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THE EFFECT OF SOLVENT-SOLUTE INTERACTIONS ON ULTRAVIOLET SPECTRAL BANDS

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A study of the shift of the absorption maxima of the $n \rightarrow \pi^*$ absorption band for mesityl oxide (unsaturated ketone) and methyl ethyl ketone (saturated ketone) has been made in a range of solvents. Specific solvent–solute interactions have been found to occur throughout the range of solvents irrespective of their hydrogen bonding ability. A similar behaviour has been found for the $\pi \rightarrow \pi^*$ absorption band of mesityl oxide and the $n \rightarrow \sigma^*$ absorption band of methyl iodide.

Ultraviolet studies of the electronic spectra of liquids and solutions have provided important evidence that in a considerable number of cases the spectral absorption bands are affected when molecules are transferred from gas phase to a solvent environment. This is due to the unequal perturbation of the ground and excited states of the molecules. Such perturbations depend on the nature of the solvent–solute interactions in the two states. Although the phenomena directly connected with the structure of the perturbed electron clouds have a more complicated behaviour, a very simple formula was indicated by Bayliss[1] who assumed that the frequency shift is proportional to the solvation energy of a classical oscillating dipole in a continuous dielectric medium of the solvent. From this assumption Bayliss arrived at a formula similar to KBM[2] expression in the case of vibrational spectra;

$$\frac{\Delta\nu}{\nu} = \frac{Cf}{\alpha\nu_0^{\,2}} \times \frac{n^2-1}{2n^2+1}$$

where f=oscillator strength of the optical transition in the absorbing solute molecule; α =polarizability of the solute active molecule; n=refractive index of the solvent; C=a constant.

This equation predicts only red shifts and a dependence of shift on only one property of the solvent (the refrective index or the dielectric constant). Bayliss and McRae[3] suggested that the blue shift (e.g. $n \rightarrow \pi^*$ transition) might arise when there is a decrease of the dipole moment of the solute during the transition. Ito *et al.*[4] have shown that the blue shift phenomenon in the $n \rightarrow \pi^*$ transition is due to cooperating effects of both electrostatic and hydrogen bonding interactions on solute molecule. McRae[5] derived an expression for the solvent-induced frequency shift, from the second order perturbation theory, taking into account all the types of interactions suggested earlier. This equation failed to account for the results in hydrogen bonding solvents.

Several workers have attempted to generalize the effect of solvents on spectra in an empirical manner. Kosower[6] has proposed that the transition energies in kcal/mole (Z-values) be adopted as empirical measures of solvent polarity. This treatment is not applicable in all cases because as the solute molecule increases in size, correlation of electronic transition with Z-values become less precise.

In the present work it has been considered that the specific solvent–solute interactions are of major importance and that such studies on simple systems are needed.

Experimental

Materials.—Mesityl oxide (B.D.H.) was fractionated and the middle fraction (b.p. 127–128°C) was used. Methyl ethyl ketone (E. Merck) was redistilled (b.p. 79.6°). Acetone (B.D.H.) was dried and its water content was checked before use by IR spectra. Methyl iodide (B.D.H.) was used as such. Only those solvents were selected which did not have any absorption in the region of interest and were equally important for their theoretical background.

Spectra.—Measurements of UV absorption spectra were made on Beckman DK-2 spectrophotometer, using matched silica cells of 1 cm or 0.5 cm thicknesses. Calibration between 340–220 mμ was carried out using 0.0400 g/litre of

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K_2CrO_4 in 0.05N KOH solution. The maxima were measured by running the spectra at the lowest speed four to five times and averaging the results.

Results and Discussion

$n \rightarrow \pi^*$ Transition

Tables 1 and 2 deal with the shifts of the absorption maxima for the $n \rightarrow \pi^*$ absorption band of mesityl oxide and methyl ethyl ketone dissolved in a wide range of solvents. Corresponding results for acetone dissolved in the same range of solvents are given in Table 3. The absorption bands of mesityl oxide, dissolved in solvents, have been reported by Kosower.[6] In the present work, more solvents have been included and the reported values have been remeasured for a complete check.

Inert solvents produce almost the same environment to a molecule as in the gas phase. The shifts of the absorption maxima have therefore been measured relative to the absorption maximum in heptane.

The relative shifts of the absorption maxima for $n \rightarrow \pi^*$ absorption band of mesityl oxide (unsaturated ketone) have been plotted against the relative shifts of the absorption maxima for $n \rightarrow \pi^*$ absorption band of acetone in the same range of solvents. Figure 1 shows that $\Delta\nu/\nu$ plot is linear and except for chloroform all the points fall very close to the straight line. This abnormal behaviour of chloroform has also been observed by Kosower[6] in the plot of transitional energies versus Z-values. The range of solvent selected in this work includes nonpolar, polar and hydrogen bonding solvents, classified earlier by Rao *et al.*[7] For hydrogen bonding solvents the shifts are, as expected, comparatively large but the values fall on the same straight line suggesting specific solvent–solute interactions. This behaviour of solvent effect on the electronic transitional bands is very much similar to the study on vibrational bands of carbonyl groups in IR spectroscopy carried out by Bellamy.[8] No such attempt has been made for UV spectra.

TABLE 1.—THE $n \rightarrow \pi^*$ ABSORPTION BAND OF MESITYL OXIDE IN SOLVENTS.

Solvents	Absorption maximum		Shift of absorption maximum cm⁻¹
	mμ	cm⁻¹	
n-Heptane	326	30680	—
n-Hexane	324	30870	190
Cyclohexane	324	30870	190
Diethylether	323	30960	280
2,2,4-Trimethylpentane	322	31060	380
Dioxane	319	31340	660
Chloroform	315	31750	1070
Acetonitrile	314	31850	1170
Isopropanol	312	32050	1370
n-Butanol	311	32160	1480
n-Propanol	311	32160	1480
Ethanol	310	32250	1570
Methanol	309	32360	1680
Ethylene glycol	305	32780	2100
Glycerine	302	33110	2430
Acetic acid	301	33220	2540
Water	298	33560	2880

TABLE 2.—THE $n \rightarrow \pi^*$ ABSORPTION BAND OF METHYL ETHYL KETONE IN SOLVENTS.

Solvents	Absorption maximum		Shift absorption maximum cm⁻¹
	mμ	cm⁻¹	
n-Heptane	278	35970	—
n-Hexane	277	36100	130
Cyclohexane	277	36100	130
Diethyl ether	277	36100	130
2,2,4-Trimethylpentane	277	36100	130
Dioxane	—	36300	330
Chloroform	—	36300	330
Acetonitrile	275	36370	400
Isopropanol	—	36560	590
n-Butanol	273	36640	670
n-Propanol	273	36640	670
Ethanol	—	36700	730
Methanol	—	36765	795
Ethylene glycol	270	37030	1060
Glycerine	269	37170	1200
Acetic acid	—	37000	1030
Water	267	37450	1480

TABLE 3.—THE $n \rightarrow \pi^*$ ABSORPTION BAND OF ACETONE IN SOLVENTS.

Solvents	Absorption maximum		Shift of absorption maximum cm⁻¹
	mμ	cm⁻¹	
n-Heptane	277	36100	—
n-Hexane	276	36220	120
Cyclohexane	276	36220	120
Diethyl ether	276	36220	120
2,2,4-Trimethylpentane	276	36220	120
Dioxane	275	36370	270
Chloroform	275	36370	270
Acetonitrile	274	36500	400
Isopropanol	272	36760	660
n-Butanol	272	36760	660
n-Propanol	272	36760	660
Ethanol	270	37030	930
Methanol	270	37030	930
Ethylene glycol	269	37170	1070
Glycerine	268	37320	1220
Acetic acid	267	37450	1350
Water	265	37750	1650

The relative shift of the absorption maxima for $n\rightarrow\pi^*$ absorption band of methyl ethyl ketone (saturated ketone) have been plotted against $\Delta\nu/\nu$ for $n\rightarrow\pi^*$ absorption band of acetone in the same range of solvents. A fairly good straight line is obtained but with a different slope from that of mesityl oxide (unsaturated ketone) shown in Fig. 1. This indicates that the properties of both solvent and solute are involved in determining the shift of the absorption maxima. The variation in slopes of the two lines for saturated and unsaturated ketones may be considered as depending upon the polaritly of C=O. If the magnitude of the shift depended solely upon some property of the solvent such as dielectric constant or refractive index,[1,5] a 45° line would be obtained for all solutes plotted one against the other.

Using compressed gases as solvents, Oksengorn[9] also studied experimentally the shift of UV absorption bands and concluded that the bulk dielectric property is not the only factor in determining the shift.

$\pi\rightarrow\pi^*$ and $n\rightarrow\sigma^*$ Transitions

Measurements for the shift of the absorption maxima of the $\pi\rightarrow\pi^*$ absorption band of mesityl oxide dissolved in a range of solvents are shown in Table 4. A plot of $\Delta\nu/\nu$ values for $\pi\rightarrow\pi^*$ against $n\rightarrow\pi^*$ absorption bands of mesityl oxide gives a straight line (Fig. 2). The need for the study of specific solvent–solute interactions has been expressed by Kosower[6] who studied $\pi-\pi^*$ transition and found that when the molecules increase in size the correlation of transition with Z-values become less precise.

The $n\rightarrow\sigma^*$ absorption band usually lies in the vacuum UV region below 190 mμ and arises from the lone pair electron transitions. Methyl iodide has been selected as it gives this band near 258 mμ which is good region for the instrument available in this laboratory. Methyl iodide is not soluble in all the solvents selected in this work and therefore, in only four solvents the $n\rightarrow\sigma^*$ absorption band has been measured (Table 5). Figure 3 shows the relative shift of the absorption maxima $\Delta\nu/\nu$ for $n\rightarrow\sigma^*$ absorption band plotted against $\Delta\nu/\nu$ for $n\rightarrow\pi^*$ absorption band of mesityl oxide. Even though a comparatively small number of solvents have been used, the type selected cover almost the same range of the shift of the absorption maxima and therefore provides reasonable test of linearity of the plot.

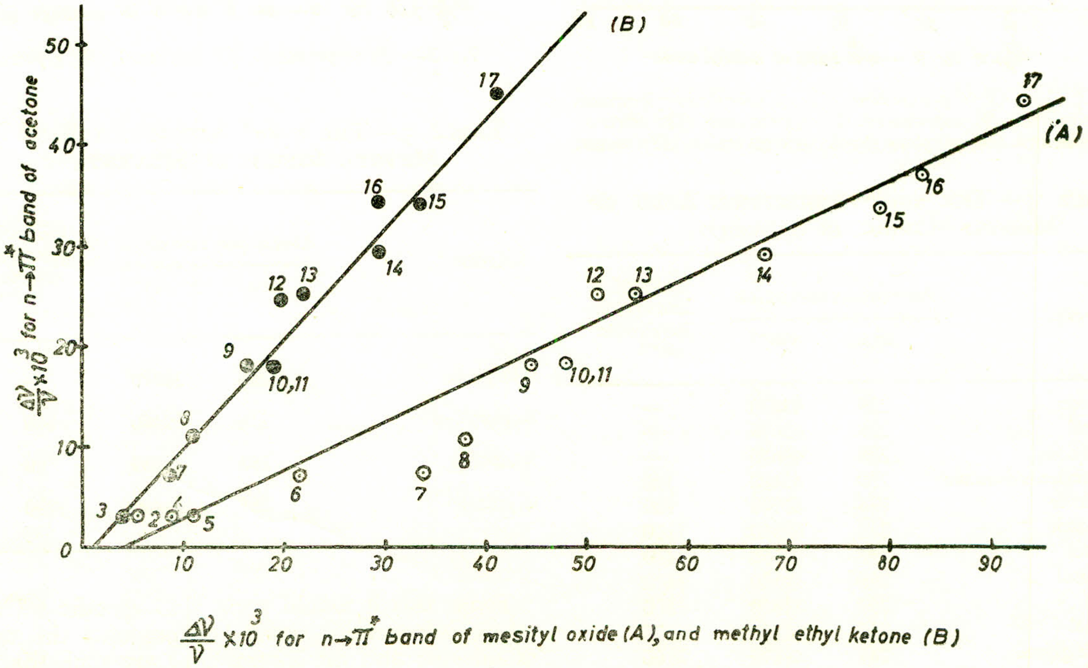

Fig. 1.— (1) n-Heptane, (2) n-hexane, (3) cyclohexane, (4) diethyl ether, (5) 2,2,4-trimethyl pentane, (6) dioxane, (7) chloroform, (8) acetonitrile, (9) isopropanol, (10) n-butanol, (11) n-propanol, (12) ethanol, (13) methanol, (14) ethylene glycol, (15) glycerine, (16) acetic acid, (17) water.

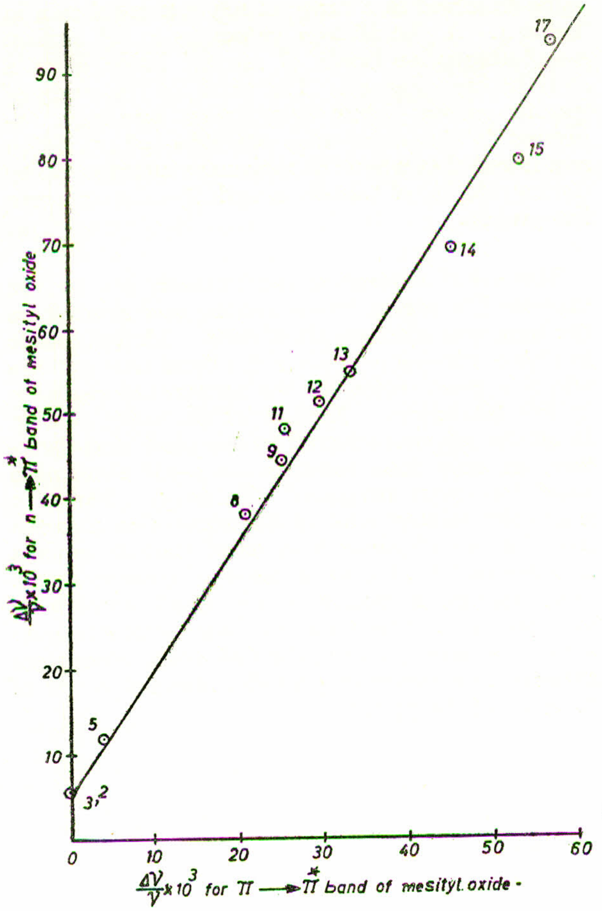

Fig. 2.— (3) (Cyclohexane, (5) 2,2,4-trimethylpentane, (8) acetonitrile, (9) isopropanol, (11) n-propanol, (12) ethanol, (13) methanol, (14) ethylene glycol, (15) glycerine, (17) water.

TABLE 4.—THE π→π* ABSORPTION BAND OF MESITYL OXIDE IN SOLVENTS.

Solvents	Absorption maximum		Shift of absorption maximum cm^{-1}
	mμ	cm^{-1}	
n-Heptane	229	43670	—
n-Hexane	229	43670	—
Cyclohexane	229	43670	—
2,2,4-Trimethylpentane	230	43480	190
Acetonitrile	234	42740	930
Isopropanol	235	42550	1120
n-Butanol	235	42550	1120
n-Propanol	235	42550	1120
Ethanol	236	42370	1300
Methanol	237	42200	1470
Ethylene glycol	241	41670	2000
Glycerine	242	41320	2350
Water	243	41150	2520

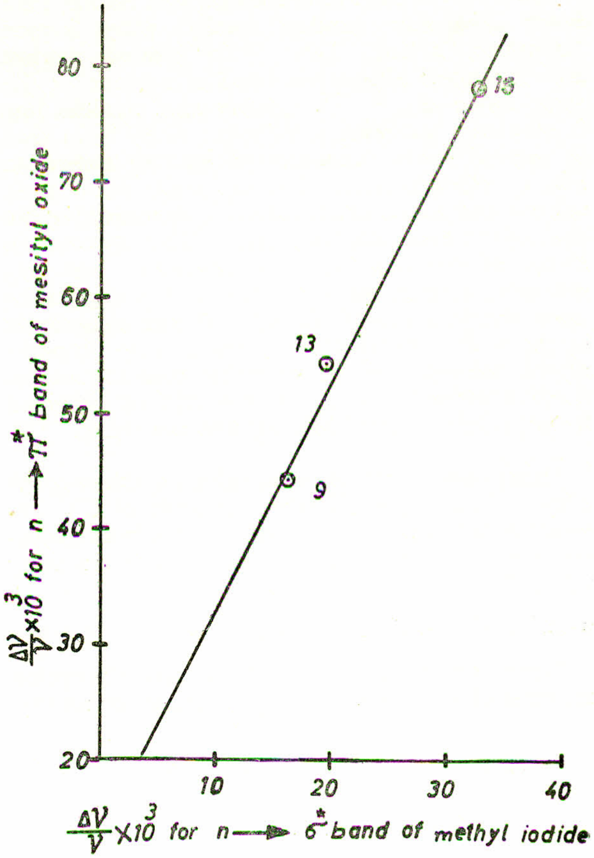

Fig. 3.— (9) Isopropanol, (13) methanol, (15) glycerine.

TABLE 5.—THE $n\rightarrow\sigma^*$ ABSORPTION BAND OF METHYL IODIDE IN SOLVENTS.

Solvents	Absorption maximum		Shift of absorption maximum cm^{-1}
	mμ	cm^{-1}	
n-Heptane	258	38770	—
Isopropanol	254	39380	610
Methanol	253	39530	760
Glycerine	251	39840	1070

From this it would seem that specific solvent–solute interactions occur throughout the range of solvents and the interactions are such that the effect on the "blue shift" absorption band (e.g. $n\rightarrow\pi^*$ and $n\rightarrow\sigma^*$ transitions) is similar to the "red shift" absorption band (e.g. $\pi\rightarrow\pi^*$ transition.)

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