

Spectral Investigations of the Influence of the Hydroxyl Solvents on the Intermolecular Interactions in Some Pyridinium Ylid Ternary Solutions

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Intermolecular interactions influence the distribution of the valence electron cloud in the spectrally active molecules causing frequency shifts in their electronic absorption and/or fluorescence spectra. In this study, spectral investigations on chemical complexes formed by hydrogen bond between the molecules of pyridinium ylid and binary solvent molecules (mixture of water and ethanol) are carried out. The long range interactions between the binary solvent and complexes formed by ylid molecules, water and ethanol are characterized using the solvatochromic effect.

Keywords: pyridinium ylids, electronic absorption spectra, water-ethanol binary solvent, hydrogen bond complexes

In the ground electronic state, ylids [1-3] are organic zwitterionic compounds with separated opposite charges on atomic groups. N-ylids have Nitrogen as positive molecular part. They are named pyridinium ylids when Nitrogen belongs to the pyridinium heterocycle. Nitrogen loses its fifth electron becoming positively charged, while the carbanion has an orbital uninvolved in a covalent bond, occupied by an electron pair (one from the two electrons being lost by the Nitrogen).

Pyridinium ylids were firstly synthesized by Krollpfeiffer and Muller [4] and by Kröhnke [5]. They can be [1, 2] carbanion mono- or di- substituted (fig.1) when the two covalent bonds of carbanion are satisfied by a hydrogen atom and by an electron withdrawing atomic group, or by two electron withdrawing atomic groups, respectively.

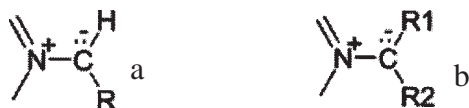


Fig.1 Carbanion monosubstituted (a) and disubstituted (b) pyridinium ylids

In the NMR spectra of some carbanion mono-substituted cycloimmonium ylids, the chemical shifts δ (ppm) of the proton bond to the ylid carbanion is in the range of 7.0-7.2 ppm, sometimes giving large signals [6-9]. For pyridinium ylid molecules [6], this fact proves the formation of a hydrogen intramolecular bond between the carbanion substitute and hydrogen from the heterocycle located near the nitrogen atom.

Pyridinium ylids have specific IR [2], visible [2, 6, 9] or NMR [6, 9] spectra. The specificity of the electronic absorption spectra of pyridinium ylids and their changes induced by the solvent action are important in the establishing of some structural features.

FT-IR spectroscopy is a valuable tool for the investigation of the delocalization degree of the electronic charge on the carbanion substitutes [2, 9]. From the IR spectra of pyridinium ylids it results that the IR band corresponding to the stretching vibrations of the $-C=O$ group attached to the carbanion shifts toward the smaller frequencies when

the electronegativity of the carbanion substitutes increases, proving a larger delocalization of the negative charge on the ylid carbanion [2].

Pyridinium ylids [2, 6-9] have an intense absorption bands in UV spectrum due to $\pi \leftrightarrow \pi^*$ transitions and a low intense band in the visible range. The visible band of pyridinium ylids [6, 10-12] was explained by the intramolecular charge transfer (ICT) transition from the carbanion to the heterocycle. The ICT visible band of pyridinium ylids shifts to blue in protic solvents, proving the presence of the specific interactions with the protons of the solvent molecules and even disappears in acids which block the non-participant electron-pair of the ylid carbanion.

According to [6], the ICT mechanism induced by light action could be schematically explained by figure 2.

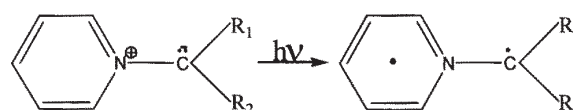


Fig.2 The mechanism of the ICT process

After the light absorption, the electronic charge density from the carbanion diminishes and the negative charge is shifted to the heterocycle. The visible ICT band belongs to a $n \rightarrow \pi^*$ type transition.

In solutions, the molecules of pyridinium ylids can participate to universal (long-range) interactions of dipolar or dispersive types. Additionally, in protic solvents, they participate to specific (quasichemical) interactions. The strength of the intermolecular interactions between the ylids and the solvent molecules depends on the degree of electronic charge delocalization on the ylid carbanion [12] and also on the solvent nature.

In the light absorption process, the electric dipole moment of the ylid molecule diminishes and the strength of interactions with the solvent molecules becomes weaker in the excited state in comparison with the ground electronic state. The visible ICT electronic absorption band of pyridinium ylids has a low intensity, disappears by protonation process and shifts to blue in the protic solvents [6, 12, 16].

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Table 1
CHEMICAL STRUCTURE OF THE STUDIED PYRIDINIUM YLIDS

Ylid	-R ₁	-R ₂	Denomination
Y ₁	COCH ₃	COC ₆ H ₅	Acetyl- Benzoyl- Pyridinium Methylid
Y ₂	CO ₂ C ₂ H ₅	CONHC ₆ H ₅	Carbetoxy-Anilido-Pyridinium Methylid
Y ₃	COC ₆ H ₅	COC ₆ H ₅	Di-Benzoyl-Pyridinium Methylid

Usually pyridinium ylids are used in situ and the knowledge about their interactions with solvents are very important. Studies about the solvent influence on the electronic spectra allow us to estimate some electro-optical parameters of the studied molecules.

The electronic absorption spectra of the dipolar compounds, such as the pyridinium ylids can be used in estimation of the solvent polarity [6, 10, 12] or of the solvent electric permittivity due to the hipsochromic shift induced in these kind of spectra by the orientation interactions. Recently, the pyridinium ylids were used to establish the composition of the first solvation sphere in ternary solutions, due to the high sensitivity to the solvent action of their visible electronic absorption band [13].

In this paper, spectral investigations of some pyridinium ylids molecules in a binary solvent consisting of a mixture of water and ethanol with different concentration are presented.

Experimental part

The binary solvent was prepared using double distilled water and spectrally grade Merck ethanol, deduced volumetrically and then the molar fraction of ethanol (x_e) was computed.

The pyridinium ylids studied in this paper are: acetyl-benzoyl-pyridinium methylid (Y₁); anilido-carbetoxy-pyridinium methylid (Y₂) and di-benzoyl pyridinium methylid (Y₃). The chemical structures of the spectrally active ylids are given in table 1.

Pyridinium ylids were prepared after known procedures [2, 5]; their structure and purity being confirmed by NMR and FT-IR spectra.

The visible spectra of the pyridinium ylids were recorded using a Specord UV VIS Carl Zeiss Jena spectrophotometer with data acquisition system. The wavenumber in the maximum of the ICT absorption band (expressed in cm⁻¹) was measured in binary solvent water-ethanol with a variable content in ethanol (expressed by the molar fraction x_e).

The ylid concentration in the ternary solutions was of about 10⁻⁴ mol / L. A Mettler MDB-5 balance ($\pm 10^{-5}$ g) was used for mass determination.

Results and discussions

Our previous studies [10, 16] of the binary solutions of Y₁, Y₂ and Y₃ ylids emphasized the presence of orientation-induction interactions in aprotic solvents and the presence of the specific interactions of the proton change type in the protic solvents. These facts were demonstrated by the presence of two curves in the plane ($\bar{\nu}(cm^{-1}), \epsilon$), where ϵ is the electric permittivity of the solvent. It was also proved the linear dependence between the wavenumber in the maximum of the ICT band $\bar{\nu}(cm^{-1})$ and the function $f(\epsilon) = \frac{\epsilon-1}{\epsilon+2}$. Such relationship suggests the presence of universal interactions in the cycloimmonium ylids and consequently, in piridinium ylids solutions [17-19].

In the plot showing the correspondence between the computed versus the experimental values of the wavenumbers in the maximum of the ylid ICT absorption band, the points corresponding to the aprotic solvents are in the vicinity of a line and points corresponding to protic solvent in the vicinity of a new line; the distance between the two line could be considered as a measure of the specific interactions strength [10, 16]. For two protic solvents with similar values of the refractive index (as water-ethanol mixtures), the dependence of $\bar{\nu}(cm^{-1})$ on the solvent electric permittivity, ϵ , evidenced the orientation type interactions of the complexes formed by hydrogen bond with the solvent molecules [12]. Consequently, for mixtures of water and ethanol in various molar fractions, only the orientation interactions produce the solvatochromism.

In this study we analyze the dependence between the wavenumbers in the maximum of ICT absorption band and the molar fraction of ethanol x_e in the binary solvent ethanol-water for three types of ylids.

Figures 3-5 present the dependences between the experimental data of the wavenumbers in the maximum ICT visible band spectra and the molar fraction of ethanol for each of the studied pyridinium ylids. Data on each graph are linear fitted (in the first approximation) by two solid lines, generically expressed by the equation:

$$\bar{\nu}(cm^{-1}) = A + B \cdot x_e \quad (1)$$

One can observe that for all of the investigated ylids, the changes of the slope of the linear dependencies take place in the vicinity of a critical value of the ethanol molar concentration, the same for all three ylids ($x_e \approx 0.78$). The slopes and the cuts to origin of the line segments are listed in table 2.

We consider that the changes in the slopes and the cuts at origin of the lines (1) are probably induced by a dominant influence of the water-ylid complexes for small ethanol molar fractions and of ethanol-ylid complexes for high molar fractions of ethanol.

From the slope values in equation (1) (table 2), it results a greater sensitivity to the solvent (considered a continuous dielectric) of the ethanol-ylid compared to the water-ylid complexes. The wavenumber in the maximum of the ICT band is larger for ethanol-ylid complexes in comparison with that in the water-ylid complexes. We suppose that the proton transfer must be interpreted as a probabilistic process in which the weak hydrogen bond can be formed and destroyed by thermal collisions, because the formation energy of the hydrogen bond formation is comparable to the thermal motion energy.

The free term in equation (1) is smaller for the binary solvent with water -ylid dominant complexes, while, in the case of ethanol-ylid dominant complexes this term is higher. Probably, the formation energy for the water-ylid

Table 2
REGRESSION COEFFICIENTS FROM EQUATION (1) AND THEIR DEVIATIONS,
CORRELATION COEFFICIENT -R, STANDARD DEVIATION-SD, NUMBER OF
POINTS -N AND PRECISION-P

PY	x_e	$A \pm \Delta A$	$B \pm \Delta B$	R	SD	N	P
Y1	$x_e > 0.78$	31186.49 ± 314.43	-4448.99 ± 351.28	0.991	58.44	5	0,0011
	$x_e < 0.78$	28480.34 ± 26.27	-1156.28 ± 78.19	0.967	75.49	17	0,0001
Y2	$x_e > 0.78$	27035.60 ± 201.54	-2674.26 ± 225.16	0.989	37.46	5	0.0013
	$x_e < 0.78$	25412.42 ± 5.75	-645.78 ± 17.11	0.995	16.52	17	0.0001
Y3	$x_e > 0.78$	28024.20 ± 146.71	-3068.77 ± 163.90	0.996	27.27	5	0.0003
	$x_e < 0.78$	26419.02 ± 5.92	-1099.47 ± 17.63	0.998	17.02	17	0.0001

complexes is higher than the formation energy for the ethanol-ylid complexes.

The changes in the slopes of the lines (1) could be explained by the replacement of the complexes ylid-water

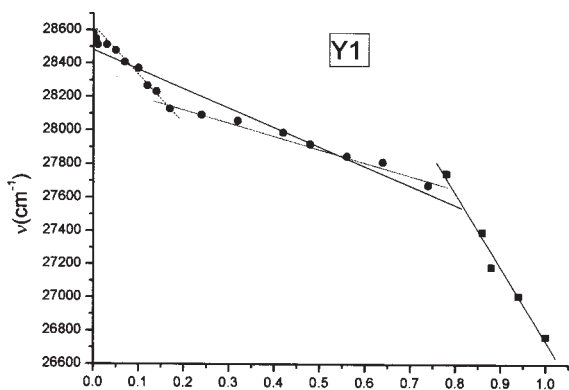


Fig. 3. $\bar{\nu}(\text{cm}^{-1})$ vs. x_e for Y_1

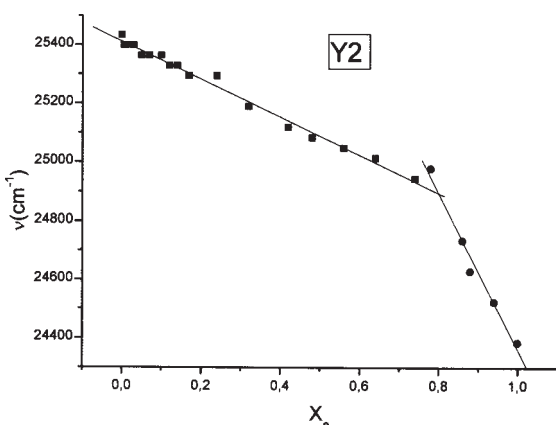


Fig. 4. $\bar{\nu}(\text{cm}^{-1})$ vs. x_e for Y_2

(formed in the very small quantities of ethanol), by complexes of the type ylid-ethanol in binary solvent with high concentrations of the alcohol.

A more detailed study of the data in the first region in figure 3 (lower values of concentration) shows that the one can do two more linear fitting of the data in this region. The new lines are plotted as broken lines. Consequently, for the case of ylid Y_1 one can see three line segments of different slopes. The segment line from the central region shows a different slope from those in the regions with small

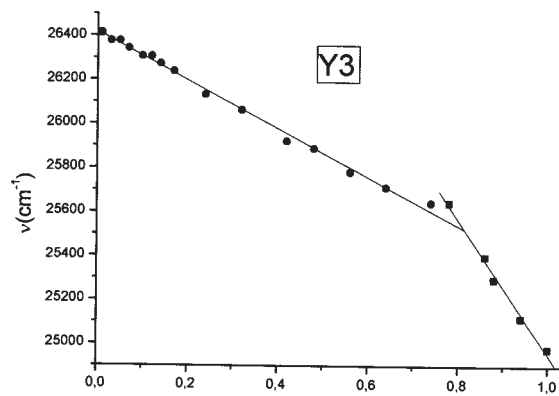


Fig. 5. $\bar{\nu}(\text{cm}^{-1})$ vs. x_e for Y_3

and high content in alcohol. Since in this region the ICT band is very large, one can suppose the presence of a mixture of complexes of two types: ylid-water and ylid-ethanol in the ternary solution.

In the plots of the ICT wavenumbers versus the ethanol molar concentrations, for the ylids Y_2 and Y_3 only two regions can be observed. It results that in these cases, for $x_e < 0.78$, differences between the complex sensitivities of water-ylid and of the mixtures water-ylid and ethanol-ylid are not reflected in the ICT band positions.

In the binary mixture of the hydroxyl solvents, molecules of ylids participate in a continuous exchange of protons both with water molecules and with ethylic alcohol (weak hydrogen bonds, with the energy of formation comparable with the thermal motion energy). Consequently, the solvatochromic effect of the solvent on the ICT visible band spectra evidences the universal interactions between the binary solvent (acting as a homogenous dielectric) and the newly formed chemical complexes.

Conclusions

The ability of the protic solvent molecules to form chemical complexes by hydrogen bond with pyridinium ylids plays an important role in the stabilization process of these zwitterionic molecules. The spectral investigations of the ICT absorption band for three types of pyridinium ylid ternary solution shows the following results. There is a linear piecewise relationship between the wave number in the maximum of ICT absorption band and the molar fraction in the binary solvent water-ethanol. The change in the slope takes place at the same critical value of the ethanol molar fraction for each of the three investigated ylids. Unfortunately, the electron spectra do not offer

enough information to determine the bonding energy and some quantum mechanical calculations become necessary.

Studies of this type can offer information on the nature of the chemical complexes formed between the molecules of pyridinium ylid and a binary solvent molecules as well as supplementary data on the dependences of their electro-optics parameters in a binary solvent with variable ethanol concentration [20-24].

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