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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 cycloimmonium 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-aprotic 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-ium 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-ium phenacylids, namely 4’-phenyl-1,2,4-triazol-1-ium phenacylid (PTPY) and 4’-phenyl-1,2,4-triazol-1-ium-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 ($\pm 10^{-5}$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 $\pm 0.5 cm^{-1}$.

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

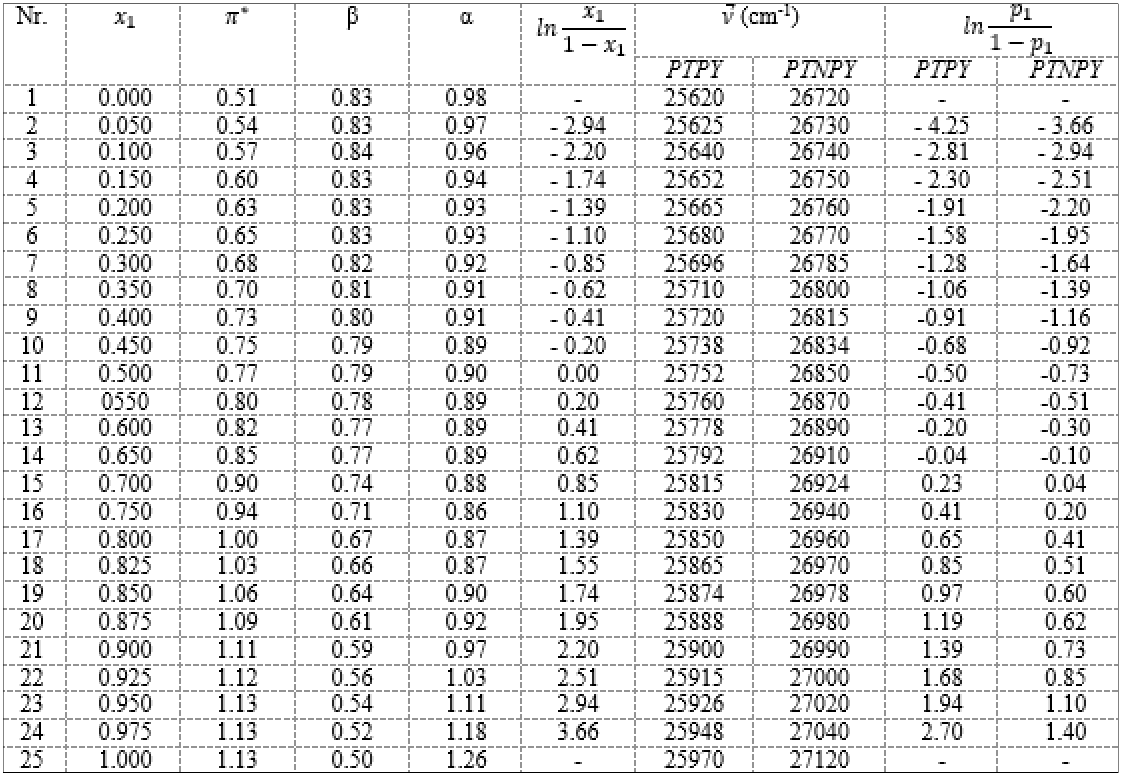
As all cycloimmonium ylids, 1,2,4-triazol-1-ium ylids show a visible electronic absorption band of low intensity, attributed to an intramolecular charge transfer (ICT) [14,24,25] from the carbanion towards the heterocycle and sensitive to the solvent nature.

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 (π^*), hydrogen-bond donor acidity (α), hydrogen bond acceptor basicity (β), has been made.

$$\bar{v}(cm^{-1}) = \bar{v}_o + C_1\pi^* + C_2\alpha + C_3\beta \qquad (1)$$

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^{-1}) inform about the sense and the magnitude of the spectral shifts recorded in the ternary solutions of ylids. The free term $\bar{v}_0$ 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 (π^*, β, α) of binary solvent water (1) + ethanol (2) [18] and wavenumbers (ν(cm^{-1})) in the maximum of the visible electronic absorption band of ylids (PTPY and PTNPY)



Nr.	x_1	π^*	β	α	$ln\frac{x_1}{1-x_1}$	$\bar{v}$ (cm^{-1})		$ln\frac{p_1}{1-p_1}$	
						PTPY	*PTNPY*	*PTPY*	*PTNPY*
1	0.000	0.51	0.83	0.98	-	25620	26720	-	-
2	0.050	0.54	0.83	0.97	- 2.94	25625	26730	- 4.25	- 3.66
3	0.100	0.57	0.84	0.96	- 2.20	25640	26740	- 2.81	- 2.94
4	0.150	0.60	0.83	0.94	- 1.74	25652	26750	- 2.30	- 2.51
5	0.200	0.63	0.83	0.93	- 1.39	25665	26760	-1.91	-2.20
6	0.250	0.65	0.83	0.93	- 1.10	25680	26770	-1.58	-1.95
7	0.300	0.68	0.82	0.92	- 0.85	25696	26785	-1.28	-1.64
8	0.350	0.70	0.81	0.91	- 0.62	25710	26800	-1.06	-1.39
9	0.400	0.73	0.80	0.91	- 0.41	25720	26815	-0.91	-1.16
10	0.450	0.75	0.79	0.89	- 0.20	25738	26834	-0.68	-0.92
11	0.500	0.77	0.79	0.90	0.00	25752	26850	-0.50	-0.73
12	0550	0.80	0.78	0.89	0.20	25760	26870	-0.41	-0.51
13	0.600	0.82	0.77	0.89	0.41	25778	26890	-0.20	-0.30
14	0.650	0.85	0.77	0.89	0.62	25792	26910	-0.04	-0.10
15	0.700	0.90	0.74	0.88	0.85	25815	26924	0.23	0.04
16	0.750	0.94	0.71	0.86	1.10	25830	26940	0.41	0.20
17	0.800	1.00	0.67	0.87	1.39	25850	26960	0.65	0.41
18	0.825	1.03	0.66	0.87	1.55	25865	26970	0.85	0.51
19	0.850	1.06	0.64	0.90	1.74	25874	26978	0.97	0.60
20	0.875	1.09	0.61	0.92	1.95	25888	26980	1.19	0.62
21	0.900	1.11	0.59	0.97	2.20	25900	26990	1.39	0.73
22	0.925	1.12	0.56	1.03	2.51	25915	27000	1.68	0.85
23	0.950	1.13	0.54	1.11	2.94	25926	27020	1.94	1.10
24	0.975	1.13	0.52	1.18	3.66	25948	27040	2.70	1.40
25	1.000	1.13	0.50	1.26	-	25970	27120	-	-

Table 2. Molar water composition (x_1), parameters (π^*, β, α) of binary solvent water (1) + methanol (2) [18] and wavenumbers (ν(cm^{-1})) in the maximum of the visible electronic absorption band of ylids (PTPY and PTNPY)

Nr.	x_1	π^*	β	α	$ln\frac{x_1}{1-x_1}$	$\vec{v}$ (cm^{-1})		$ln\frac{p_1}{1-p_1}$	
						PTPY	*PTNPY*	*PTPY*	*PTNPY*
1	0.000	0.58	0.74	1.14	-	25640	26810	-	-
2	0.050	0.61	0.74	1.13	- 2.94	25645	26820	- 4.18	- 3.41
3	0.100	0.64	0.74	1.12	- 2.20	25650	26828	- 3.48	- 2.79

4	0.150	0.66	0.74	1.10	- 1.74	25660	26840	- 2.74	- 2.16
5	0.200	0.70	0.74	1.09	- 1.39	25668	26850	-2.38	-1.91
6	0.250	0.73	0.74	1.07	- 1.10	25680	26864	-1.98	-1.56
7	0.300	0.76	0.74	1.06	- 0.85	25692	26880	-1.67	-1.23
8	0.350	0.78	0.72	1.04	- 0.62	25710	26892	-1.31	-1.02
9	0.400	0.82	0.72	1.04	- 0.41	25720	26910	-1.14	-0.74
10	0.450	0.85	0.71	1.02	- 0.20	25738	26924	-0.86	-0.54
11	0.500	0.88	0.70	1.03	0.00	25756	26942	-0.61	-0.30
12	0550	0.91	0.68	1.02	0.20	25774	26960	-0.38	-0.06
13	0.600	0.95	0.66	1.01	0.41	25792	26978	-0.16	0.17
14	0.650	0.98	0.65	1.01	0.62	25815	26990	0.12	0.33
15	0.700	1.01	0.63	1.01	0.85	25840	27002	0.43	0.49
16	0.750	1.04	0.61	1.02	1.10	25865	27022	0.76	0.77
17	0.800	1.06	0.59	1.06	1.39	25882	27038	1.01	1.02
18	0.825	1.08	0.58	1.07	1.55	25892	27042	1.17	1.09
19	0.850	1.09	0.56	1.09	1.74	25904	27050	1.39	1.23
20	0.875	1.10	0.55	1.12	1.95	25918	27060	1.67	1.42
21	0.900	1.11	0.54	1.13	2.20	25926	27068	1.87	1.60
22	0.925	1.11	0.52	1.17	2.51	25940	27072	2.30	1.70
23	0.950	1.12	0.52	1.19	2.94	25952	27089	2.84	2.19
24	0.975	1.12	0.51	1.22	3.66	25960	27107	3.48	3.20
25	1.000	1.14	0.49	1.23	-	25970	27120	-	-

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	$\bar{\nu}_0 + \Delta\bar{\nu}_0$	$C_1 \pm \Delta C_1$	$C_2 \pm \Delta C_2$	$C_3 \pm \Delta C_4$
Water + Ethanol	PTPY	24680 ± 676	676 ± 54	413 ± 119	243 ± 47
Water + Ethanol	PTNPY	25381 ± 414	795 ± 128	668 ± 286	365 ± 112
Water + Methanol	PTPY	25839 ± 118	329 ± 32	$- 601 \pm 77$	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 acceptance of the hydroxyl solvent protons described by $C_2\alpha$ term. In this type of solutions, the hydrogen bonds realized by solvent acceptance of protons are of small probability. They determine approximately 5-2% contribution to the total spectral shift.

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. crt.	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	7
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	0550	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	7

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. crt.	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	0550	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

16	0.750	49	31	20	71	26	3
17	0.800	52	29	19	71	26	3
18	0.825	53	28	19	71	26	3
19	0.850	53	27	20	71	27	2
20	0.875	54	26	20	71	27	2
21	0.900	55	24	21	71	27	2
22	0.925	55	23	22	70	28	2
23	0.950	54	23	23	70	28	2
24	0.975	54	21	25	70	28	2
25	1.000	54	20	26	70	28	2

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.

$$ln\frac{p_1}{1-p_1} = mln\frac{x_1}{1-x_1} + n\frac{w_2-w_1}{kT} \qquad (2)$$

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.

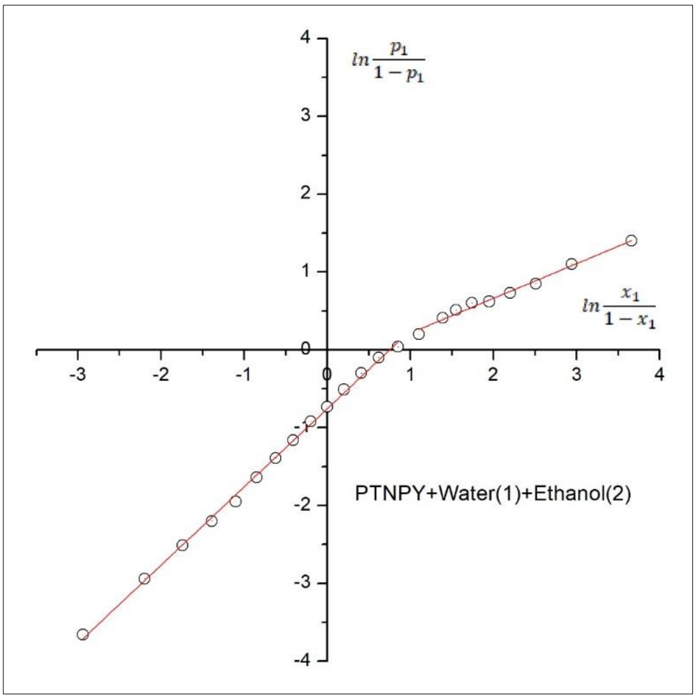


Figure 1. ln p_1/(1-p_1) vs. ln x_1/(1-x_1) for binary solution PTNPY + Water (1) + Ethanol (2)

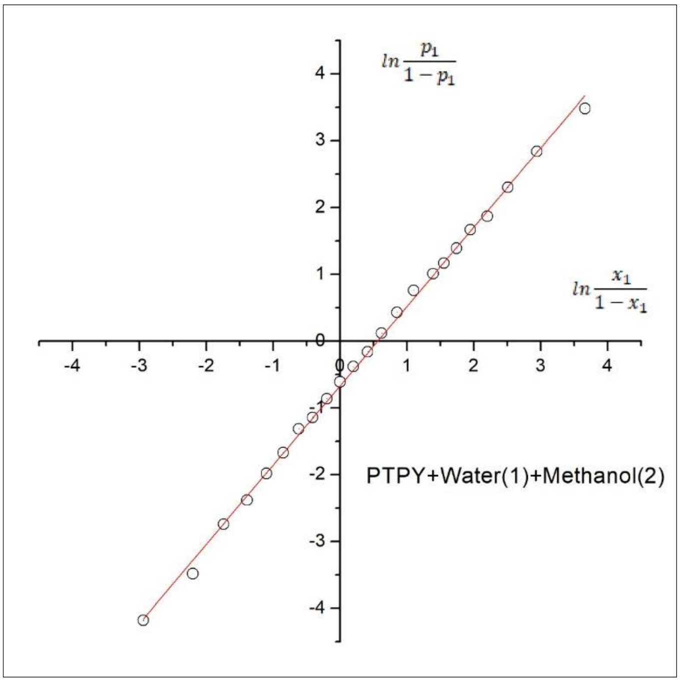


Figure 2. $ln\frac{p_1}{1-p_1}$ vs. $ln\frac{x_1}{1-x_1}$ for binary solution PTPY + Water (1) + Methanol (2)

The average statistic weights [21, 22] in the first solvation shell of the spectrally active molecules can be computed using relations (3).

$$p_1 = \frac{\bar{\nu}_t - \bar{\nu}_2}{\bar{\nu}_1 - \bar{\nu}_2} \quad \text{and} \quad p_1 + p_2 = 1 \qquad (3)$$

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

References

1. ZUGRAVESCU I., PETROVANU M., *N-Ylid Chemistry*, Academic Press, New York, 1976.
2. PETROVANU M., LUCHIAN C., SURPATEANU G., BARBOIU V., 1,2,4-Triazolium ylures I. Synthèsis et stréréochimie des réactions de cycloaddition aux composés á liaison ethylenique active, *Rev. Roum. Chim.*, **24**(5), 1979, 733-744.
3. SURPATEANU G., CAEA N., SUFLETEL L., GRANDCLAUDON P., Synthesis characterization of new azatriazolium ylids, Rev. Roum. Chim., **40** (6), 1995, p. 133-136.
4. PETROVANU M., LUCHIAN C., SURPATEANU G., BARBOIU V., CONSTANTINESCU M., 1,2,4-Triazolium ylures VIII. Réactions des triazolium phénacylures avec les hétérocumulènes, *Tetrahedron*, **39**(14), 1983, 2417-2420.
5. LARS-FLORI C., Triazole antifungal agents in invasive fungal infections; a comparative review, *Drug*, **71**(18), 2011, 2405-2411.
6. GRANBERG K., SLASSI A., STEFANAC T., WALLBERG A., WIPO Patent 2009/054787A1, April 30, 2009.
7. JAGEROVIC N., CUMELLA-MONTANCHEZ J., GOYA-LAZA M., DORDAL-ZUERAS A., CUBERES-ALTISENT M.R., EP patent 1 921 073 A1, May 14, 2008; also U.S. Patent 8,349,878B2 Jan 5, 2013.
8. BONANOMI G., DI FABIO R., FAZZOLARI E., HAMPRECHT D., MICHELI F., TARSI L., TERRENI S., WIPO Patent 2007/022933 A1, March 3, 2007.
9. SHAH M.H., MHASALKAR M.Y., PATKI V.M., DELIWALA C.V., STETH U.K., New 1,2,4 (H) triazole derivatives as diuretic agents, *J. Pharm. Sci.*, **58**, 1969, 1398-1401.
10. TAN X., FURIO L., REBOUD RAVAUX M., VILLOUTREIX B.O., HOVNANIAN A., AMRE C. EL., 1,2,4 Triazole derivatives as transient inactivators of kallikreins involved in skin diseases, *Bioorg. Med. Chem. Lett.*, **23**(13), 2013, 4547-4551.

11. AL-OMAR M.A., AL-ABDULAAH E.S., SHEHATA I.A., HABIB E.E., IBRAHIM T.M., EL EMAM A.A., Synthesis, antimicrobial and anti-inflammatory activities of novel 5-(1-Adamantyl-4-arildeneamino-3-mercapto-1,2,4-triazoles and related derivatives, *Molecules* **15**(4), 2010, 2526-2550.
12. CHEN X., SHI Y.-M., HUANG C., XIA S., YANG L.-J., YANG X.-D., Novel dibenzo[b, d]furan–1H-1,2,4-triazole derivatives: Synthesis and antitumor activity, *Anti-Cancer Agents in Medicinal Chemistry*, **16**(3), 2016, 377 - 386.
13. CLOSCA V., PUICA MELNICIUC N., BENCHEA A.C., Dorohoi D.O., Intermolecular interactions in ternary solutions of some 1,2,4 triazolium ylids studied by spectral means, *Proc. of SPIE*, **9286**, 92862T-1, 2014.
14. CLOSCA V., PUICA MELNICIUC N., CLOSCA M., AVADANEI I.M., DOROHOI D.O., Spectral study of (4'-phenyl)-1,2,4-triazol-1-ium phenacylid (PTPY) in ternary solutions, *Ukr. J. Phys.*, **63**(7), 2018, 592-599.
15. DOROHOI D.O., DIMITRIU D.G., DIMITRIU M., CLOSCA V., Specific interactions in N-ylid solutions, studied by nuclear magnetic resonance and electronic absorption spectroscopy, *J. Mol. Struct.*, **1044**, 2013, 79-86.
16. MELNICIUC PUICA N., IVAN L.M., CLOSCA V., DOROHOI D.O., Electro-optical and spectral comparative study of some triazol-1-ium methylids with biomedical applications, *Rev. Chim.*, **70**(3), 2019, 956-960.
17. DOROHOI D.O., AVADANEI I.M., POSTOLACHE M., Characterization of the solvation spheres of some dipolar spectrally active molecules in binary solvents, *Optoel. Adv. Mat. –Rapid Comm.* **2**(8), 2008, 511-514.
18. BUHVESTOV U., RIVED R., RÁFOLS C., BOSCH E., ROSE M., Solute-solvent and solvent-solvent interactions in binary solvent mixtures. Part 7. Comparison of the enhancement of the water structure in alcohol-water mixtures measured by solvatochromic indicators, *J. Phys. Org. Chem.*, **11**, 1998, 185-192.
19. ROSES M., BUHVESTOV U., RAFOLS C., RIVED F., BOSCH E., Solute-solvent and solvent-solvent interactions in binary solvent mixtures. Part 6. A quantitative measurement of the enhancement of water structure in 2-methylpropane-2-ol-water and propane-2-ol-water mixtures by solvatochromic indicators, *J. Chem. Soc. Perkin Trans*. **2**, 1997, 1341-1348.
20. POP V., DOROHOI D.O., DELIBAS M., Consideration on the statistic model of the intermolecular interactions in ternary solutions, *An. Stiint. Univ. Al. I. Cuza, Iasi, s.Ib, Fizica*, **32**, 1986, 79-84.
21. DOROHOI D.O., POP V., Spectral shifts in the electronic absorption spectra of some cycloimmonium ylids in ternary solutions, *An. Stiint. Univ. Al. I. Cuza, Iasi, s.Ib, Fizica*, **33**, 1987, 78-85.
22. AVADANEI M., DOROHOI D.O., Interaction energy in pairs of pyridazinium ylids-solvent molecules estimated by spectral means within the cell ternary solution model, *Ukr. J. Phys.*, **57**(2), 2012, 118 -122.
23. DOROHOI D.O., Electronic spectroscopy of N-ylids, *J. Mol. Struct.*, **704**(1-3), 2004, 31-43.
24. DULCESCU M.M., STAN C., DOROHOI D.O., Spectral investigations of the influence of the hydroxyl solvents on the intermolecular interactions in some pyridinium ylid ternary solutions, *Rev. Chim.*, **61**(12), 2010, 1219-1222.
25. DOROHOI D.O., CREANGA D.E., DIMITRIU D.G., MOROSANU A.C., GRITCO TODIRASCU A., MARICIUC G. GR., PUICA MELNICIUC N., ARDELEAN E., CHEPTEA C., Computational and spectral means for characterizing the intermolecular interactions in solutions and for estimating excited state dipole moment of solute, *Symmetry*, **12**, 1299, 2020, 1-23. doi:10.3390/sym2081299.
26. IVAN L.M., DIMITRIU D.G., GRITCO-TODIRASCU A., DOROHOI D.O., CHEPTEA C., Excited state dipole moments of two pyridazinium p-nitro-phenacylids estimated from solvatochromic study, Spectrosc. Lett., 53, 2020, 1-11.

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