INTERMOLECULAR INTERACTIONS IN HOMOGENEOUS SOLUTIONS

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Abstract

Intermolecular interactions in liquid solutions are evidenced by the spectral shifts of the electronic spectra of homogeneous solutions in which spectrally active molecules are used as sounds measuring the intensity of the internal field of forces. Some pyridazinium ylids used as potential drugs were considered as spectrally active substances and the spectral shifts in binary and ternary solutions were measured in their electronic visible absorption spectra.The contribution of each type of intermolecular interactions was separated by using Bakhshiev theory of liquid homogeneoue solution. In influence of the chemical structure on the spectral shifts was evidenced.

Keywords: *intermolecular interactions, (p-chloro)-p-phenyl-pyridazinium benzoyl-methylid, (p-bromo)-p-phenyl-pyridazinium benzoyl –methylids.*

Introductions

The spectrally active molecules in liquid solutions can measure the strength of the intermolecular interactions by the modifications of their electronic spectra [Reichardt, 2003, Mc Rae, 1957]. In the theories regarding the solvent influence on the electronic spectra, the spectral shifts, $\Delta\bar{\nu}$ (expressed in cm^{-1}), recorded in a given solvent $\bar{\nu}_{solv.}$ related to the gaseous phase $\bar{\nu}_{vap.}$ of the spectrally active molecule;

$$(1) \quad \Delta\bar{\nu} = \bar{\nu}_{solv.} - \bar{\nu}_{vap.}$$

are correlated with physical parameters of the both solvent and spectrally active molecules. The total spectral shift in simple liquids is due to the orientation-induction ($\Delta\bar{\nu}_{orict-ind}$), polarization ($\Delta\bar{\nu}_{polar}$) and/or to the dispersion ($\Delta\bar{\nu}_{disp}$) interactions.

$$(2) \quad \Delta\bar{\nu} = \Delta\bar{\nu}_{orient.-ind.} + \Delta\bar{\nu}_{polar.} + \Delta\bar{\nu}_{disp.}$$

Bakhshiev [Bakhshiev, 1972] obtained the following expressions for each type of interactions:

$$(3)\quad \Delta\bar{\nu}_{orient.-ind} = \frac{2n^2+1}{n^2+2}\left[\frac{2\mu_g\left(\mu_g-\mu_e\cos\varphi\right)}{r^3}\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right)+\frac{\mu_g^2-\mu_g^2}{r^3}\frac{n^2-1}{n^2+2}\right]$$

$$(4)\quad \Delta\bar{\nu}_{polar.} = \frac{he^2 f}{8\pi m\nu_{00}r^3}\frac{n^2-1}{2n^2+1}$$

$$(5)\quad \Delta\bar{\nu}_{disp.} = \left(\alpha_g-\alpha_e\right)\left(\frac{3}{2r^3}\frac{II'}{I+I'}\right)\frac{n^2-1}{n^2+2}$$

In relations (3)-(5), n and ε are the refractive index and electric permittivity of the solvent, μ and α denominate the electric dipole moment and the polarizability in the ground (g) and in the excited (e) states of the spectrally active molecules, e and m are the charge and the mass of the electron, h is Planck constant, I and I' are the ionization potentials of the solvent and spectrally active molecules, f is the oscillator strength for the studied electronic transitions, ν_{00} is the wave number of the pure electronic transition and r is the mean radius of a spectrally active molecule.

Usually, for a great number of solvents, the ratio $\frac{2n^2+1}{n^2+2}$ is a number in the range 1.3-1.6. By considering this ratio as being a constant, independent on the solvent nature, the sum (2) of the terms (3), (4) and (5) can be re-written as separate terms representing orientation and inductive-polarization-dispersive interactions [Dorohoi, 2004, Pop 1994], especially when dipolar molecules are included in the liquid solutions.

Let be $f(\varepsilon)=\frac{\varepsilon-1}{\varepsilon+2}$ and $f(n)=\frac{n^2-1}{n^2+2}$ the ratios dependent on the solvent nature in relations (3)-(5). The wave numbers in the maxim of the electronic absorption band can be computed by using relation (6).

$$(6)\quad \nu_{calc.} = \nu_{vap.} + C_1 f(\varepsilon) + C_2 f(n)$$

The term $\nu_{vap.}$ has the significance of the wave number in the maximum of the electronic band in the vaporous state of the spectrally active molecule. The coefficients $\nu_{vap.}$, C_1 and C_2 can be obtained by a method of multi-parameter linear regression [Henrion, 1988] applied to the experimental data referring to the wave numbers, refractive index and electric permittivity measured in each solvent.

According to relations (1-5), the second term, $C_1 f(\varepsilon)$ in relation (6) gives the contribution of the orientation forces to the total spectral shift, and the third one, $C_2 f(n)$, gives the supply of the inductive-polarization-dispersive forces to the total spectral shift. The separation of the inductive, polarization and dispersive interaction supply from the total spectral shift is a difficult problem, because the theories express these interactions by the same function of the refractive index.

When the experimental values of the wave numbers in different solvents are plotted versus the calculated by formula (6) wave numbers, the deviations of the obtained points related to the first bisectrice give the spectral shifts due to the specific interactions[Pop, 1997, Dorohoi, 1993]. This type of interactions is neglected in the theory about the influence of the universal interactions on the electronic spectra [Reichardt, 2003, Mc Rae, 1957, Bakhshiev, 1972].

Pyridazinium ylids are cycloimmonium ylids having as cation a pyridazinium derivative [Zugravescu, 1966; Dorohoi, 1977; Dorohoi, 1994; Dorohoi, 2006].

All cycloimmonium ylids have a very sensitive to the solvent influence visible band attributed to an intramolecular charge transfer from the carbanion to the heterocycle [Dorohoi 2004, Zugravescu 1966; Dorohoi 2006] as in figure 2 is suggested.

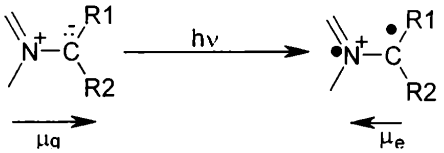

Fig. 2: Intramolecular charge transfer for visible absorption band of cycloimmonium ylids.

This band shifts to blue when an aprotic solvent is substituted by a protic one, or one non-polar solvent is substituted by a polar one. This band disappears in acid solutions in which the lone pair electrons of carbanion are blocked in the protonation process.

Experimental

The studied ylids differ by the chemical structure of the cation substituents. The carbanion substituents are listed in table 1.

Table 1: Chemical structure of the studied pyridazinium ylids

Ylid	Cation	R_1	R_2
Y_1	p-chloro-p-phenyl-pyridazinium	Hydrogen	Benzoyl
Y_2	p-bromo-p-phenyl-pyridazinium	Hydrogen	Benzoyl

A Specord UV-VIS spectrophotometer was used for spectra recordings. The refractive index and the electric permittivity of each solvent were measured as it is shown in [Pop, 1997, Dorohoi, 1993].

The electronic spectra of the studied pyridazinium ylids in ethanol solutions and in ethanol solutions with propionic acid (ylid/acid was mole/mole) are given in figure 3.

The wavenumbers of the electronic absorption spectra of the studied compounds were correlated with the solvent parameters.

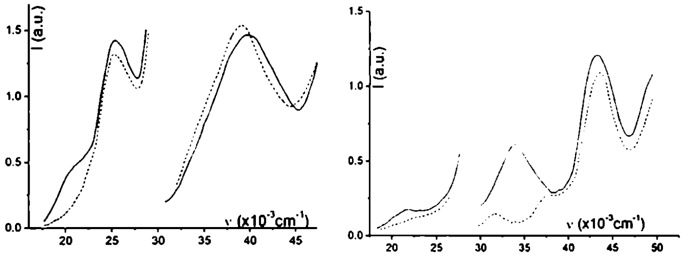

Fig. 3: UV VIS spectra of some cycloimmonium ylids in ethanol. a) p-(p-chloro-phenyl)-pyridazinium-benzoylmethylid ;b) p-(p-bromo-phenyl)-pyridazinium-benzoylmethylid; dotted line corresponds to the same solution with propionic acid

From figure3 it results the disappearance of the charge transfer electronic absorption bands in the presence of the propionic acid.

Results and Discussions

If the general theory of universal interactions is used, a relation of the type (6) permits to obtain by a multi-parameter regression [Henrion, 1988], the values of the coefficients $\nu_{vap.}$, C_1 and C_2 on the basis of the experimental data. The results obtained in this study are given in relations (7) - (8).

$$(7)\quad \nu_1 = 21730 + 615\frac{\varepsilon - 1}{\varepsilon + 2} + 5258\frac{n^2 - 1}{n^2 + 2}$$

$$(8)\quad \nu_1 = 21030 + 614\frac{\varepsilon - 1}{\varepsilon + 2} + 3639\frac{n^2 - 1}{n^2 + 2}$$

Table 2: Supply in cm^{-1} of different type of interactions in the absorption spectrum of the studied pyridazinium ylids

Type of interaction	Benzene		Acetone	
	Y_1	Y_2	Y_1	Y_2
$C_1f(\varepsilon)$ (orientation)	184	184	533	533
$C_2f(n)$ (induction-dispersion)	1551	1073	1167	808

In table 2 the supply of each type of interactions is given for the studied spectrally active molecules. It results that in a non-polar solvent (benzene) the dispersive-induction-polarization interactions are prevalent, while, in a polar solvent (acetone), the orientation interactions become more important for the total spectral shift measured in ylid solutions.

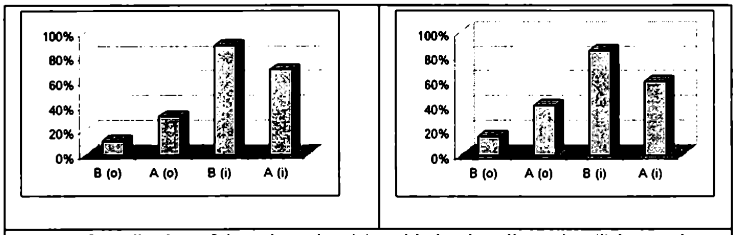

Fig. 4: Contribution of the orientation (o) and induction-dispersive (i) interactions in benzene (B) and acetone (A)

In figure 4 the considered solvents were benzene (B) and acetone (A). The contribution of orientation interactions was denominated by "o" and the induction-dispersive interactions by "i".

A great supply has the induction dispersive interactions in benzene for the both ylids. The smallest contribution was determined for the orientation interactions in benzene.

Conclusions

The existent theories regarding the solvent influence on the electronic absorption spectra of organic compounds neglect the specific interactions; consequently in the case of the spectrally active molecules with proton acceptor character, a supplemental term must be introduced for the protic solutions in which the specific interactions have an important role.

For these cases a term proportional with the proton degree of freedom in OH bond must be added to the terms describing the supply of the universal interactions in solutions of the proton acceptors spectrally active molecules.

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