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Spectral Insights on Intermolecular Interactions in Solutions of Some Zwitterionic Compounds

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3 Spectral Insights on Intermolecular Interactions in Solutions of Some Zwitterionic Compounds

Dana Ortansa Dorohoi
and Dan Gheorghe Dimitriu

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Abstract
The solvatochromic features of some zwitterionic compounds in different solutions allow to establish the nature of intermolecular interactions and to evaluate their contribution to the spectral shifts measured in electronic spectra. Some molecular descriptors of spectrally active molecules were estimated from the solvatochromic analysis.
3.1 INTRODUCTION

The atomic systems (atoms, molecules, molecular complexes, and so on) contain electric charges in a continuous motion. Owing to instantaneous dipole moment created by the fluctuations in the motion of the valence electrons, each atomic system creates an instantaneous radial electric field acting on neighboring systems, even if it is neutral from the electric point of view.

The intensity of the electric field in condensed media depends on the reciprocal actions between the components. Onsager (cited by McRae 1956) introduced the notion of internal reactive electric field in condensed media, suggesting the reciprocal influence between the atomic systems. In the internal reactive electric field, the particles possess potential energy which depends on their chemical nature and on the modifications induced in electro-optical parameters by external agents (pressure, temperature, irradiative fields, etc.).

The internal reactive electric field from liquids is difficult to be measured because any device introduced in liquid can perturb the internal forces. The strength of the reactive internal field in liquids can be evaluated only through the modifications induced in the molecular parameters reflected in electronic spectra.

The molecular spectra offer information regarding the strength of the electric fields acting on the spectrally active molecules introduced in small concentrations in condensed media. Especially the electronic (absorption and fluorescence) spectra based on modifications induced by light in the valence molecular electronic cloud offer global information regarding the reactive electric field action on the liquid components. In this aim, spectrally active molecules are introduced in small amounts \((10^{-3}–10^{-5}\ \text{mol/L})\) as “probes” able to give information about the local reactive electric field in the studied liquid. The liquid must solve the spectrally active molecules and must be transparent in the spectral range of the solute spectra.

The spectral changes induced by liquid are related to the band position (given by the wavenumber \(\nu\ (\text{cm}^{-1})\) in the band maximum) and/or to the spectral intensity of the electronic band.

3.2 INTERMOLECULAR INTERACTIONS IN LIQUID SOLUTIONS

The intermolecular interactions from liquids can be classified (McRae 1956, Mataga and Kubota 1970, Bakhshiev 1972, Suppan 1990) into universal (long range) and specific (short range, or quasi-chemical) interactions.

The first type of interactions exerts a global influence on the spectrally active molecules. They are nonoriented, nonsaturated, and can cause spectral shifts of the electronic (absorption and/or fluorescence) bands.

The specific interactions consist of processes with charge transfer between the atomic systems such as hydrogen bonds, or electron transfer. Specific interactions act locally, being evidenced especially in vibration (IR or Raman) spectra, but they can cause supplementary spectral shifts in electronic spectra directly affected by universal forces.
Many chemical and physical processes take place in solutions, being influenced by the solvent nature. The solvent effects depend on the chemical structure of the solute molecules and on the magnitude of the changes in their electro-optical parameters (electric dipole moment, polarizability, ionization potential, etc.) induced by external agents, such as the irradiative fields.

The knowledge of the nature and strength of intermolecular interactions in liquids is very important because most of the chemical reactions take place “in situ” being directly affected by the solvent nature (Wypych 2001, Reichardt 2003).

Usually, the solutions for which the electronic spectra are recorded contain small amounts of spectrally active molecules. In these conditions, the distances between the spectrally active molecules are too large that the interactions between them are negligible.

The solvent molecules create concentric shells having the solute molecule in their center. The internal electric field acting in the point in which the spectrally active molecule is placed modifies the charge distribution and electro-optical parameters of this molecule. The relative distances between the energetic levels of the solute molecule are also modified in the solvation process.

At room temperature, the molecules composing a studied solution are in their ground state. In the light interaction process, the solvent keeps its ground state (being transparent in the searched spectral range), while the solute molecules absorb radiation, passing in excited electronic states. According to Frank–Condon principle (Bayliss and McRae 1954), the electronic transitions are very quick. So, after absorption, the excited solute molecule is in a destabilized state because the solvent arrangement corresponds to the energetic conditions of its ground state. The solvent relaxation process needs a time interval higher compared to the life time of the excited state. In the case of the excited states with a long life time, the solvent molecules can reorient in the electric field created by the solute-excited state dipole moment and the solute molecule becomes stabilized by the new arrangement of the solvent molecules. This phenomenon modifies the energetic levels of the spectrally active molecules and changes the wavenumber in the maximum of the electronic absorption band.

The absorption process takes place between two electronic levels of the spectrally active molecule. The stabilization energies are usually different in the two electronic levels responsible for the absorption band appearance. Their difference determines the spectral shift of the electronic band in the wavenumber scale relative to its position in the gaseous phase corresponding to the isolated molecule (Bakhshiev 1961, Mataga and Kubota 1970, Stone 2013).

The spectral method offering information on intermolecular interactions in solutions is noninvasive; it does not change the internal equilibrium of forces because spectrally active molecules are used as “probes,” no big devices are compared to the molecular dimensions.

In the first stage of the research on intermolecular interactions in solutions, multiple attempts were made in order to evidence some correlations between the spectral characteristics and the micro- and macroscopic parameters of solutions. The spectral shifts were correlated with the solvent refractive index (n), electric permittivity (ε),
ionization potential ($I$), and so on, in order to establish the general characteristics of intermolecular interactions in liquid solutions.

Unfortunately, the liquid phase is very complex, both by the chemical structure of its components and by gentle equilibrium between the potential energy of the molecules in the internal reactive field and the energy of thermal motion which continuously modifies the composition of the molecular shells surrounding the spectrally active molecules and so, the solvation energy of each solute molecule. This fact can be easily evidenced in multicomponent solutions.

The liquid complexity is the cause that the developed theories regarding intermolecular interactions cannot be applied on a large category of liquids.

Some models (McRae 1956, Bakhshiev 1961, Abe 1965) developed for various liquids have limited applicability due to some simplifying hypotheses corresponding to the type of liquid for which they are made. For example, in most of the theoretical descriptions, the specific interactions are neglected, and even there are experimental evidences for their presence in the majority of liquids (Reichardt 2003).

In order to accord the theory with the experiment, the researchers added empirical terms to the theoretical relations to describe the influence of the specific interactions on the electronic spectra.

Some known empirical scales (Kosower 1958, Kamlet et al. 1977, Catalan 2009) were proposed. The solvents are arranged according to their spectral influence on the related compounds from the structural point of view (Benchea et al. 2014, Babusca and Dorohoi 2016).

3.3 COMPUTATIONAL METHODS IN DESCRIBING INTERMOLECULAR INTERACTIONS IN SOLUTIONS

In the specialized literature, there are tendencies to select only the results that confirm the considered models and in which the supplementary spectral shifts are attributed to various specific interactions. This procedure makes such verifications inconvenient and could be considered as nonobjective.

Based on the theoretical and empirical dependences between the spectral shifts and the solution parameters, computational methods were applied to experimental data in order to establish the contribution of different types of interactions to the wavenumber in the maximum of the electronic (absorption and/or fluorescence) bands. Relations of the type

$$\nu = \nu_0 + C_1 \epsilon + C_2 f(n) + C_3 \beta + C_4 \alpha + \cdots$$  \hspace{1cm} (3.1)

are usually applied to experimental data in order to establish the regression coefficients $C_1$, $C_2$, ..., $C_n$, which in existent theories are dependent on the microscopic parameters of the spectrally active molecules (Dorohoi 2010).

The regression parameters show, by their magnitude and sign, the sensibility of the spectrally active molecule to the interactions described by the corresponding term and the sense of the spectral shift in the wavenumber scale, respectively.

The greatest value of one regression coefficient demonstrates that the intermolecular interaction described by the corresponding term is dominant in solution.
The negative signs of the terms in relation (3.1) determine the bathochromic (toward red) shift of the electronic bands due to the corresponding effects. Contrarily, the positive signs of the terms in Equation 3.1 determine the hypsochromic effect, shifting the electronic bands to blue.

Great correlation coefficient ($R$) and small standard deviation (SD), resulted from the statistical analysis, demonstrate the applicability of the model (described by the non-null regression coefficients $C_i$, $i = 1, 2, \ldots, n$) of Equation 3.1 to the studied solution.

### 3.4 ZWITTERIONIC COMPOUNDS

The multitude of compounds in organic chemistry is essentially based on the covalent bonds among atoms. The covalent bonds between atoms with different chemical structure have polar character, due to the higher electron density near the more electronegative atom. The chemical compounds containing basic and acid groups able to neutralize each other are named zwitterionic. The structure of a zwitterionic compound can be written with one negative and one positive charges placed on different atoms.

#### 3.4.1 CYCLOIMMONIUM YLIDS AS ZWITTERIONIC COMPOUNDS

The ylidic bond is realized between two charged (one heteroatom and one carbanion) atoms having an orbital occupied by two electrons uninvolved in the covalent bond. The term ylid (Johnson 1966, Zugravescu and Petrovanu 1976) was introduced by Witting in 1944. It suggests both the presence of a free valence and the anionic nature of this kind of molecules.

$N$-ylids are compounds in which a nitrogen atom is covalently bonded to carbanion. If the nitrogen atom belongs to a heterocycle (see Figure 3.1a), the compounds are named cycloimmonium ylids (Zugravescu and Petrovanu 1976).

As cation, the positive part of the cycloimmonium ylids (Johnson 1966, Zugravescu and Petrovanu 1976) can be one heterocycle, most common being pyridine, iso-quinoline, pyridazine, phthalazinium, and so on.

Having in view the carbanion structure, cycloimmonium ylids can be classified into carbanion mono- and carbanion disubstituted ones, if they possess one proton or one atomic group as $R_1$ substituent, respectively. The $R_2$ substituent must be a high electronegative atomic group in order to assure the ylid stability. The carbanion

![Figure 3.1](a) Chemical structure of cycloimmonium ylids; (b) ICT mechanism in the case of cycloimmonium ylids.)
symmetrically disubstituted cycloimmonium ylids has two identical substituents \( R_1 = R_2 \). Symbiosis effect has been emphasized in the case of the symmetrically substituted carbanion (Surpateanu and Dorohoi 1977, Dorohoi, 2007).

The cycloimmonium ylid stability depends on the chemical nature of both the heterocycle and the groups covalently bonded to the ylid carbanion. The greater the capacity of the groups attached to the carbanion to accept the negative charge and of the heterocycle to bear positive charge, the higher the ylid stability is. The carbanion-disubstituted cycloimmonium ylids are more stable than the carbanion-monosubstituted ones. The highest stability is obtained for the carbanion disubstituted with strongly electronegative atomic groups (Surpateanu et al. 1975, Dorohoi 2004).

Cycloimmonium ylids are nucleophilic compounds (Gheorghies et al. 2008, Dorohoi et al. 2013), which can react with a large variety of organic compounds. As a participant to cycloaddition reactions, the cycloimmonium ylids are precursors (Melnig et al. 2006) for new heterocycle compounds.

### 3.4.2 Spectral Study of Cycloimmonium Ylids Using the Solvent Empirical Polarity

In absorption, all cycloimmonium ylids show a visible electronic band classified into an intramolecular charge transfer (ICT) (see Figure 3.1b) from the carbanion toward the heterocycle (Dorohoi et al. 1994, 2012, Dimitriu et al. 2008, Closca et al. 2014a). This electronic band is very sensitive to the solvent nature and it disappears in acid media, due to ylid protonation at the carbanion level (Gheorghies et al. 2008, Dorohoi et al. 2013).

In chemistry, the cycloimmonium ylids can be used as acid–basic indicators because this band is very sensitive to the solution pH (Zugravescu and Petrovanu 1976, Dulcescu and Dorohoi 2009).

The linear dependence of \( E_{\text{max}} \) (kcal/mol) versus \( Z \) (kcal/mol) (Figure 3.2 and Tables 3.1 and 3.2) proves the ICT nature of the visible band of cycloimmonium ylids (Dorohoi 2004, Dulcescu et al. 2010a,b, Homocianu et al. 2011a,b). This assertion is based on the ICT in 1-ethyl-4-carbomethoxy-pyridinium iodide responsible for the visible band considered (Kosower 1958, 1968) as an indicator of the solvent polarity.

Being very sensitive to the solvent nature, the visible ICT band of cycloimmonium ylids can give information about the nature and the strength of intermolecular interactions in solutions (Gheorghies et al. 2010, Closca et al. 2014a). So, the cycloimmonium ylids can be used as sounders in estimating the internal reactive field created by the solvent in the place of the solved molecule (Figure 3.3).

The slopes and the cuts at the origin of the equations

\[
E_{\text{max}} \text{ (kcal/mol)} = mZ \text{ (kcal/mol)} + n
\] (3.2)

depend both on the heterocycle nature and on the carbanion substituents (Dorohoi 2004, Closca et al. 2014b, Babusca and Dorohoi 2016). The carbanion mono-substituted cycloimmonium ylids are a few sensitive to the solvent nature (see Table 3.2).
As dipolar molecules, cycloimmonium ylids participate essentially to orientation–induction interactions which are stronger in their ground state, compared to the excited electronic state. This fact can be explained due to the charge transfer from carbanion to the heterocycle, causing the decrease of the ylid dipole moment. The cycloimmonium ylids are also nucleophilic compounds able to participate to proton changes with hydroxyl solvents, accepting protons from acidic (HBD) solvents such as alcohols or acids. This phenomenon was demonstrated by the aspects of the graphs of the wavenumber $\nu$ (cm$^{-1}$) in the maximum of the ICT band versus electric permittivity of the solvents (see Figure 3.4). In these graphs (Dorohoi 2004, 2006,
TABLE 3.1
Energy in the Maximum of the Visible ICT Band of Some Cycloimmomium Ylids in Binary Solutions

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( Z ) (kcal/mol)</th>
<th>( \varepsilon )</th>
<th>( iQCM )</th>
<th>( iQDiCM )</th>
<th>( iQCBM )</th>
<th>( CuPNiPY )</th>
<th>( CuPABM )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorobenzene</td>
<td>59.1</td>
<td>5.62</td>
<td>51.0</td>
<td>60.8</td>
<td>63.5</td>
<td>57.0</td>
<td>57.5</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>60.3</td>
<td>6.02</td>
<td>–</td>
<td>61.5</td>
<td>63.5</td>
<td>56.9</td>
<td>58.0</td>
</tr>
<tr>
<td>Anisal</td>
<td>60.6</td>
<td>4.33</td>
<td>–</td>
<td>62.1</td>
<td>65.0</td>
<td>56.9</td>
<td>57.7</td>
</tr>
<tr>
<td>Benzene</td>
<td>62.4</td>
<td>2.27</td>
<td>51.5</td>
<td>60.5</td>
<td>63.2</td>
<td>–</td>
<td>57.5</td>
</tr>
<tr>
<td>Chloroform</td>
<td>63.2</td>
<td>4.81</td>
<td>51.7</td>
<td>63.0</td>
<td>65.3</td>
<td>57.6</td>
<td>59.3</td>
</tr>
<tr>
<td>Dichloroethane</td>
<td>63.2</td>
<td>10.36</td>
<td>–</td>
<td>62.5</td>
<td>64.6</td>
<td>–</td>
<td>58.2</td>
</tr>
<tr>
<td>Pyridine</td>
<td>64.0</td>
<td>12.4</td>
<td>51.5</td>
<td>61.5</td>
<td>65.0</td>
<td>56.9</td>
<td>58.2</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>64.2</td>
<td>8.93</td>
<td>51.7</td>
<td>62.8</td>
<td>65.0</td>
<td>57.7</td>
<td>58.1</td>
</tr>
<tr>
<td>Iso-amyl acetate</td>
<td>64.4</td>
<td>4.8</td>
<td>–</td>
<td>62.1</td>
<td>65.0</td>
<td>57.8</td>
<td>57.7</td>
</tr>
<tr>
<td>Acetone</td>
<td>65.7</td>
<td>20.7</td>
<td>–</td>
<td>62.8</td>
<td>64.6</td>
<td>58.0</td>
<td>58.6</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>68.5</td>
<td>36.7</td>
<td>51.6</td>
<td>63.5</td>
<td>65.0</td>
<td>57.6</td>
<td>58.8</td>
</tr>
<tr>
<td>Dimethylsulfoxide</td>
<td>71.1</td>
<td>46.7</td>
<td>51.4</td>
<td>64.2</td>
<td>65.7</td>
<td>57.8</td>
<td>59.2</td>
</tr>
<tr>
<td>Diacetalcohol</td>
<td>74.7</td>
<td>18.2</td>
<td>51.9</td>
<td>65.7</td>
<td>68.1</td>
<td>58.9</td>
<td>60.5</td>
</tr>
<tr>
<td>Iso-propyl alcohol</td>
<td>76.3</td>
<td>17.9</td>
<td>–</td>
<td>65.7</td>
<td>60.7</td>
<td>59.4</td>
<td>61.8</td>
</tr>
<tr>
<td>( n )-Butyl alcohol</td>
<td>77.7</td>
<td>17.51</td>
<td>51.3</td>
<td>66.5</td>
<td>70.2</td>
<td>60.2</td>
<td>61.8</td>
</tr>
<tr>
<td>( n )-Hexyl alcohol</td>
<td>78.2</td>
<td>12.5</td>
<td>51.3</td>
<td>65.7</td>
<td>69.7</td>
<td>59.2</td>
<td>61.5</td>
</tr>
<tr>
<td>( n )-Propyl alcohol</td>
<td>78.2</td>
<td>20.33</td>
<td>–</td>
<td>66.5</td>
<td>70.6</td>
<td>59.6</td>
<td>61.8</td>
</tr>
<tr>
<td>( n )-Octyl alcohol</td>
<td>79.1</td>
<td>9.80</td>
<td>51.3</td>
<td>65.7</td>
<td>69.7</td>
<td>59.2</td>
<td>61.5</td>
</tr>
<tr>
<td>( n )-Amyl alcohol</td>
<td>79.4</td>
<td>14.8</td>
<td>51.8</td>
<td>65.7</td>
<td>69.7</td>
<td>59.6</td>
<td>61.5</td>
</tr>
<tr>
<td>Ethanol</td>
<td>79.6</td>
<td>24.5</td>
<td>51.3</td>
<td>67.7</td>
<td>70.6</td>
<td>60.0</td>
<td>62.1</td>
</tr>
<tr>
<td>Iso-butyl alcohol</td>
<td>80.6</td>
<td>18.1</td>
<td>51.4</td>
<td>66.5</td>
<td>70.4</td>
<td>59.6</td>
<td>62.0</td>
</tr>
<tr>
<td>Formamide</td>
<td>81.0</td>
<td>84.00</td>
<td>52.0</td>
<td>68.9</td>
<td>71.5</td>
<td>59.6</td>
<td>63.5</td>
</tr>
<tr>
<td>( n )-Benzy1 alcohol</td>
<td>82.1</td>
<td>13.5</td>
<td>51.6</td>
<td>66.9</td>
<td>70.4</td>
<td>–</td>
<td>62.1</td>
</tr>
<tr>
<td>Methanol</td>
<td>83.6</td>
<td>32.7</td>
<td>51.5</td>
<td>68.5</td>
<td>72.4</td>
<td>–</td>
<td>63.5</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>85.1</td>
<td>37.70</td>
<td>51.7</td>
<td>68.9</td>
<td>72.8</td>
<td>60.6</td>
<td>64.2</td>
</tr>
</tbody>
</table>

Significance of the notations: \( iQCM \), iso-quinolinium carbethoxy methylid; \( iQDiCM \), iso-quinolinium dicarbethoxy methylid; \( iQCBM \), iso-quinolinium carboethoxy-benzoyl-methylid; \( CuPNiPY \), \( p \)-cumyl-pyridazinium-\( p \)-nitrophenacylid; \( CuPABM \), \( p \)-cumyl-pyridazinium-acetyl-benzoyl-methylid.

Dimitriu et al. 2008, Gheorghies et al. 2008, Homocianu et al. 2011a,b) for the same value of the electric permittivity, the protic solvents are placed to higher wavenumbers on the second curve expressing this dependence. At the same time, the aprotic solvents determine the first curve placed on the smaller values of the wavenumbers (see Figure 3.4a and b).

The distance between the two curves containing the aprotic and protic solvents, respectively, can be considered as a measure for the specific interactions of the hydrogen bond type between the ylid and hydroxyl solvent. This distance is proportional...
Spectral Insights on Intermolecular Interactions in Solutions

3.6 SOME DESCRIPTORS OF CYCLOIMMONIUM YLIDS ESTIMATED FROM SOLVATOCHROMIC STUDY

The solvatochromic studies corroborated with the theories about the simple liquids can give information about the strength of the molecular interactions in liquid solutions. The electro-optical parameters in the excited states of the spectrally active molecules can be estimated by the magnitude of the frequency shifts in electronic spectra. The existent theories regarding the solvent influence on the electronic absorption and fluorescence spectra permit to estimate some electro-optical parameters in the molecular-excited states. The theory developed by McRae and modified by Bakhshiev permits to estimate the dipole moments of the spectrally active (in

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|}
\hline
\textbf{C\% Ethanol in Water} & \textbf{\(Z\) (kcal/mol)} & \textbf{\(E_{\text{max}}\) (kcal/mol)} & \textbf{CuNiPY} \\
98 & 80.2 & 59.7 & 62.5 \\
96.9 & 80.8 & 60.0 & 62.7 \\
95.0 & 81.2 & 60.1 & 62.8 \\
92.0 & 82.0 & 60.2 & 62.9 \\
90.0 & 82.5 & 60.2 & 63.0 \\
85.0 & 83.8 & 60.3 & 63.5 \\
80.0 & 84.8 & 60.4 & 63.8 \\
75.0 & 85.7 & 60.6 & 64.2 \\
70.0 & 86.4 & 60.7 & 64.4 \\
\hline
\textbf{C\% Acetone in Water} & & & \\
99.0 & 68.1 & 58.3 & 58.9 \\
95.0 & 72.9 & 58.8 & 59.6 \\
93.0 & 74.8 & 58.9 & 60.0 \\
90.0 & 76.6 & 59.1 & 60.5 \\
85.0 & 78.8 & 59.7 & 61.0 \\
75.0 & 80.7 & 60.0 & 61.8 \\n70.0 & 82.1 & 60.3 & 62.5 \\
65.0 & 83.2 & 60.6 & 62.5 \\
60.0 & 84.3 & 60.9 & 63.2 \\
55.0 & 85.5 & 61.2 & 63.5 \\
\hline
\end{tabular}
\caption{Energy in the Maximum of the Visible ICT Band of Some Cycloimmonium Ylids in Ternary Solutions Ethanol + Water and Acetone + Water}
\end{table}

with the contribution of the specific interactions to the total spectral shift recorded in the electronic absorption spectra of cycloimmonium ylids.
absorption and/or fluorescence) molecules in both electronic states participating to the electronic transitions. In relation (3.1), the significance of the regression coefficient $C_1$ is given by relations

$$C_{1g} = \frac{2}{h c r^3} \frac{2n^2 + 1}{n^2 + 2} \mu_g (\mu_e - \mu_g \cos \phi)$$

(3.3)

$$C_{1e} = \frac{2}{h c r^3} \frac{2n^2 + 1}{n^2 + 2} \mu_e (\mu_e - \mu_g \cos \phi)$$

(3.4)

In relations (3.3) and (3.4), the parameters have the following significance: $\mu$ is the electric dipole moment in the ground ($g$) and in excited ($e$) electronic states of the solute molecule; $\phi$ is the angle between the dipole moments in the electronic states participating to the absorption/fluorescence transition, $h$ is Planck’s constant, $c$ is the velocity of light, and $r$ is the solute Onsager radius.

FIGURE 3.3 $E_{\text{max}}$ (kcal/mol) versus $Z$ (kcal/mol) for CuPNiPY and CuPABM in ternary solutions ethanol + water + cycloimmonium ylids.
For the molecules with electronic absorption ($a$) and fluorescence ($f$) bands, such as the pyridazinium ylids, both the ground state and the excited state dipole moments can be estimated, as it is described below (Dorohoi 2006, Dorohoi et al. 1998). The studied molecules have the structural formula from Figure 3.5 and the attached substituents from Table 3.3. Pyridazinium ylids from Table 3.3 show visible absorption and fluorescence bands (Pop et al. 1994).

**FIGURE 3.4** $\bar{\nu}$ (cm$^{-1}$) versus $\varepsilon$ for iQDiCM and CuPABM cycloimmonium ylids in binary solutions.

**FIGURE 3.5** Chemical structures of the fluorescent pyridazinium ylids.
The cycloimmonium ylids’ denomination from Table 3.3: Pyridazinium-\( (p\)-methoxy-benzoyl) phenacylid (PMBP); \( p\)-phenyl-pyridazinium-(\( p\)-methoxy-benzoyl)-phenacylid (PPMBP); \( p\)-tolyl-pyridazinium-di-benzoyl methylid (TPDiBM); and \( p\)-cumyl-pyridazinium-(acetyl-benzoyl) methylid (CPABM).

The wavenumber in the maximum of the ylids from Table 3.3 was correlated with the solvent electric permittivity (\( \varepsilon \)), refractive index (\( n \)), and spectral shift of the hydroxyl proton measured in nuclear magnetic resonance (NMR) spectra. The dependence of the type

\[
\nu = \nu_0 + C_1 \frac{\varepsilon - 1}{\varepsilon + 2} + C_2 \frac{n^2 - 1}{n^2 + 2} + C_3 \delta_{OH}
\]  

(3.5)

where \( \delta_{OH} \) is the chemical shift (in ppm) measured in the NMR spectrum of the protic solvent.

The statistical analysis using relations (3.3) and (3.4) both in absorption and fluorescence emphasized the regression coefficients from Table 3.4.

Table 3.5 contains the values of the electric dipole moment in the ground state and the molecular radius of pyridazinium ylids (computed by HyperChem 8.0.6 using PM3). The excited state dipole moments, the angle \( \phi \) between dipole moments, and the transition dipole moment are also listed in Table 3.5.

From the data of Table 3.5, it results in the decrease of the molecular dipole moment in the absorption process. The small values of the dipole moment in the excited state determine the dispersion–polarization nature of the intermolecular forces between the solute and the solvent molecules, while in the ground state of pyridazinium ylids, the dipolar orientation–induction interactions are dominant. The solvation energy by orientation–induction interactions is smaller in the ylid-excited state than in its ground state. For similar structures, the same conclusions can be drawn (Pop et al. 1994, Gheorghies and Dorohoi 2008).

The reciprocal orientation of the dipole moments in the electronic states participating in the photon absorption is shown in Figure 3.6.

In order to estimate the dipole moments in the electronic states participating in the absorption/emission process responsible for the visible band appearance, Equations 3.3 and 3.4 were solved having in view the values of the coefficients in multilinear regression applied to the spectral data. In accordance with Table 3.5 and

<table>
<thead>
<tr>
<th>Name</th>
<th>( R_1 )</th>
<th>( R_2 )</th>
<th>( R_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PMBP)</td>
<td>–H</td>
<td>–H</td>
<td>–COC(_2)H(_5)–OCH(_3) (( p ))</td>
</tr>
<tr>
<td>(PPMBP)</td>
<td>–C(_6)H(_5)</td>
<td>–H</td>
<td>–COC(_2)H(_5)–OCH(_3) (( p ))</td>
</tr>
<tr>
<td>(TPDiBM)</td>
<td>–C(_6)H(_4)–CH(_3) (( p ))</td>
<td>–COC(_2)H(_5)</td>
<td>–COC(_2)H(_5)</td>
</tr>
<tr>
<td>(CPABM)</td>
<td>–C(_6)H(_4)–CH(_3)(CH(_3)) (( p ))</td>
<td>–COCH(_3)</td>
<td>–COC(_2)H(_5)</td>
</tr>
</tbody>
</table>
Equations 3.3 and 3.4, there are two solutions for the excited state dipole moment; the first corresponds to the null value and the latter to $\mu_e = \mu_g \cos \phi$. The values of the ground-state dipole moment in the case $\mu_e = 0$, obtained for the system of Equations 3.3 and 3.4, are written in the last row of Table 3.5.

The hydrogen bonds possible to be made between the nonparticipant electrons of the ylid carbanion and the hydroxyl groups of alcohol or acids are weaker in the excited state of the cycloimmonium ylid molecules. The estimation of a null contribution of the orientation–induction forces in fluorescence spectra proves that by

### Table 3.4
Regression Coefficients, Correlation Coefficient, and Standard Deviation for Spectral Absorption and Fluorescence Data of the Studied Pyridazinium Ylids Analyzed with Formula (3.1)

<table>
<thead>
<tr>
<th>Ylid</th>
<th>PMBP</th>
<th>PPMBP</th>
<th>TPDibM</th>
<th>CPABM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{\nu}_0 \pm \Delta \bar{\nu}_0$ (cm$^{-1}$)</td>
<td>20550 ± 280</td>
<td>19870 ± 130</td>
<td>20200 ± 150</td>
<td>20080 ± 130</td>
</tr>
<tr>
<td>$\bar{\nu}_0' \pm \Delta \bar{\nu}_0'$ (cm$^{-1}$)</td>
<td>19710 ± 360</td>
<td>19310 ± 260</td>
<td>19560 ± 260</td>
<td>19666 ± 360</td>
</tr>
<tr>
<td>$\Gamma^a \pm \Delta \Gamma^a$ (cm$^{-1}$)</td>
<td>867 ± 330</td>
<td>683 ± 351</td>
<td>829 ± 208</td>
<td>720 ± 280</td>
</tr>
<tr>
<td>$\Gamma^a' \pm \Delta \Gamma^a'$ (cm$^{-1}$)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\gamma{\Delta \Gamma^a}$ (cm$^{-1}$)</td>
<td>9±6</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\bar{\nu}_e \pm \Delta \bar{\nu}_e$ (cm$^{-1}$)</td>
<td>-1076 ± 520</td>
<td>-1920 ± 700</td>
<td>-2016 ± 750</td>
<td>-5060 ± 2318</td>
</tr>
<tr>
<td>$\Gamma^a \pm \Delta \Gamma^a$ (cm$^{-1}$)</td>
<td>0</td>
<td>0</td>
<td>176 ± 27</td>
<td>192 ± 16</td>
</tr>
<tr>
<td>$\gamma{\Delta \Gamma^a}$ (cm$^{-1}$)</td>
<td>0</td>
<td>37 ± 12</td>
<td>0</td>
<td>42 ± 22</td>
</tr>
<tr>
<td>$R_e$</td>
<td>0.93</td>
<td>0.95</td>
<td>0.91</td>
<td>0.99</td>
</tr>
<tr>
<td>$R'_e$</td>
<td>0.91</td>
<td>0.90</td>
<td>0.93</td>
<td>0.92</td>
</tr>
<tr>
<td>SD$^a$</td>
<td>76</td>
<td>80</td>
<td>96</td>
<td>130</td>
</tr>
<tr>
<td>SD$^c$</td>
<td>88</td>
<td>105</td>
<td>77</td>
<td>117</td>
</tr>
</tbody>
</table>

### Table 3.5
Ground $\mu_g$ (D) and Excited $\mu_e$ (D) States Dipole Moments, Angle $\phi$ (degree) between Them, and the Transition Dipole Moment $\Delta \mu_{eg}$ (D) of the Studied Pyridazinium Ylids

<table>
<thead>
<tr>
<th>Ylid</th>
<th>PMBP</th>
<th>PPMBP</th>
<th>TPDibM</th>
<th>CPABM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_g$ (D) (computed by PM3)</td>
<td>8.30</td>
<td>5.20</td>
<td>8.10</td>
<td>6.50</td>
</tr>
<tr>
<td>$\gamma$ (Å) (computed by PM3)</td>
<td>10</td>
<td>8</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>$\mu_e$ (D)</td>
<td>1.78</td>
<td>1.57</td>
<td>1.66</td>
<td>0.73</td>
</tr>
<tr>
<td>$\phi$ (degree)</td>
<td>77.62</td>
<td>76.04</td>
<td>78.15</td>
<td>81.90</td>
</tr>
<tr>
<td>$\Delta \mu_{eg}$ (D)</td>
<td>7.73</td>
<td>6.30</td>
<td>7.58</td>
<td>5.14</td>
</tr>
<tr>
<td>$\gamma$ (degree)</td>
<td>167.62</td>
<td>166.15</td>
<td>168.15</td>
<td>171.56</td>
</tr>
<tr>
<td>$\mu_g$ (D) for $\mu_e = 0$</td>
<td>8.11</td>
<td>5.15</td>
<td>7.93</td>
<td>6.31</td>
</tr>
</tbody>
</table>
excitation both in protic and in aprotic solvents, the electric dipole moment of cycloimmonium ylids is smaller than the dipole moment in their ground state.

3.7 TERNARY SOLUTIONS OF CYCLOIMMONIUM YLIDS INTERACTION ENERGY IN THE GROUND STATE OF THE MOLECULAR PAIRS

Some interesting results can be obtained in solvatochromic analysis of the ternary solutions of cycloimmonium ylids. In this kind of studies, the difference between interactions energies in the molecular pair made by the solute molecule and the molecules of the two miscible solvents (one active and one inactive from the molecular interactions point of view) is estimated. One can exemplify by the ternary solutions made in a binary solvent containing one protic and one aprotic liquid. As nucleophilic molecules cycloimmonium ylids participate to specific interactions of the type of hydrogen bonds and in this context, the protic solvent can be considered more active than the aprotic ones from the interactions point of view.

As it was established in Chapter 2, the cell model of the ternary solutions (Mazurenko 1972, Perov 1980, Pop et al. 1986) can be applied to some cycloimmonium ylids having triazolium derivatives as the heterocycle. The similar dependences with those established in Chapter 2 can be obtained for other cycloimmonium ylids. We resume only the values of the potential energy in molecular pairs of the types cycloimmonium ylid–active solvent and cycloimmonium ylid–inactive solvent. Estimations (see Tables 3.6 through 3.8) are made for the experimental results obtained in diluted solutions and refer to the ground state of the molecular pairs, as it results from the theoretical model (Pop et al. 1986, Dorohoi and Pop 1987).

When one protic and one aprotic solvents compose the binary solvent, the difference between the molecular pairs energy is proportional to the energy of the hydrogen bond, especially when the macroscopic parameters of the two solvents have appropriate values (in order to equalize the universal interactions of the solute molecule with the two solvents) (Dorohoi et al. 2008, Avadanei et al. 2011, 2015).

In the case of a binary solvent containing two hydroxyl components, the difference $\omega_2 - \omega_1$ is very small, because the specific interactions have contributions in the two terms of the differences (Dulcescu et al. 2010a,b).
### TABLE 3.6
Difference of Energies in Molecular Pairs Realized by Phthalazinium Dibenzoyl Methylid (Melniciuc-Puica et al. 2012) and Solvent Molecules in Ternary Solutions

<table>
<thead>
<tr>
<th>Binary Solvent</th>
<th>$m \pm \Delta m$</th>
<th>$n \pm \Delta n$</th>
<th>$R$</th>
<th>$kT(n \pm \Delta n)10^{-20}$ (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water + ethanol</td>
<td>0.674 ± 0.049</td>
<td>0.605 ± 0.188</td>
<td>0.998</td>
<td>0.245 ± 0.076</td>
</tr>
<tr>
<td>Proionic acid + chloroform</td>
<td>1.8583 ± 0.096</td>
<td>3.587 ± 0.178</td>
<td>0.997</td>
<td>1.451 ± 0.072</td>
</tr>
<tr>
<td>Octanol + dichloroethane</td>
<td>1.267 ± 0.010</td>
<td>3.055 ± 0.022</td>
<td>0.999</td>
<td>1.236 ± 0.009</td>
</tr>
</tbody>
</table>

### TABLE 3.7
Difference of Energies in Molecular Pairs Realized in Ternary Solutions by Cycloimmonium Di-Carboethoxy Methylids (Having Pyridinium and Iso-Quinolinium as Heterocycles)

<table>
<thead>
<tr>
<th>Ylid</th>
<th>$m \pm \Delta m$</th>
<th>$n \pm \Delta n$</th>
<th>$R$</th>
<th>$kT(n \pm \Delta n)10^{-20}$ (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDCM</td>
<td>0.976 ± 0.030</td>
<td>−0.093 ± 0.046</td>
<td>0.99</td>
<td>−0.037 ± 0.018</td>
</tr>
<tr>
<td>iQDCM</td>
<td>0.953 ± 0.021</td>
<td>−0.285 ± 0.032</td>
<td>0.99</td>
<td>−0.115 ± 0.013</td>
</tr>
</tbody>
</table>


PDCM—pyridinium dicarboethoxy-methylid. iQDCM—iso-quinolinium-dicarboethoxy-methylid.

Binary solvent: ethylene glycol + dioxane.

### TABLE 3.8
Difference of Energies in Molecular Pairs Realized in Ternary Solutions by Cycloimmonium Carboethoxy-Anilido-Methylids (Having Pyridinium and Iso-Quinolinium as Heterocycles)

<table>
<thead>
<tr>
<th>Ylid</th>
<th>$m \pm \Delta m$</th>
<th>$n \pm \Delta n$</th>
<th>$R$</th>
<th>$kT(n \pm \Delta n)10^{-20}$ (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCAM</td>
<td>1.229 ± 0.039</td>
<td>3.326 ± 0.089</td>
<td>0.99</td>
<td>1.345 ± 0.036</td>
</tr>
<tr>
<td>iQCAM</td>
<td>1.325 ± 0.078</td>
<td>3.714 ± 0.178</td>
<td>0.98</td>
<td>1.503 ± 0.071</td>
</tr>
</tbody>
</table>


PCAM—pyridinium carboethoxy anilido methylid. iQCAM—iso-quinolinium carboethoxy anilido methylid.

Binary solvent: octanol + dichloromethane.
In Chapter 2, some results obtained for the carbanion monosubstituted triazolium ylids in ternary solutions are detailed.

### 3.8 CONCLUSIONS

Zwitterionic compounds show visible electronic bands with ICT. They are very sensitive to the solvent nature. The energies in the maximum of the ICT bands of cycloimmonium ylids linearly depend on the solvent empirical polarities defined by Kosower.

The protic and aprotic solvents are separated on two distinct curves in the graphs $\tilde{\nu}$ (cm$^{-1}$) versus $\varepsilon$ due to the supplementary shift caused by hydrogen bonds between the cycloimmonium ylids carbanion and the hydroxyl group of the protic solvents.

When cycloimmonium ylids are spectrally active both in absorption and fluorescence spectra, the dipole moments in the electronic states participating to the electronic transition and the angle between them can be estimated from the solvent influence of the solvent on electronic spectra.

Spectral study in ternary solutions of cycloimmonium ylids permits to estimate, in the limits of the cell model of multicomponent solutions, the difference between the energies in molecular pairs achieved between ylid molecules and the molecules of the two components of the binary solvent. If the binary solvent contains one protic and one aprotic solvent, the energy difference is proportional to the contribution of the hydrogen bond to the total spectral shift.

Solvatochromic study of cycloimmonium ylids contributes to obtain information both on the electro-optical parameters of these molecules and on the contribution of each type of intermolecular interactions to the spectral shift measured in each solvent.

### REFERENCES


Spectral Insights on Intermolecular Interactions in Solutions

Catalan, J. 2009. Toward a generalized treatment of the solvent effect based on four empirical scales: Dipolarity (SdP, a new scale); Polarity (SP); Acidity (SA); Basicity (SB) of the medium. J. Phys. Chem. 113:5951–5960.


