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LINEAR SOLVATION ENERGY CONCEPT ON INFRARED SPECTRA OF DONORS ON COMPLEX FORMATION WITH HALOGENS AND INTERHALOGENS

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ABSTRACT

The effect of environments on the frequency shift has been explained in terms of degree of charge transfer. Fruitful suggestions have been made in order to correlate the frequency shift with solvent properties such as π^* values, dielectric constant and refractive index of these solvents. It may be concluded that with the increase of π^* values of the solvents, the frequency shift increases and the solvent effects on ground state of the complexes definitely depend on both polarity and polarizabilty terms.

INTRODUCTION

The vibrational spectrum of a molecule is affected markedly by environmental factors. The changes in the shape, frequency and intensity of bands are observed while going from one solvent to another. The spectral changes due to solvents may throw some light on the intermolecular forces. Several attempts had been made[1–3] to predict types of intermolecular interactions. It was observed that on increasing the solvent polarity, the charge transfer band shift to the higher energy. Kosower[4] has explained the solvent effects by giving more emphasis to the dative bond structure of the ground state. Person *et al.*[5–6] pointed out that there were always two types of interactions (i) donor–solvent and (ii) acceptor–solvent type. If solvent stabilization of the excited state is greater than for the ground state, there may be a shift to lower energies of the charge transfer band on moving from vapour to solution. But the reasons for changes in the vibrational spectra resulting from medium effect have not yet been sufficiently clear.

An attempt has been made in the present investigations to apply several solvent parameters along with the concept of linear solvation energy relationship[7–9] (LSER'S) to the donors on complex formation with halogens and interhalogens.

EXPERIMENTAL

Materials : α–Picoline (α–pic) and β–picoline (β–pic), 2,5–dimethylpyridine (Lut) were dried over KOH and BaO for several days and distilled under reduced pressure. 2–bromopyridine (Fluka, AG), 2–chloropyridine (Aldrich Chemicals) were used as such. Iodine

was resublimed and dried over P_2O_5. ICl (E Merck) was purified by usual method[10]. IBr and BrCl were prepared as given in literature[10]. All the solvents used in this study were purified as described in literature[11] given.

Preparation of the complexes : The complexes of α–picoline, β–picoline, lutidine, 2–bromopyridine and 2–chloropyridine with I_2, Br_2, ICl and IBr were prepared as described previously[12,13,14,15]. All the complexes were recrystallised from spectrograde methanol dried over vaccum desiccator and analyzed (Table–1).

Spectra : The infra–red spectra were recorded using an IR Perkin–Elmer Model 880 double beam spectrophotometer in the range 1200–200 cm^{-1}. The accuracy is ± 2 cm^{-1} (2000–200 cm^{-1}). For solutions, path–length of the cells varied from 0.02 to 0.11 mm.

RESULTS AND DISCUSSION

The solvents used in this study are not sufficiently strong donors to displace the substitute pyridines from the complex.

It is observed that the vibration, which are sensitive to the degree of electron transfer, move in the same direction through a series of environments of increasing polarity as they do in a series of complexes, where the acceptor strength increases. This is observed for ν_1 (ring) and ν_{6a} (X–sensitive) modes because these are the most sensitive modes of vibration of α–picoline, β–picoline, 2–bromopyridine, 2–chloropyridine and 2,5–dimethylpyridine. It is clear that the frequency shifts of these sensitive vibrations are definitely dependent upon a common factor and should, therefore, be directly related to each other.

Marked changes of frequency have been observed for other X–sensitive modes with the change of polarity of the solvents. The reason is that the polarity of the environment is obtained by plotting frequency shift of $\Delta\nu_1$ against $n^2–1/2n^2 + 1$ of the solvents (Fig.1), where n is the refractive index of the solvent used. Similar linear trend is also observed by plotting $\Delta\nu_1$ against $\varepsilon–1/2\varepsilon+1$. It is seen that smaller is the solvent shifts, the worse is the scatter of the experimental points. From the $n^2 –1/2n^2 + 1$ and $\varepsilon–1/2\ \varepsilon+ 1$ plots of same complex, it may be assumed that the simple theory of dipole–dipole interaction describes an effect, which is important for solvents of different polarity and polarizability functions and finally, which have got correlation with the frequency shift for a particular complex.

The variation of $\Delta\nu_1$ against S_m^{16} values of solvents for all the complexes has also been reported (Table 2). Here, we have observed that with increasing polarity, the frequency shifts ($\Delta\nu_1$) for all the complexes are greatly enhanced. This is expected only, when the ground state is more polar than the excited state.

Table 1.

Compounds	M.pt.°C	Total Halogen Content %	
		Calcd.	Found
β–pic–I_2	61.0	73.16	71.00%
α–pic–ICl	76.5	63.00	62.80%
α–pic–Br_2	69.0	63.20	60.50%
Lut–ICl	89.0	60.29	60.25%
Lut–IBr	83.0	65.92	65.70%
β–pic–ICl	56.5	63.00	62.30%
β–pic–IBr	62.5	69.00	68.80%
2–bromopy–ICl	121.0	50.70	50.10%
2–bromopy–IBr	81.0	56.70	56.00%
2–chloropy–ICl	81.0	60.00	59.80%

To get adequate explanation of solvent effect, finally the concept of linear solvation energy relations like $\nu = \nu_o + s\,\pi^*$ was used with usual significance of each term. In this study, a correlation is made of the π^* scale of solvent polarities with the infra–red frequency shift for most of the sensitive modes of the donors on complex formation with the acceptors. Some excellent correlation's have been observed between the frequency shift of ν_{6a} modes of the donors with π^* scale of solvent polarities (Fig. 2). In all the cases of solvents rights from extremely non–polar solvent like C_6H_6 to polar solvent like CH_2Cl_2, the ν_{6a} modes of the donors shows adequate response to changing to higher frequency region. It is also observed from the Table 3 that the value of 's' is always positive, which may probably be due to the fact that the ground state

Table 2

Solvents	$\frac{\varepsilon - 1}{2\varepsilon + 1}$	$\frac{n^2 - 1}{2n^2 + 1}$	$5 + S_M$	$\Delta\nu_1$ of the complexes, cm^{-1}					
				β–pic–ICl	β–pic–IBr	Lut–ICl	Lut–IBr	2-bromo-py–ICl	2-bromo-py–IBr
CH_2Cl_2	0.420	0.170	4.447	32	29	20	17	17	15
$CHCl_3$	0.356	0.209	4.114	29	27	18	15	16	14
C_6H_6	0.220	0.227	3.255	28	26	17	14	15	13
CS_2	0.261	0.261	2.398	25	24	15	15	14	12

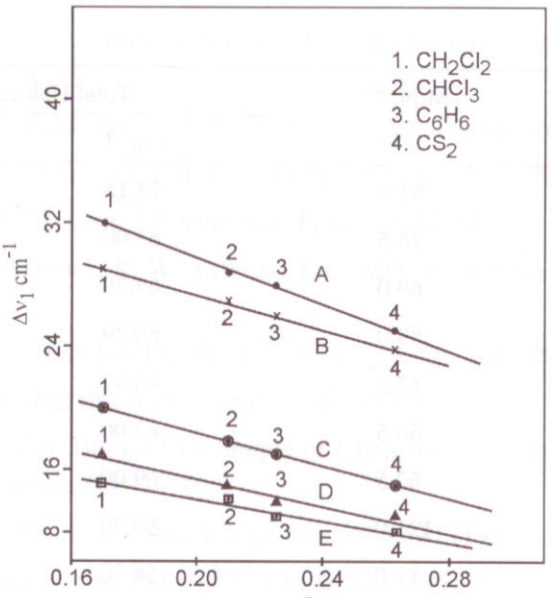

Fig. 1. Plot of $\frac{n^2-1}{2n^2+1}$ against $\Delta\nu_1$ of Complexes

A = β–pic–ICl; B = β–pic–IBr; C = Lut–ICl; D = Lut–IBr and E = 2–bromopy – IBr

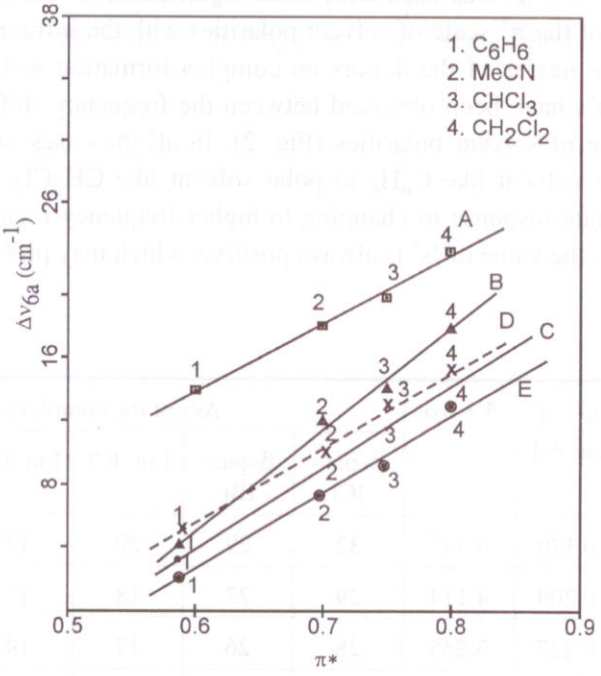

Fig. 2. Plot of π^* values of solvents against $\Delta\nu_{6a}$ of complexes :

A = β–pic–I_2 ; B = α–pic–ICl; C = α–pic–Br_2; D = Lut – ICl; E = Lut – IBr

polarity of the complexes increases with the increasing values of π^* of the solvents, the frequency shift increase and the solvation effects on ground state of the complexes definitely depend on both polarity and polarizability terms.

Table 3

Solvents	π* of Solvents	Compounds	$\Delta\nu_{6a}$ (cm^{-1})	s
CH_2Cl_2	0.802	β–pic–I_2	23	28.6
		α–pic–ICl	18	22.4
		α–pic–Br_2	14	17.4
		Lut–ICl	15	18.7
		Lut–IBr	13	16.0
$CHCl_3$	0.760	β–pic–I_2	20	26.3
		α–pic–ICl	14	18.4
		α–pic–Br_2	12	15.8
		Lut–ICl	13	17.1
		Lut–IBr	9	11.8
MeCN	0.713	β–pic–I_2	18	25.2
		α–pic–ICl	12	16.8
		α–pic–Br_2	9	12.6
		Lut–ICl	10	14.0
		Lut–IBr	7	9.67
C_6H_6	0.588	β–pic–I_2	14	23.8
		α–pic–ICl	4	6.8
		α–pic–Br_2	3	5.1
		Lut–ICl	5	8.5
		Lut–IBr	2	3.4

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