Spectral Study of Two Carbanion Mono-substituted 4’-phenyl-1,2,4-triazol-1-ium Phenacylids in Binary Protic Solvents

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Abstract: The visible electronic absorption band of two 4’-phenyl-1,2,4-triazol-1-ium phenacylids was studied in two binary solvents: water (1) + ethanol (2) and water (1) + methanol (2) with variable content in water. The nature and the contribution of the intermolecular interactions to the spectral shifts in ternary solutions of the studied ylids were estimated based on the Kamlet Taft parameters (π*, α and β) previously measured by Buhvestov and all. The influence of the universal and specific interactions on the visible electronic band of the studied ylids depends on the water concentration in binary solvent. At small water concentrations in binary solvent, the hydrogen complexes of the type ylid-alcohol are predominant, while at high water concentrations, the complexes made by hydrogen bonds between water and ylid molecules prevail. The difference between the energies corresponding to molecular pairs of the types: ylid-water and ylid-alcohol was estimated based on the statistic cell model of the ternary solutions.

Keywords: 1,2,4-triazol-1-ium phenacylids; Kamlet Taft parameters; intermolecular interactions in ternary protic solutions of ylids; cell model of ternary solutions

1. Introduction
Triazol-1-ium ylids are dipolar and polarizable molecules with opposite charges separated on the positive nitrogen belonging to the triazolium ring and on a negatively charged carbon, named carbanion and covalently bonded to two substituents [1-3]. In the carbanion mono-substituted ylids, one from the substituents is hydrogen atom and the second is an electronegative atomic group, while in those carbanion di-substituted the both electron withdrawing substituents assure more stability of these compounds.

Triazolium ylids are used as precursors in obtaining new heterocycle derivatives [3,4] with important applications in pharmaceutical industry. Pharmacological activity, clinical implications, efficiency and costs of triazolium agents are reflected briefly in the review published by Flori [5] and their biological applications are underlined in a multitude of publications [6-10]. For example, some triazolium derivatives were tested [11] against a panel of positive and negative Gram bacteria and Candida albicans, showing good or moderate activities. Many 1,2,4 triazolium derivatives exhibit antimicrobial [11], antifungal [5] antitumor [12] anti-inflammatory [11], analgesic [6], diuretic [9] properties and so on.

All reactions of triazolium derivatives are made in situ. So, knowledge about their interactions with the liquids in which are solved are of a great importance. Previous studies give some conclusions regarding intermolecular interactions in 1,2,4-triazolium ylids in solutions [13-15] and also in other cyclomimonium ylid solutions [16,17], based on the visible electronic absorption band of these compounds which is very sensitive to the solvent nature. They emphasized the presence of the universal interactions in a-protic solvents and supplementary of the specific interactions in the protic solvents [16]. The spectral study in different solvents with various physical-chemical properties becomes very difficult due to the small solubility of triazolium ylids. Some researches regarding the ternary solutions of

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1,2,4 triazolium ylids in protic and aprotic solvents established correlations between the energies in molecular pairs of the types ylid-protic solvent and ylid-aperotic solvent molecules [13,14].

Now, in this study, one uses a binary solvent composed by water and one alcohol (ethanol, or methanol) in order to study the difference between the strength of the hydrogen bond made between the studied ylids and hydroxyl solvents and to characterize the composition of the first solvation shell formed around the complex realized by hydrogen bond. This quantitative study became possible due to the measurement of the binary solvent parameters at different compositions by Buhvestov and all [18].

Water and ethanol are non-toxic biological liquids due to their physical and chemical properties. This paper deals with the spectral study of ternary solutions of 1,2,4 triazolium ylids in binary solvents water (1) + ethanol (2) of different molar concentrations. The binary solvent water (1) + methanol is used here for comparison reasons, having in view the similar properties of the two alcohols. The nature and the strength of the intermolecular interactions in the ternary solutions of the types: ylid + water (1) + ethanol (2) and ylid + water (1) + methanol (2) are established based on LERS analysis of the spectral data with Kamlet Taft binary solvent parameters previously determined by Buhvestov and all [18,19].

Supplementary information regarding the contribution of the specific interactions in the ternary solutions are added to the previous results obtained in the study of the influence of the binary solvent containing one protic and one non-protic solvent and some cycloimmonium ylids [14-17].

The contribution of each type of intermolecular interactions on the wavenumber of the visible band of two triazolium methylids is now estimated for the case of binary protic solvents.

The statistic cell model of ternary solutions [20-23] developed for spectral data was used to estimate the difference between the interaction energies in molecular pairs of the types: ylid-water (1) and ylid–ethanol (2) and also ylid-water (1) and ylid–methanol (2).

The interaction energy between two molecules is very difficult to be estimated by other methods and the cell model of the ternary solutions allows to estimate it. The difference between the potential energies in molecular pairs formed by the spectrally active molecules (triazol-1-iium methylid) with the hydroxyl solvents permits a comparison between the strength of the specific interactions in the two types of protic solvents.

2. Materials and methods

Two carbanion mono-substituted 1,2,4-triazol-1-iium phenacylids, namely 4’-phenyl-1,2,4-triazol-1-iium phenacylid (PTPY) and 4’-phenyl-1,2,4-triazol-1-iium-4’’-nitro-phenacylid (PTNPY) were studied in the two binary solvents obtained by mixing in molar fractions water with ethanol, respectively with methanol.

The ylids were prepared by the salt method [2-4] and purified as it is described in [2]. Their purity was checked by elemental analysis and their structure as clarified by spectral (IR and NMR) means.

The spectrally grade alcohols (ethanol and methanol) were purchased from Merck Company. Initially they were used without purification. Bi-distilled water was obtained in our laboratory.

The weightings were made at a Mettler MDB-5 balance (±10^−5 g).

The visible electronic absorption spectra of the ternary solutions were recorded at a Specord UV Vis Carl Zeiss Jena spectrophotometer with data acquisition system having the accuracy of about ±0.5 cm^−1.

The wavenumber (expressed in cm^−1) in the maximum of the visible electron absorption band of ylids was measured in each binary solvent achieved in molar fractions with a step of 0.05. The ternary solutions were carefully prepared and measurements were repeated twice.

The binary solvents parameters and the wavenumbers in the maximum of the visible band of 1,2,4-triazolium ylids are listed in Tables 1 and 2.

3. Results and discussions

As all cycloimmonium ylids, 1,2,4-triazol-1-iium ylids show a visible electronic absorption band of low intensity, attributed to an intramolecular charge transfer (ICT) [14,24,25] from the carbanion towards the heterocycle and sensitive to the solvent nature.
Using the binary solvent Kamlet Taft parameters determined by Buhvestov and all. [17] for water (1) + ethanol (2) and water (1) + methanol (2), a multilinear correlation of the type (1) between the wavenumber in the maximum of the ICT visible electronic absorption band of the studied ylids and the solvent parameters: dipolarity/polarizability indicator ($\pi^*$), hydrogen-bond donor acidity ($\alpha$), hydrogen bond acceptor basicity ($\beta$), has been made.

$$\bar{\nu}(cm^{-1}) = \nu_0 + C_1\pi^* + C_2\alpha + C_3\beta$$  \hfill (1)

The regression parameters of relation (1), established using ORIGIN 08 and the data from Tables 1 and 2, are given in Table 3. The regression coefficients in relation (1) give information about the intermolecular interactions in the studied solutions. The sign and magnitude of the coefficients $C_1 - C_3$ (expressed in $cm^{-2}$) inform about the sense and the magnitude of the spectral shifts recorded in the ternary solutions of ylids. The free term $\nu_0$ signifies the wavenumber of the studied electronic absorption band in vacuum. The values of these coefficients are listed in Table 3. All regression coefficients are positive, excepting $C_2$ for the case of ternary solutions water (1) + ethanol (2) + PTPY. As it results from this assertion, the wavenumber in the maximum of the visible electronic absorption band increases with the water content in the binary solvent.

### Table 1. Molar water composition ($x_1$), parameters ($\pi^*$, $\beta$, $\alpha$) of binary solvent water (1) + ethanol (2) [18] and wavenumbers ($\nu$ $cm^{-1}$)) in the maximum of the visible electronic absorption band of ylids (PTPY and PTNPY)

| Nr. | $x_1$ | $\pi^*$ | $\beta$ | $\alpha$ | $ln\frac{x_1}{1-x_1}$ | $\nu$ $cm^{-1}$ | $ln\frac{p_1}{1-p_1}$ |
|-----|-------|---------|---------|----------|------------------------|-----------------|-----------------------|
|     |       |         |         |          |                        |                 |                       |
| 1   | 0.000 | 0.51    | 0.33    | 0.98     | -                      | 25620           | 26720                 |
| 2   | 0.050 | 0.54    | 0.33    | 0.97     | -2.94                  | 25625           | 26730                 |
| 3   | 0.100 | 0.57    | 0.34    | 0.96     | -2.20                  | 25640           | 26740                 |
| 4   | 0.150 | 0.60    | 0.33    | 0.94     | -1.74                  | 25652           | 26750                 |
| 5   | 0.200 | 0.63    | 0.33    | 0.93     | -1.39                  | 25665           | 26760                 |
| 6   | 0.250 | 0.65    | 0.33    | 0.93     | -1.10                  | 25680           | 26770                 |
| 7   | 0.300 | 0.68    | 0.32    | 0.92     | -0.83                  | 25690           | 26780                 |
| 8   | 0.350 | 0.70    | 0.31    | 0.91     | -0.52                  | 25700           | 26800                 |
| 9   | 0.400 | 0.73    | 0.30    | 0.90     | -0.41                  | 25720           | 26815                 |
| 10  | 0.450 | 0.75    | 0.29    | 0.89     | -0.20                  | 25730           | 26830                 |
| 11  | 0.500 | 0.77    | 0.29    | 0.90     | 0.00                   | 25752           | 26850                 |
| 12  | 0.550 | 0.80    | 0.28    | 0.89     | 0.20                   | 25760           | 26870                 |
| 13  | 0.600 | 0.82    | 0.27    | 0.89     | 0.41                   | 25778           | 26890                 |
| 14  | 0.650 | 0.85    | 0.26    | 0.89     | 0.62                   | 25792           | 26910                 |
| 15  | 0.700 | 0.89    | 0.25    | 0.89     | 0.80                   | 25815           | 26930                 |
| 16  | 0.750 | 0.92    | 0.24    | 0.88     | 1.00                   | 25830           | 26940                 |
| 17  | 0.800 | 0.97    | 0.23    | 0.87     | 1.19                   | 25850           | 26960                 |
| 18  | 0.825 | 1.00    | 0.22    | 0.87     | 1.39                   | 25860           | 26970                 |
| 19  | 0.850 | 1.03    | 0.21    | 0.86     | 1.57                   | 25865           | 26970                 |
| 20  | 0.875 | 1.06    | 0.20    | 0.87     | 1.75                   | 25865           | 26970                 |
| 21  | 0.900 | 1.11    | 0.19    | 0.86     | 1.94                   | 25865           | 26970                 |
| 22  | 0.925 | 1.12    | 0.18    | 0.86     | 2.12                   | 25865           | 26970                 |
| 23  | 0.950 | 1.13    | 0.17    | 0.86     | 2.31                   | 25865           | 26970                 |
| 24  | 0.975 | 1.13    | 0.16    | 0.86     | 2.50                   | 25865           | 26970                 |
| 25  | 1.000 | 1.13    | 0.15    | 0.86     | 2.70                   | 25865           | 26970                 |

### Table 2. Molar water composition ($x_1$), parameters ($\pi^*$, $\beta$, $\alpha$) of binary solvent water (1) + methanol (2) [18] and wavenumbers ($\nu$ $cm^{-1}$)) in the maximum of the visible electronic absorption band of ylids (PTPY and PTNPY)

| Nr. | $x_1$ | $\pi^*$ | $\beta$ | $\alpha$ | $ln\frac{x_1}{1-x_1}$ | $\nu$ $cm^{-1}$ | $ln\frac{p_1}{1-p_1}$ |
|-----|-------|---------|---------|----------|------------------------|-----------------|-----------------------|
|     |       |         |         |          |                        |                 |                       |
| 1   | 0.000 | 0.58    | 0.74    | 1.14     | -                      | 25640           | 26810                 |
| 2   | 0.050 | 0.61    | 0.74    | 1.13     | -2.94                  | 25645           | 26820                 |
| 3   | 0.100 | 0.64    | 0.74    | 1.12     | -2.20                  | 25650           | 26828                 |

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The spectral shifts measured in the studied ternary solutions are not so great, because the both liquids composing the binary solvent are protic solvents and specific interactions between the solvents and between them and the solute are possible. In the mixtures of hydroxyl liquids the specific interactions can modify their action on the solute molecules by their improved structure [18, 19] due to hydrogen bonds acting between water, alcohol or between water-alcohol. The spectral data from Tables 1 and 2 offer the possibility estimating the strength of the intermolecular interactions of the studied ylids with the liquids composing the binary solvent.

**Table 3. Regression parameters in relation (1) for the studied ternary solutions**

| Solvent         | Ylid   | $\nu_0 + \Delta \nu_0$ | $C_1 \pm \Delta C_1$ | $C_2 \pm \Delta C_2$ | $C_3 \pm \Delta C_4$ |
|-----------------|--------|------------------------|-----------------------|-----------------------|-----------------------|
| Water + Ethanol | PTPY   | 24680 ± 676            | 676 ± 54              | 413 ± 119             | 243 ± 47              |
| Water + Ethanol | PTPY   | 25381 ± 414            | 795 ± 128             | 668 ± 286             | 365 ± 112             |
| Water + methanol| PTPY   | 25839 ± 118            | 329 ± 32              | -601 ± 77             | 44 ± 37               |
| Water + methanol| PTNPY  | 26249 ± 201            | 526 ± 55              | 35 ± 131              | 197 ± 63              |

The contributions of the intermolecular interactions to the total spectral shift of the visible electronic absorption band of 1,2,3-triazolium ylids in the binary protic solvents used in this research are listed in Tables 4 and 5. Some differences between the actions of the two binary solvents on the ylid molecules can be emphasized based on the contribution (expressed in percentages) of each type of interaction on the total spectral shift, as it follows:

- In water (1) + ethanol (2) solvents, the universal interactions are predominant and their strength increases with the water molar fraction in liquid mixture;
- At small water molar concentrations, the contribution of the specific interactions is approximately 50% and it decreases (up to 40%) with increasing of the molar concentration of water in ternary solutions. The strength of specific interactions by hydrogen bonds and ylid molecules are proportional with the sum of the terms $C_3 \beta$ (for hydrogen bonds received by solvent molecules, HBD) and $C_4 \alpha$ (for hydrogen bonds received by ylid molecules, HBA).
- In water (1) + methanol (2) binary solvent, the specific interactions of PTPY (expressed by the term $C_4 \alpha$) are predominant (Table 4). They contribute to the total spectral shifts of the ylid electronic absorption band with 60-40%. The contribution of universal interactions in this binary solvent is between 28-52% and increases with the water molar fraction in binary solvent. The negative value of the term $C_3 \beta$ in relation (1) shows that in this binary solvent, the specific interactions in which the ylid molecules give protons for the hydroxyl molecules shift the visible electronic absorption band to smaller wavenumbers compared to the position of this band in aprotic solvents [13,14]. The formation of...
hydrogen bonds by ylid donating protons is of small probability and its influence on the spectral shifts is reduced to about 7%.

- In the case of ternary solutions water (1) + methanol (2) + PTNPY, the universal interactions determine the 55 -70% from the spectral shifts of the electronic absorption spectra of ylid. The specific interactions determine the rest of the spectral shifts; dominant being the hydrogen bond realized by ylid. The specific interactions determine the rest of the spectral shifts; dominant being the hydrogen bonds realized by ylid donating protons is of small probability and its influence on the spectral shifts is reduced to about 7%.

**Table 4.** Contribution of various types of interactions between the PTPY and binary solvent molecules to the total spectral shift recorded in each binary solvent after kamlet taft representation

| Nr. | $x_1$ | Water + Ethanol | Water + Methanol |
|-----|-------|-----------------|------------------|
|     |       | $C_1\pi^*$ | % | $C_2\alpha$ | % | $C_3\beta$ | % | $C_1\pi^*$ | % | $C_2\alpha$ | % | $C_3\beta$ | % |
| 1   | 0.000 | 37       | 37 | 26       | 28 | 65       | 6 |
| 2   | 0.050 | 39       | 36 | 25       | 29 | 64       | 7 |
| 3   | 0.100 | 40       | 36 | 24       | 30 | 63       | 7 |
| 4   | 0.150 | 42       | 35 | 23       | 30 | 63       | 7 |
| 5   | 0.200 | 43       | 34 | 23       | 32 | 61       | 7 |
| 6   | 0.250 | 44       | 34 | 22       | 33 | 61       | 6 |
| 7   | 0.300 | 45       | 33 | 22       | 34 | 60       | 6 |
| 8   | 0.350 | 46       | 33 | 21       | 35 | 59       | 6 |
| 9   | 0.400 | 47       | 32 | 21       | 36 | 58       | 6 |
| 10  | 0.450 | 47       | 31 | 21       | 37 | 57       | 6 |
| 11  | 0.500 | 49       | 31 | 20       | 38 | 56       | 6 |
| 12  | 0.550 | 50       | 30 | 20       | 40 | 54       | 6 |
| 13  | 0.600 | 51       | 29 | 20       | 41 | 53       | 6 |
| 14  | 0.650 | 52       | 29 | 19       | 42 | 52       | 6 |
| 15  | 0.700 | 54       | 27 | 19       | 44 | 50       | 6 |
| 16  | 0.750 | 56       | 26 | 18       | 45 | 49       | 6 |
| 17  | 0.800 | 58       | 24 | 18       | 46 | 47       | 6 |
| 18  | 0.825 | 59       | 23 | 18       | 47 | 46       | 7 |
| 19  | 0.850 | 60       | 22 | 18       | 48 | 45       | 7 |
| 20  | 0.875 | 61       | 21 | 18       | 49 | 44       | 7 |
| 21  | 0.900 | 61       | 20 | 19       | 49 | 44       | 7 |
| 22  | 0.925 | 61       | 19 | 20       | 50 | 43       | 7 |
| 23  | 0.950 | 60       | 18 | 22       | 50 | 43       | 7 |
| 24  | 0.975 | 60       | 17 | 23       | 50 | 42       | 8 |
| 25  | 1.000 | 59       | 17 | 24       | 52 | 41       | 8 |

**Table 5.** Contribution of various types of interactions between the PTNPY and binary solvent molecules to the total spectral shift recorded in each binary solvent after kamlet taft representation

| Nr. | $x_1$ | Water + Ethanol | Water + Methanol |
|-----|-------|-----------------|------------------|
|     |       | $C_1\pi^*$ | % | $C_2\alpha$ | % | $C_3\beta$ | % | $C_1\pi^*$ | % | $C_2\alpha$ | % | $C_3\beta$ | % |
| 1   | 0.000 | 31       | 43 | 26       | 55 | 40       | 5 |
| 2   | 0.050 | 33       | 42 | 25       | 56 | 39       | 5 |
| 3   | 0.100 | 34       | 42 | 24       | 58 | 38       | 4 |
| 4   | 0.150 | 35       | 41 | 24       | 59 | 37       | 4 |
| 5   | 0.200 | 36       | 41 | 23       | 61 | 35       | 4 |
| 6   | 0.250 | 37       | 40 | 23       | 62 | 34       | 4 |
| 7   | 0.300 | 38       | 39 | 23       | 63 | 33       | 4 |
| 8   | 0.350 | 40       | 38 | 22       | 64 | 32       | 4 |
| 9   | 0.400 | 41       | 37 | 28       | 66 | 31       | 3 |
| 10  | 0.450 | 42       | 37 | 21       | 66 | 30       | 4 |
| 11  | 0.500 | 42       | 37 | 21       | 67 | 29       | 4 |
| 12  | 0.550 | 43       | 36 | 21       | 68 | 29       | 3 |
| 13  | 0.600 | 44       | 35 | 21       | 69 | 28       | 3 |
| 14  | 0.650 | 45       | 34 | 21       | 70 | 27       | 3 |
| 15  | 0.700 | 47       | 33 | 20       | 71 | 26       | 3 |
It is possible that in binary solvent water + methanol the interactions between the alcohol molecules to be strengthen than between their molecules and the ylid molecules. The differences between the percentages for HBA and HBD contributions to the total spectral shift in binary solvent water + methanol of the two ylid are probably caused by the nitro group in PTNPY molecules.

In the second step of our research, the statistic cell model previously developed [20,21] and applied to some spectrally active molecules [13,14,17] was used here to characterize the first solvation shell of ylid molecules and to estimate the potential energy of interactions in molecular pairs of the types: ylid-water and ylid-alcohol.

In this aim, relation (2), obtained in the statistic cell model of ternary solutions has been used.

\[
\ln \frac{p_1}{1-p_1} = m \ln \frac{x_1}{1-x_1} + n \frac{w_2-w_1}{kT}
\]  

(2)

In relation (2) \(p_1\) and \(p_2 = 1 - p_1\) are the average statistic weights of the two hydroxyl solvents in the first solvation shell of the solute molecule, \(x_1\) and \(x_2\) are the molar fractions of the two solvents in the bulk solution, \(w_1\) and \(w_2\) are the interaction energies in the molecular pairs of the types: water (1)-ylid and alcohol (2)-ylid, respectively. The indices (1) and (2) refer to the solvent influence on the visible band of ylid; solvent giving a large spectral shift is noted by (1). It is usually considered as 'active' solvent. The solvent with index (2) gives smaller shifts of the spectral bands and is considered as a 'few active' or 'inactive' from the interactions point of view.

![Figure 1. ln p_1/(1-p_1) vs. ln x_1/(1-x_1) for binary solution PTNPY + Water (1) + Ethanol (2)](image)
The average statistic weights \([21, 22]\) in the first solvation shell of the spectrally active molecules can be computed using relations (3).

\[
p_1 = \frac{\bar{v}_1 - \bar{v}_2}{\bar{v}_1 - \bar{v}_2} \quad \text{and} \quad p_1 + p_2 = 1 \quad (3)
\]

When a relation of the type (2) can be evidenced for the spectral data, it results that the statistic cell model of ternary solutions is applicable and the intercept \(n\) signifies the difference between interaction energies in molecular pairs of the types: water (1)-ylid and alcohol (2)-ylid, noted by \(w_1\) and \(w_2\), respectively.

In Figures 1 and 2 are illustrated two dependences for the studied ternary solutions.

The slopes and intercepts of the lines (2), obtained based on the spectral data from Tables 1 and 2 are listed in Table 6. From Figures 1 and 2 it results that the slopes decrease for high water molar concentrations in binary solvent, showing changes in specific interaction nature when the composition of the binary solvent varies. From Table 6 it results changes in the slope and the cut at origin for both ylids in binary solvent water +ethanol and also for PFNPY in water + methanol. As exception, (see Figure 2 and Table 6) a single line was obtained when the molar fraction of water was varied, for ternary solution Water (1) + Methanol (2) + PTPY.

**Table 6.** Slopes and intercepts for relation (2)

| Solvent       | \(x_1\) | Ylid  | \(m \pm \Delta m\) | \(n \pm \Delta n\) | \((w_2 - w_1) \times 10^{20}\) J | R  |
|---------------|---------|-------|---------------------|---------------------|---------------------------------|----|
| Water + Ethanol | < 0.5   | PTPY  | 1.21 ± 0.06         | -0.34 ± 0.09        | -0.139                          | 0.98 |
|               | > 0.5   | PTPY  | 0.88 ± 0.01         | -0.56 ± 0.02        | -0.229                          | 1   |
|               | < 0.7   | PTNPY | 1.01 ± 0.01         | -0.75 ± 0.01        | -0.306                          | 1   |
|               | > 0.7   | PTNPY | 0.45 ± 0.02         | -0.23 ± 0.04        | -0.094                          | 0.99 |
| Water + Methanol | < 0.6   | PTNPY | 1.08 ± 0.02         | -0.33 ± 0.03        | -0.135                          | 0.98 |
|               | > 0.6   | PTNPY | 0.87 ± 0.03         | -0.25 ± 0.05        | -0.102                          | 1   |
|               | 0÷1     | PTPY  | 1.07 ± 0.01         | -0.67 ± 0.02        | -0.274                          | 1   |

In the last column of Table 6 are noted the differences \(w_2 - w_1\) (expressed in J) for the molecular pairs formed by hydrogen bonds in the studied ternary solutions. The energy in molecular pairs is very hardly to be estimated by usual techniques, so the values obtained for \(w_2 - w_1\) are important, especially for developing the models of liquids in which specific interactions act.
In the case of the binary solvent water (1) + ethanol (2), all differences $w_2 - w_1$ are negative, showing that $|w_2| > |w_1|$: the interaction energy in molecular pair ethanol-ylid is higher in modulus as the modulus of interaction energy in molecular pair water – ylid, for both solute molecules.

The values of the difference $w_2 - w_1$ is comparable for PTPY at all molar concentrations of the binary solvent water (1) + ethanol (2) and also for PTNPY in the case $x_1 < 0.50$. In the case of PTNPY in water + ethanol solutions, for $x_1 > 0.50$, the intercept is smaller than for intercept corresponding to the small concentrations of water.

For the binary solvent water (1) + methanol (2), the difference $w_2 - w_1$ is also negative, but it is higher in modulus for PTPY than for PTNPY. The difference $w_2 - w_1$ differs for small and high water molar concentrations in the binary solvents, indicating the prevalence of complexes of the types: alcohol-ylid or water-ylid as function of the water content in the binary solution. The slope modification has been not observed in the case of ternary solution water (1) + methanol (2) + PTNPY. In graph from Figure 2 the change in the slope of the line is not observable when the water concentration increases in ternary solution.

The results obtained in this study are sustained by another recent published articles regarding the solvatochromic behavior of cycloimmonium ylids [25, 26]

4. Conclusions

In the protic solvents, the studied ylids participate to specific interactions of the hydrogen types and the formed complexes interact with the binary solvent. For small water concentrations, the complexes alcohol – ylid are predominant and, at higher water concentration the complexes water – ylid prevail in the studied ternary solutions.

The theory of the cell statistic model of a diluted solution in binary solvent can be applied to the spectral data obtained in this research. The intercepts obtained for the lines (2) are very small because in the difference $w_2 - w_1$ the energies corresponding to hydrogen bonds in molecular pairs of the types ylid-water and ylid-alcohol cannot be identified because they are subtracted.

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