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# SOLVATOCHROMIC STUDY OF TWO PYRIDAZINIUM YLIDS BINARY SOLUTIONS

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Abstract: The wavenumbers in the maximum of intramolecular charge transfer (ICT) visibile band of two pyridazinium ylids binary solutions were analized using Kamlet and Taft empirical parameters and the Hildebrand's solubility parameter. The Hildebrand's solubility parameter values,  $\delta_H^2$ , measures the energy needed to separate the solvent molecules. A linear solvation energy relationship (LSER) allows separating the contributions of different types of interactions to the total spectral shift. The supply of universal and specific interactions as well as the supply of solvent-solvent interactions to the total spectral shifts was calculated.

# Keywords: pyridazinium ylids, intramolecular charge transfer (ICT), Hildebrand's solubility parameter, LSER.

### 1. Introduction

Pyridazinium ylids are amphionic compounds having positive Nitrogen belonging to the azo-heterocycle, covalently bonded to a mono- or a di-substituted negative carbanion [1, 2]. Pyridazinium ylids are highly reactive organic compounds due to their strong nucleophiles character. The disubstituted pyridazinium ylids are more stable therefore they can be used as analytical reagents [2, 3], semiconducting materials [4, 5], as acid –basic indicator due to their specific colour [2].

The monosubstituted pyridazinium ylids are less stable [6] comparatively with the disubstituted pyridazinium ylids and they are used as intermediates in organic synthesis [7-9] in order to obtain compounds with biological activity [10] and nanomaterials with fluorescent properties [10,11].

The intermolecular interactions were studied by UV-Vis spectroscopy means.

The pyridazinium ylids show a visible absorption band due to the transfer of the carbanion non-bonded electrons toward to the pyridazinium heterocycle. This band position and intensity depend on the solvent nature [13] and on the carbanion substituents [14, 15]. The ICT visible absorption band shifts to blue (negative solvatochromism) when solvent polarity increases. This band disappears in acids where the non-participating electrons of the carbanion are captured by the OH groups resulted from the acid dissociation [16].

The goal of this paper is to evaluate the contributions of different types of interactions to the total spectral shifts, including the solvent-solvent interactions neglected. that are usually The multiparameter scale of Kamlet and Taft [17, 18] and the Hildebrandt solubility parameter [19, 20] were used for separate contributions of solute-solvent the interactions solvent-solvent and

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interactions, respectively.

### 2. Experimental

In this paper, the studied ylids are spectrally active molecules and their structure is presented in Figure 1 and Table 1.

The ylids under study were obtained



Figure 1: Structural features of the ylids under study.

Table 1 Substituents R,  $R_1$ ,  $R_2$  and name of the ylids under study

by the methods described in [2].

without other purification.

The solvents used for binary

solutions were bought from Merck and used

$\frac{1}{1000}$								
Ylid	R	$R_{I}$	$R_2$	Name				
Ylid 1	Н	Н	$COC_6H_4(NO_2)_p$	p phenyl-pyridazinium p nitrophenacylid				
Ylid 2	$CH(CH_3)_2$	COCH <sub>3</sub>	$COC_6H_5$	p cumyl-pyridazinium- acetyl-benzoyl methylid				

The electronic absorption spectra were recorded with a Specord UV-Vis Carl Zeiss Jena spectrophotometer with a data acquisition system.

# 3. Results and discussions

The ICT visible bands of the ylids under study in solvents having different physico-chemical parameters have been recorded and the wavenumbers expressed in cm<sup>-1</sup> in their maximum are listed in Table 2. The Kamlet and Taft parameters values and the solubility parameter  $\delta_{H}^2$  values were taken from References [17-20].

The  $\pi^*$  scale is a measure of the dipolarity/polarizability of the solvent. The  $\alpha$  scale is an empirical measure of the solvent acidity in a solute-solvent hydrogen bond. The  $\beta$  scale is an empirical measure of solvent basicity in a solute-solvent hydrogen bond. In order to count the solvent-solvent interactions Hildebrand's solubility parameter was introduced. The solubility parameter indicates the relative solvency behaviour of a specific solvent [20].

In the multiparameter approach a

linear solvation energy relationships of the type 1 (LSER) [19] is used in order to correlate solvent parameters with solute physicochemical properties such as solubility, equilibrium constant or wavenumber in the maximum of an UV/Vis, IR, or NMR band.

$$\widetilde{\nu} = \widetilde{\nu}_0 + C_1 \pi^* + C_2 \alpha + C_3 \beta + C_4 \delta_H^2(1)$$

where  $\tilde{\nu}$  is the wavenumber in the maximum of absorption band,  $\tilde{\nu}_0$  is the regression value of wavenumber in the reference solvent, C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> are the regression coefficients which describe the sensitivity of the solute to the solvent parameters  $\pi^*$ ,  $\alpha$ ,  $\beta$ ,  $\delta_H^2$ , respectively. Depending on the solute-solvent interactions, one or more terms can be neglected.

The correlation coefficient improved when the term which describes the basicity of the solvent,  $\beta$ , was eliminated from Eq. 1 for the disubstituted carbanion ylid (Ylid 2). That means that the hydrogen bond acceptor (HBA) interactions can be neglected for Ylid 2. For Ylid 1 HBA interactions cannot be eliminated from LSER.

Nr	Solvent	Ylid1	Ylid2	$\pi^*$	α	β	$\delta_{\rm H}^2$
111.	Solvent	$\widetilde{v}$ (cm <sup>-1</sup> )	$\widetilde{\nu}$ (cm <sup>-1</sup> )				$(J \text{ cm}^{-3})$
1	Formamide	20641	22215	0.97	0.71	0.48	1544.49
2	Ethane1.2-diol	21131	22460	0.92	0.90	0.52	894.01
3	Methanol		22215	0.60	0.98	0.66	876.16
4	Ethanol	20886	20991	0.54	0.86	0.75	676.00
5	n-Propyl alcohol	20781	21620	0.52	0.84	0.90	620.01
6	Dimethylformamide	20151	20571	0.88	0.00	0.69	615.04
	(DMF)						
7	Dimethylsulfoxide	20116	20711	1.00	0.00	0.76	600.25
	(DMSO)						
8	1-Butanol	20711	21620	0.47	0.84	0.84	542.89
9	Pyridine	19906	20361	0.87	0.00	0.64	479.61
10	Acetone		20501	0.62	0.08	0.48	408.04
11	1.2 Dichloroethane		20361	0.81	0.00	0.00	400.00
12	Chlorobenzene	20291	20116	0.68	0.00	0.07	376.36
13	Trichloromethane	20291	20396	0.69	0.20	0.10	361.00
14	Benzene		20116	0.55	0.00	0.10	353.44
15	Ethyl acetate		20291	0.45	0.00	0.45	345.96

Table 2 Wavenumbers in the maximum of visible absorption band of the studied ylid,  $v(cm^{-1})$ , Kamlet and Taft's parameters,  $\pi^*$ ,  $\alpha$ ,  $\beta$ , Hildebrand's parameter, $\delta_H$  ( $J^{1/2}*cm^{-3/2}$ ), square value of Hildebrand'parameter,  $\delta_H^2$  ( $J^*cm^3$ )

In order to establish the influence of solvent-solvent interactions, the wavenumbers in the maximum of ICT absorption band were analyzed using multiple linear regressions fitting with

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Kamlet and Taft parameters and then with Kamlet and Taft parameters and the solubility parameter  $(\delta_{H}^{2})$ . The correlations improved when the solvent-solvent interactions were taken into account (Table 3).

Table 3 Correlations coefficient, R, standard deviation, SD, number of validated points, N,for the Equations from the Table 3

	Ylid 1		Ylid 2			
$v = v_0 + C_1 \pi^* + C_2 \alpha + C_3 \beta + C_4 \delta_H^2$			$v = v_0 + C_1 \pi^* + C_2 \alpha + C_4 \delta_H^2$			
R	SD N		R	SD	N	
0.89	133 10		0.90	260	15	
$v = v_0 + C_1 \pi^* + C_2 \alpha + C_3 \beta$			$\nu = \nu_0 + C_1 \pi^* + C_2 \alpha$			
R	SD	Ν	R	SD	Ν	
0.87	139 10		0.89	271	15	

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he regression coefficients  $\tilde{v}_0$ , C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C4 ylids under study are listed in Table 4.

Tuble 4 C	<i>Table 4 Coefficients of Eq. (1), obtained from multiple thear regression analysis</i>									
YLID	$(cm^{-l})$	$C_1$ (cm <sup>-1</sup> )	$C_2$ (cm <sup>-1</sup> )	$C_3$ ( $cm^{-l}$ )	$C_4$ $(cm^2/J)$					
Ylid1	19899±221	640±340	$1132 \pm 170$	-211±139	-0.35±0.20					
Ylid2	19429±314	882±555	1560±279		$0.59 \pm 0.41$					

Table 4 Coefficients of Eq. (1), obtained from multiple linear regression analysis

The negative coefficients,  $C_3$  and  $C_4$  for Ylid 1 indicate bathochromic shifts due to HBA and solvent-solvent interactions.

wavenumbers in the maximum of ICT band was obtained (R=0.94, SD=78.85 N=9 for Ylid 1 and R=0.90, SD=266.76, N=15 for Ylid 2) as one can see in Figure 2.

A good linear correlation between the calculated and the experimental values of the



Figure 2: v<sub>calculated</sub> vs. v<sub>experimental</sub> for the studied ylids

Spectral shifts due to the universal forces between solute and solvent molecules are measured by the term  $C_1\pi^*$ . The contribution of the solvent-solvent interaction to the total spectral shift is

measured by term  $C_4 \delta_H^2$ .

The terms  $C_2\alpha$  and  $C_3\beta$  describe the role of the specific HBD and HBA interactions, respectively, to the total spectral shift.

			Ylid 1				Ylid 2		
Nr.	Solvent	$P\pi^*$	Ρα	Ρβ	$P \delta_H^2$	$P\pi^*$	Ρα	$P \delta_H^2$	
		(%)	(%)	(%)		(%)	(%)	(%)	
1	Formamide	30	39	5	26	30	39	32	
2	Ethane1.2-diol	29	50	5	15	30	51	19	
3	Methanol	-	-	-		21	59	20	
4	Ethanol	20	57	9	14	21	60	18	
5	n-Propyl alcohol	20	56	11	1	21	61	17	
6	Dimethylformamide (DMF)	61	0	16	23	68	0	32	
7	Dimethyl sulfoxide(DMSO)	63	0	16	21	71	0	29	
8	1-Butanol	19	59	11	12	20	64	16	
9	Pyridine	*	*	*	*	73	0	27	
10	Acetone	-	-	-	-	60	14	26	
11	1.2 Dichloroethane	-	-	-	-	75	0	25	
12	Chlorobenzene	75	0	3	23	73	0	27	
13	Trichloromethane	54	28	3	15	54	27	19	
14	Benzene	-	-	-	-	70	0	30	
15	Ethyl acetate	-	-	-	-	66	0	34	

Table 5 Contribution of different type of interaction, in percentage, to the total spectral shifts

\* eliminated by the statistical analysis

The contribution of different types of interaction to the total spectral shift, in percentage is listed in Table 5.

In protic solvents the specific interactions prevails while in aprotic solvents the universal interactions are

predominant. The contribution of the solvent-solvent interactions to the total spectral shifts is bigger in aprotic solvents than in protic ones.

#### 4. Conclusions

The wavenumbers in the maximum of the visible band of the ylids under study

depend linearly on the parameters  $\pi^*$ ,  $\alpha$ ,  $\beta$  and  $\delta_H^2$  (LSER).

The HBA interactions can be neglected in binary solutions of the carbanion disubstituted ylid (Ylid 2).

The correlation between the experimental and the calculated values of the wavenumbers in the maximum of the absorption band improves by using the

solubility Hildebrand's parameter.

The contribution of solvent-solvent interactions to the spectral shifts is bigger for the carbanion disubstitued ylid (Ylid 2) than for monosubstituted ylid (Ylid 1).

The solvent–solvent interactions have an important role to the spectral shifts for both studied ylids.

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