Intermolecular Interactions in Binary Solutions of 3-*(p-cumyl)-pyridazinium-benzoyl-2,4,6 picryl methylid* (CPBPM) Described by Catalan's Parameters

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The wavenumbers in the maximum of the visible absorption band of a carbanion disubstituted ylid in binary solutions were correlated with the solvent Catalan's parameters. The supply of universal and specific interactions to the total spectral shift was established. The hydrogen bonds were recomputed for CPBPM in water solution using HyperChem 8.06 Programme.

Keywords: 3-(p-cumyl)-pyridazinium-benzoyl-2,4,6 picryl methylid (CPBPM), Catalan's parameters, protic solvents, aprotic solvents, hydrogen bonds

3-(p-cumyl)-pyridazinium-benzoyl-2,4,6 picryl methylid (CPBPM) is a zwitterionc compound [1-5] having a disubstituted negative carbanion covalent bounded with a positive Nitrogen from the pyridazinium heterocycle.

The studied ylid has a visible absorption band due to an intramolecular charge transfer (ICT) from the carbanion to heterocycle (fig.1) [6-10]. This band is very sensitive to the solvent nature. In protic solvents and in polar ones the spectral shifts are towards blue. It means that the ylid dipole moment decreases by excitation and so, the solvation energy in the excited state is smaller than in the ground state [7-9].

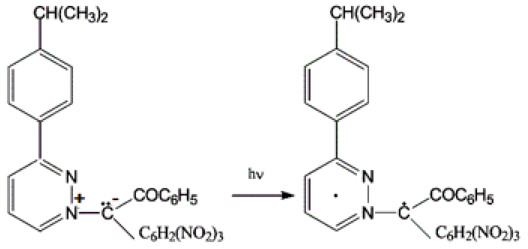

Fig. 1 The intramolecular charge transfere (ICT) mechanism

Among its various applications (acid-base indicator [1], precursor of new heterocyclic compounds) CPBPM has pharmaceutical potential [11, 12].

Compared with gaseous phase, in wich a spectrally active molecule could be considered isolated, free of external forces, in solutions this molecule is under the influence of solvent molecules.

Between spectrally active molecules and solvent ones act universal (long range) and specific (quasi-chemical, short range) forces.

The electric field created by the solvent molecules modifies the electron valence cloud of the spectrally active molecule and minimizes the ground state energy compared with that of the same isolated molecule. Depending on the changes induced by electronic transition responsible for the absorption band appearance, the energy in the excited state can differ by that coresponding in the ground state of the molecule. So, by passing the spectrally active molecule from its gaseous phase to homogenous solution, the electronic absorption band is shifted in the wavenumber scale with the difference between the molecular solvation energies, ΔW_e and ΔW_g in the electronic states participating to the absorption process.

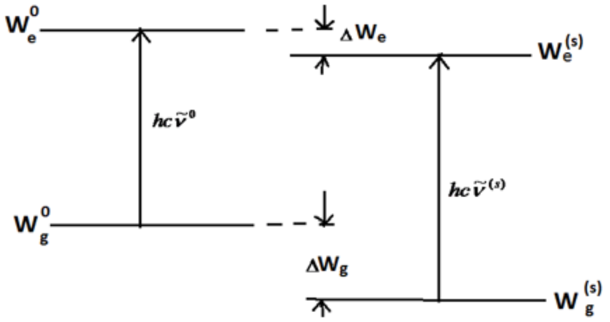

Fig. 2 Spectral shift due to the solvation process

Figure 2 illustrates a scheme of the ICT electronic absorption transition in two of the spectrally active substance (gaseous and solution phase).

$$hc(\tilde{\nu}^{(s)} - \tilde{\nu}^{(0)}) = \Delta W_e - \Delta W_g \qquad (1)$$

The spectral shift measured in the maximum of the electronic absorption band due to the solvation process is proportional with the difference of the solvation energies in the electronic states participating to the absorption process (eq. 1)

A series of researches explained the spectral shift recorded in absorption spectra by using the liquid theories. But the exitent theories are not generalized to the large variety of liquids and obtained formulas [13, 14] can not describe the shifts in each solvent with the same precision.

In order to clasify solvents taking in consideration their action on the molecules with similar structure, some empirical scales were proposed [15-22].

Catalan et al. [20, 21] introduced a new multiparameter scale based on solvent dipolarity/polarizability (SPP scale), solvent acidity (SB scale) and solvent basicity (SB scale).

Two probes which show a positive solvatochromic effect: 2-amino-7-nitofluorene (DMNAF) and its homomorph 2-fluoro-7-nitrofluorene (FNF) were used to

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measure the dipolarity/polarizability. The difference $\Delta\tilde{\nu} = \tilde{\nu}(FNF) - \tilde{\nu}(DMNAF)$ was taken as a measure of solvent dipolarity/polarizability (SPP scale). The references for normalize the SPP scale are the gas phase (SPP=0.000) and dimethyl sulfoxides (DMSO) (SPP=1.000). The SPP scale is defined as:

$$SPP(solvent) = \frac{\Delta\tilde{\nu}(solvent) - \Delta\tilde{\nu}(gas)}{\Delta\tilde{\nu}(DMSO) - \Delta\tilde{\nu}(gas)} = \frac{\Delta\tilde{\nu}(solvent) - 4692}{2119} \quad (2)$$

SB is the hydogen-bond acceptor (HBA) basicity scale. The probes used were 5-nitroindoline (NI) and its homomorph 1-methyl-5- nitroindoline. (MNI). The two homomorphs have the same HBA properties as well as similar dipole moments and polarizabilities. Thus, they exhibit the same sensitivity to changes in solvent dipolarity/ polarizability and should only register a change in the solvent's HBA basicity. The difference $\Delta\tilde{\nu} = \tilde{\nu}(MNI) - \tilde{\nu}(NI)$ is used to measure the ability of solvent to accept hydrogen-bonds. In order to normalize the SB solvent scale two references was taken: the gas phase (SB=0.000) and tetramethyl-guanidine (TMG) (SB=1.000).

$$SB(solvent) = \frac{\Delta\tilde{\nu}(solvent) - \Delta\tilde{\nu}(gas)}{\Delta\tilde{\nu}(TMG) - \Delta\tilde{\nu}(gas)} = \frac{\Delta\tilde{\nu}(solvent) - 1570}{1735} \quad (3)$$

A solvent hydrogen-bond donor (HBD) acidity scale (SA scale) was developed by Catalan et al., using the homomorphic merocyanines 1-methyl-4-[(4-oxocyclohexaienylidene)-ethylidene]-1,4-dihydropyridine with o,o'-di-tert-butylstilbazolium betaine (DTBSB) in position α,α'-to the carbonyl group and o-tert-butylstilbazolium betaine (TBSB) in position α –to the carbonyl group.

Thedifference $\Delta\tilde{\nu} = \tilde{\nu}(TBSB) - [1.405 \cdot \tilde{\nu}(DTBSB) - 6289]$ was used to define SA scale.

In order to obtain a normalized scale of near-zero HBD acidity for non-HBD solvents and a value of roughly unity for HBD solvents, the SA scale was defined as follows [23,24]:

$$SA(solvent) = \frac{\Delta\tilde{\nu}(solvent)}{\Delta\tilde{\nu}(ethanol)} \cdot 0.4 = \frac{\Delta\tilde{\nu}(solvent)}{1300} 0.4 \quad (4)$$

The probe mentionated above (DTBSB and TBSB) are protonated by strongly acidic solvents. In order to extend the SA scale for acidic solvents it was used 3,6-diethyltetrazine (DETZ) as a suitable probe.

Experimental part

The CPBPM was prepared in the Labs of Alexandru Ioan Cuza University as it was described in [1].

The solvents purchased from Merck Company were of spectrally grade and if it was necessary they were purified as it is described in [25].

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

The solutions concentration was of about 10^{-4} mol/L. Glass cuvettes of 1 cm thickness were used.

The Hyperchem 8.06 Programme [26] was used for geometrical optimization of the ylid molecule and for recomputing hydrogen bonds. It was set up a periodic solvent box having the dimensions: x=11Å, y=7Å, z=17Å. The maximum number of water molecules for the chosen box dimensions was 44 and the minimum distance between solute and solvent molecules was 2.3Å.

Results and discussions

The ICT visible band of CPBPM in solvents having different physicochemical parameters has been recorded and the wavenumber in its maximum is listed in table 1.

Table 1

THE CATALAN'S PARAMETERS: SPP, SA, SB, THE WAVENUMBERS IN THE MAXIMUM OF THE VISIBLE ABSORPTION BAND OF CPBPM ,$\tilde{\nu}$ (cm^{-1})

Group	Nr.	Solvent	SPP	SA	SB	$\tilde{\nu}$ (cm^{-1})
Aldehydes and ketones	1	Acetone	0.881	0.000	0.475	21520
Esters	2	Ethyl acetate	0.795	0.000	0.542	21485
	3	Iso amyl acetate	0.752	0.000	0.481	21520
Amides	4	DMF	0.954	0.031	0.613	21520
	5	Formamide	0.833	0.549	0.414	21690
Sulfoxides	6	DMSO	1.00	0.072	0.647	21520
Pyridines	7	Pyridine	0.922	0.033	0.581	21590
Arenes and Alkylarenes	8	Benzene	0.667	0.000	0.124	21380
Haloalkanes and Haloalkenes	9	DCE	0.890	0.030	0.126	21520
	10	DCM	0.876	0.040	0.178	21520
	11	Cloroform	0.786	0.047	0.071	21520
Alcohols and water	12	Diaceton alcohol	0.883	0.010	0.537	21725
	13	iso propyl alcohol	0.848	0.283	0.830	21865
	14	n Butyl alcohol	0.837	0.341	0.809	21865
	15	n Hexyl acohol	0.810	0.315	0.879	21865
	16	n Propyl alcohol	0.847	0.367	0.782	21935
	17	n Octyl alcohol	0.785	0.299	0.923	21830
	18	n Amyl alcohol	0.817	0.319	0.860	21865
	19	Ethanol	0.853	0.400	0.658	21935
	20	iso butyl alcohol	0.832	0.311	0.828	21900
	21	n Benzyl alcohol	0.886	0.409	0.461	21865
	22	Methanol	0.857	0.605	0.545	21935
	23	Water	0.962	1.062	0.025	22080
Aliphatic Polyalcohols	24	Ethylene glycol	0.932	0.717	0.534	21970

Table 2
CHARACTERISTICS OF EQ. (5) FOR BINARY SOLUTIONS OF CPBPM

$\tilde{\nu}_0$ (cm^{-1})	a (cm^{-1})	b (cm^{-1})	c (cm^{-1})	R	SD	N	Eliminated solvents
21534.05 ± 151	-158.82 ± 176.22	685.25± 48.44	279.57 ± 45.06	0.92	58.09	22	5.12

A multilinear dependence of the type (5) proposed by Catalan was used to describe the spectral shifts of CPBPM measured in the solvents from table 1.

$$\tilde{\nu} = \tilde{\nu}_0 + aSPP + bSA + cSB \qquad (5)$$

A good corelation was obtained as one can see in table 2 . The probes used by Catalan have bathocromic shifts and CPBPM shows hypsochromic shifts. This fact explains the negative sign of SPP coefficient.

The calculated wavenumbers in the maximum of the ICT absorption band of CPBPM using equation (5) are plotted versus the corresponding experimental values in figure 3.

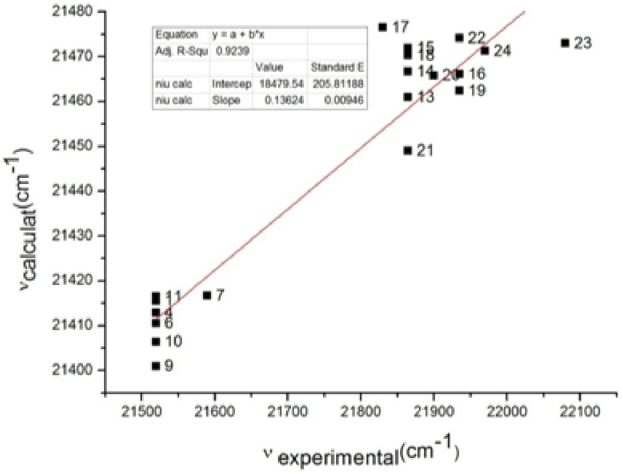

Fig.3. $\tilde{\nu}_{calculat}$(cm^{-1}) versus $\tilde{\nu}_{experimental\ t}$(cm^{-1})

There is a good linear correlation between the calculated and experimental values of the wavenumbers in the maximum of the visible ICT band of CPBPM (R=0.92, SD=7.83).

The contributions to the total spectral shift in (cm^{-1}) and in percentage of each type of interaction in a given solvent were evaluated and listed in table 3.

The HBD interactions are absent or weak in non-protic solvents and only induction-orientations dipolar universal interactions ($a \cdot SPP$) and HBA specific interactions are responsible for spectral shifts due to the solvation process (table 3).

The protic solvents contribute to specific HBD interactions and cause supplementary deviation of the visible ICT band of CPBPM. In protic solvents, besides the universal interactions, specific interactions cause supplementary spectral shifts of visible the absorption band of CPBPM.

The recomputed hydrogen bonds (dashed lines) in solution of CPBPM in water using Hyperchem 8.06 Programme is shown in figure 4.

As one can see in table 3, for water solution the HBD interactions is prevail. The most likely atom of spectrally active molecule that would achieve a hydrogen bond is one of the Oxigen atoms of the picryl substituents (fig. 4).

Table 3
SUPPLY, EXPRESSED IN cm^{-1} AND IN PERCENTAGE OF UNIVERSAL (a . SPP) AND SPECIFIC (b . SA AND c . SB) INTERACTIONS TO TOTAL SPECTRAL SHIFT IN BINARY SOLUTIONS OF CPBPM

Nr.	Solvent	$\lvert a \cdot SPP \rvert$ (cm^{-1})	P_{SPP}(%)	$b \cdot SA$ (cm^{-1})	P_{SA}(%)	$c \cdot SB$ (cm^{-1})	P_{SB}(%)
1	Acetone	139.71	51	0	0	132.80	49
2	Ethyl acetate	126.07	45	0	0	151.53	55
3	Iso amyl acetate	119.25	47	0	0	134.47	53
4	DMF	151.29	44	21.24	6	171.38	50
5	Formamide	Eliminated by the statistical analysis					
6	DMSO	158.58	41	49.34	13	180.88	46
7	Pyridine	146.21	44	22.61	7	162.43	49
8	Benzene	105.77	75	0	0	34.67	25
9	DCE	141.14	72	20.56	10	35.23	18
10	DCM	138.92	64	27.41	13	49.76	23
11	Cloroform	124.64	71	32.21	18	19.85	11
12	Diaceton alcohol	Eliminated by the statistical analysis					
13	iso propyl alcohol	134.48	24	193.92	35	232.04	41
14	n Butyl alcohol	132.73	22	233.67	40	226.17	38
15	n Hexyl acohol	128.45	22	215.85	37	245.742	41
16	n Propyl alcohol	134.32	22	251.49	42	218.62	36
17	n Octyl alcohol	124.49	21	204.89	35	258.04	44
18	n Amyl alcohol	129.56	22	218.59	37	240.43	41
19	Ethanol	135.27	23	274.10	46	183.96	31
20	iso butyl alcohol	131.94	23	213.11	37	231.48	40
21	n Benzyl alcohol	140.50	26	280.27	51	128.88	23
22	Methanol	135.90	19	414.58	59	152.37	22
23	Water	152.55	17	727.74	82	6.99	1
24	Ethylene glycol	147.80	19	491.32	62	149.29	19

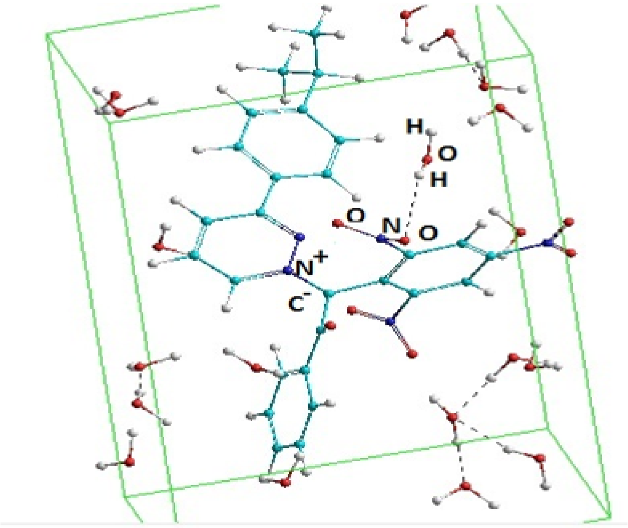

Fig. 4 Hydrogen bonds in binary solution of CPBPM in water

Conclusions

The general SPP scale of solvent dipolarity/polarizability and specific SA and SB scales are orthogonal to one another [20,22] and can be used to analyse the solvent effects on the absorption spectra.

The HBD interactions do not contribute to the spectral shifts of the absorption band of CPBPM in used aprotic solvents from aldehydes and ketones, esters and arenes and alkylarenes groups. For this solvents, the supply of universal forces and of the HBA interactions to the toatal spectral shifts of the absorption band are aproximatively equal. In the other aprotic solvents the supply of HBD interactions to the total spectral shifts is small.

In protic solvents the specific interactions (HBD and HBA) are predominant, while the supply of the universal interactions is smaller.

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