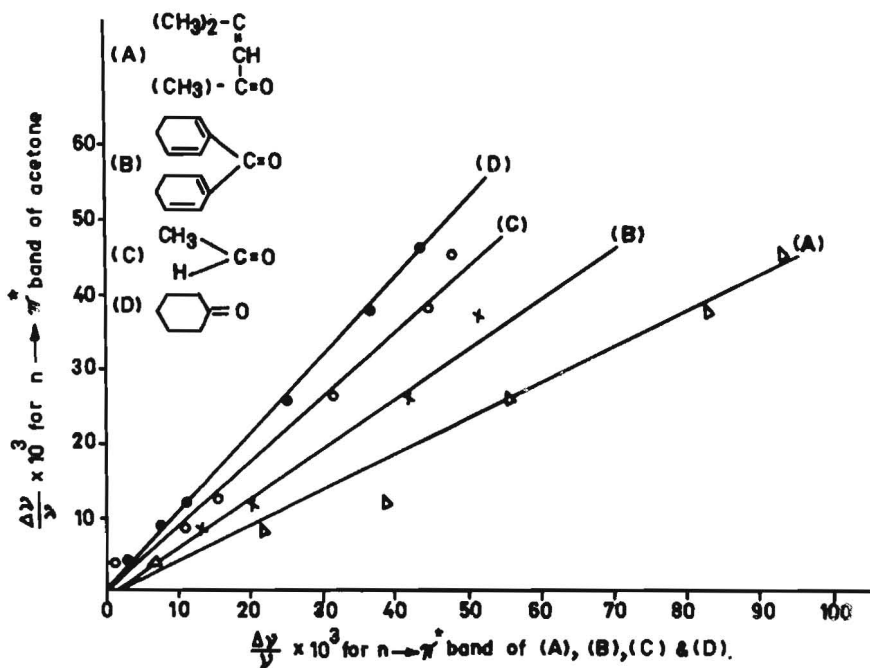


FIG.1

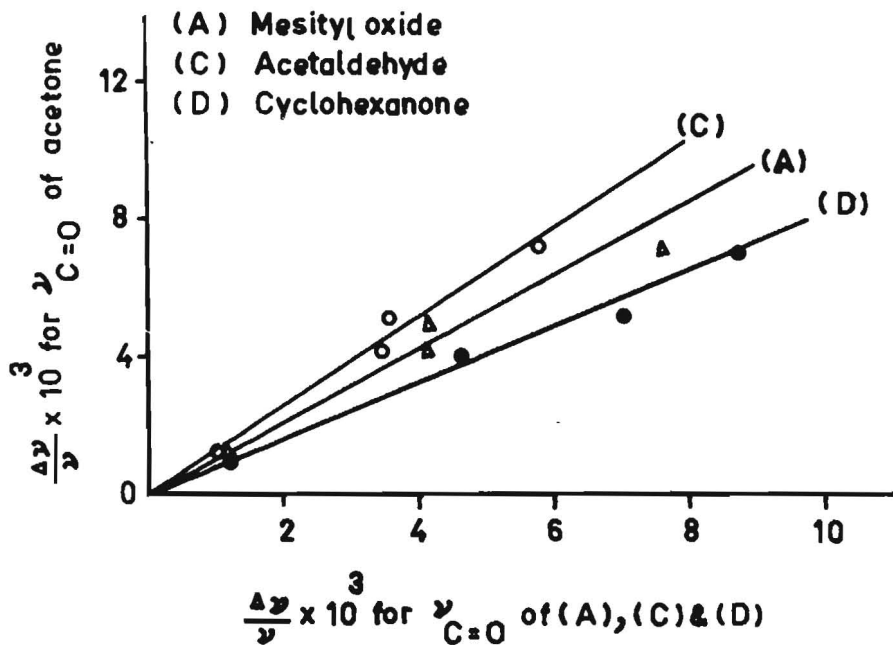


FIG.2



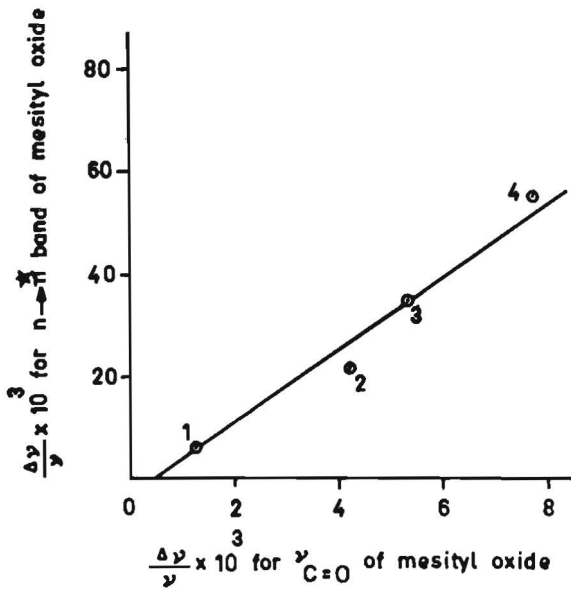
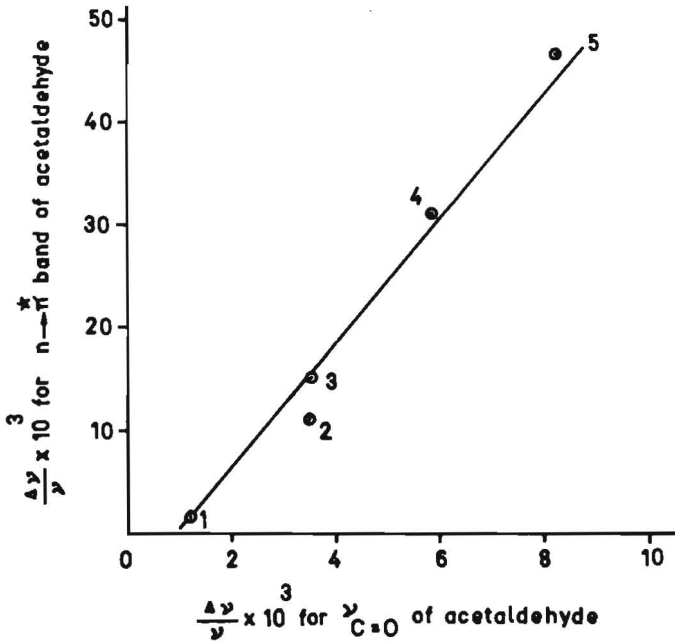


FIG-3

## دراسة العلاقة المتبادلة بين أطياف امتصاص الأشعة تحت الحمراء وال فوق بنفسجية في تفاعلات محاليل المذيبات ، مركبات الكربوناييل

أزهر م . سيد ، محمد أ . صومالي وم . أ . قدوس  
 مختبر الجودة النوعية ، وزارة التجارة ، جدة ، المملكة العربية السعودية  
 ومختبرات PCSIR ، كراتشي .

امتصاص الأشعة تحت الحمراء وال فوق بنفسجية الناشئ عن مجموعة الكربوناييل من مركبات مختلفة قد درست في مجالات واسعة من المحاليل بالإضافة إلى الماء .  
 امتصاص الأشعة تحت الحمراء قيس بواسطة ATR. التغيرات الظاهرة الناشئة عن المذيب تؤثر في الالكترونية وترددات التوصيل لمجموعة الكربوناييل قد نوقشت في دراسة المقارنة .