Spectral and Thermodynamical Studies on iso-Quinolinium Carbethoxy Methylid (iQCEM) Solutions with Binary Solvent Water (W) + Ethanol (E)

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The electronic absorption spectra of iso-Quinolinium Carbethoxy Methylid (iQCEM) in binary solvents water + ethanol in twenty two different ratios were analyzed in order to obtain information about the water content in the first solvation shell of iQCEM in the studied ternary solutions. The main result of this investigation is given by the approximately equal values found for water molar fraction in the all ternary solutions and water average statistic weight in the first solvation shell of iQCEM for all water+ ethanol binary solvents. Also the estimation of the excited state dipole moment was carried out based on the molecular modelling results and the solute molecule solvatochromic behaviour.

Keywords: iso-quinolinium ylid, ternary mixtures, electronic absorption spectra, semi-empirical molecular modelling

Iso-quinolinium ylids [1-3] are zwitterionic compounds with basic character in which the nitrogen atom is covalently bonded to a carbon, named carbanion. The carbanion monosubstituted iso-quinolinium methylidys contain two substituents at their carbanion (one hydrogen atom and one electronegative atomic group). They are less stable compared with the bi-substituted ones (with two electronegative substitutes at carbanion). The isoquinolinium carbethoxy methylid (iQCEM) stability increases with the electronegativity of the carbanion substituents. The molecule of iQCEM is a carbanion monosubstituted ylid having as substituents hydrogen and carbethoxy group bonded to the carbanion.

All cycloimmonium ylids exhibit an electronic absorption band in the visible range attributed to an intramolecular charge transfer (ICT) from the carbanion towards the heterocycle [1-6]. This band is very sensitive to the solvent nature. For this reasons, iso-quinolinium ylids can be used as spectrally active probes in the visible range, when the intermolecular interactions are studied. In the aprotic solvents, cycloimmonium ylids can be involved in universal interactions of orientation, induction and/or polarization types, while in the protic solvents, the spectrally active molecules can also be involved in specific interactions of the hydrogen bond type [4-6].

One of the most active solvent from the intermolecular interactions point of view is water. As a polar solvent, water is a hydroxyl-type compound able to develop hydrogen bonds with cycloimmonium ylids. Alcohols can also be involved in hydrogen bonding with iQCEM. Complexes formation of water-water, water-ethanol, water-iQCEM, ethanol-ethanol and ethanol-iQCEM type can be explained by hydrogen bonds yielding in water + ethanol + iQCEM ternary solutions with different molar concentrations characterizing the binary solvent (i.e. water + ethanol).

In ternary solutions containing solvents with hydroxyl group in their molecules, like water, ethanol and iQCEM studied inhere, the two hydroxyl solvents compete to occupy the first solvation shell around the ylid. This fact induces a degree of non-homogeneity of ternary solutions of iQCEM. So, the molar ratio, \( x_i \), of the active solvent (considered here as being water) can differ by the average statistic weight, \( p_i \), of this solvent in the first solvation shell [7-10].

\[
x_i = \frac{c_i \frac{\rho_i}{M_i}}{c_i \frac{\rho_1}{M_1} + c_2 \frac{\rho_2}{M_2}}
\]

\[
p_i = \frac{x_1 \exp\left(-\frac{w_1}{kT}\right)}{x_1 \exp\left(-\frac{w_1}{kT}\right) + x_2 \exp\left(-\frac{w_2}{kT}\right)}
\]

where \( c_i \) is the volumetric concentration of the \( i \) component, \( \rho_i \) and \( M_i \) are its density and respectively its molar mass, \( w_i \) is the intermolecular solute-solvent interaction energy, \( T \) is the absolute temperature and \( k \) is the Boltzmann constant. As it results from the definition relations (1) and (2), \( x_i \) and \( p_i \) must have different values, depending only on the volumetric concentrations, \( c_i \) and \( c_2 \), of the two solvents and on their density, \( \rho_i, i = 1,2 \) and molar mass, \( M_i, i = 1,2 \). The average statistic weight \( p_i \) supplementary depends on the strengths of pair - interactions between (solute-solvent) and (solute-solvent) molecules. From the theoretical point of view, \( x_i \) must differ from \( p_i \). Some parameters which indicate the solution non-ideality were defined in order to characterize the spatial domains neighboring the spectrally active molecules.

The preferential solvation constant, \( K_{12} \) defined by Frankel and co-workers [11] can be also considered an indicator of the ternary solution non-homogeneity.

\[
K_{12} = \left( \frac{p_1}{1 - p_1} \right) \left( \frac{1 - x_1}{x_1} \right)
\]

When \( K_{12} > 1 \), it results \( p_1 > x_1 \). In this case, the average statistic weight of the active solvent in the first solvation shell of the spectrally active molecule iQCEM is higher than...
its bulk fraction in the binary solvent. Due to the specific interactions in which iQCEM can be involved, its ternary solutions achieved with hydroxyl solvents are usually not thermodynamically ideal. The parameter $\Delta \tilde{\nu}$ (cm\(^{-1}\)) indicates the non-ideality of the ternary solutions [12].

$$\Delta \tilde{\nu} = \tilde{\nu}_t - (x_1 \tilde{\nu}_1 + x_2 \tilde{\nu}_2) \quad (4)$$

In relation (4), the wavenumber difference $\Delta \tilde{\nu}$ (cm\(^{-1}\)) is expressed as function of the wavenumber of the ICT band of iQCEM recorded in ternary solutions, $\tilde{\nu}_t$, and in the two solvents (water) and (ethanol), respectively $\tilde{\nu}_1$ and $\tilde{\nu}_2$.

The excess function or preferential solvation [13] $\delta$ represents a measure of the extent of the preferential solvation of the solute molecule in the active solvent indexed by "1".

$$\delta_i = p_i \cdot x_i \quad (5)$$

Each parameter defined by relations (3)-(5) offers information about the preferential solvation of iQCEM in the protic active solvent of the binary mixture considered in this study.

The purpose of this study was to verify the results obtained for ternary solutions of some other cycloimmonium ylids investigated in previous studies [14-16] regarding their preferential solvation for the case of iQCEM in water + ethanol binary solvent. There are methods for establishing the ternary solutions properties [17, 18] based on experimental or computational procedures. The method used in this paper for the characterization the first solvation shell composition is one of the few methods which correlate the spectral and computational approaches.

**Experimental part**

The studied ylid, iQCEM, was synthesized as it was described in [1-3] and its purity was verified by chemical and spectral means. The ternary solutions were achieved in volumetric concentrations (by calculating molar fractions and spectral means. The ternary solutions were described in [1-3] and its purity was verified by chemical and spectral means. The ternary solutions were achieved in volumetric concentrations (by calculating molar fractions and spectral means. The ternary solutions were described in [1-3] and its purity was verified by chemical and spectral means. The ternary solutions were achieved in volumetric concentrations (by calculating molar fractions and spectral means. The linear dependence between the wavenumber $\tilde{\nu}$ (cm\(^{-1}\)) in the ICT band maximum of iQCEM and the function of $\varepsilon$ (dielectric constant of binary solvent), defined by:

$$f(\varepsilon) = \frac{\varepsilon - 1}{\varepsilon + 2}$$

(6)

describes the orientation-induction interactions in ternary solutions [2]. The linear dependence:

$$\tilde{\nu} = C_1 f(\varepsilon) + \tilde{\nu}_c$$

(7)

contains two regression coefficients, $C_1$ and $\tilde{\nu}_c$. The first coefficient depends on the dipole moments of the spectrally active molecule in its electronic states participating to the ICT transition while the second one contains the contribution of the wavenumber for the gaseous phase ($\tilde{\nu}_c$) and the eventual contributions of other universal interactions.

![Fig. 1 Optimized chemical structure of iQCEM](image)

![Fig. 2. E\(_{\text{max}}\) (kcal/mol) vs. Z (kcal/mol) for the visible band of iQCEM](image)

Both water and ethanol hydroxyl molecules can participate to hydrogen bonds with solute molecules of iQCEM. Consequently, a ternary solution results as a mixture of complexes realized by hydrogen bonds of the types: iQCEM-ethanol and iQCEM-water. Those molecular systems have electronic absorption bands in the visible range, while the complexes water-water, water-ethanol and ethanol-ethanol are inactive in the visible range.

The weak hydrogen bonds as those occurring between ylid molecule and water or ethanol consist in proton exchange between hydroxyl solvent and ylid molecules. It results that, at equal molar concentrations of the two solvents, the stronger hydrogen bond will be predominant. Or, it is possible that both complexes to be of similar values of energy and the solvent to interact with the two complexes by orientation-induction interactions. This type of interactions is described by function (7); the coefficient $C_1$ can be expressed [2] by the function (8):

$$E_{\text{max}} = C_1 f(\varepsilon) + \text{constant}$$

(8)
In relation (8), \( \mu_g \) and \( \mu_e \) are the dipole moments in the ground and excited states of the complex, \( r \) is the radius of the complex, \( h \) - Planck constant and \( c \) - light velocity in vacuum.

The excited state dipole moment of iQCEM was assessed with relation (8) using the value of \( C_1 \) established from the solvatochromic effect of the binary solvent water + ethanol and the value of \( \mu_g \) computed by semi-empirical method PM3. The determined value of \( \mu_e \) can contain the changes due to hydrogen bond formation and could be attributed to the excited state of the complex iQCEM-hydroxyl solvent. The dependence of the type (7) is illustrated in figure 3.

The linear dependence illustrated in figure 3 indicates the prevalence of the orientation-induction interactions in ternary solutions iQCEM + water + ethanol. The complexes iQCEM-water and iQCEM-ethanol interact with the binary solvent by orientation-induction forces of the same magnitudes, so the prevalence of one type of complex does not change drastically the slope in the linear fit (7) as it happens for the carbanion monosubstituted ylids [15,16]. The binary solvent dielectric constant increases with the water content in ternary solution and the slope of the line (7) is a constant parameter. From the value of this slope, noted by \( C_1 \), in relation (7), the dipole moment of the hydrogen bond-complex realized by iQCEM with water or ethanol can be evaluated if the dipole moment in its ground state is estimated by HyperChem computations. For the excited state of the complex, a value of about \( \mu_e = 2.64 \)D (for the case of \( \cos \phi = -1 \) and \( \mu = 4.98 \)D resulted from semi-empirical molecular modeling) has been determined. For the solutions iQCEM + water + ethanol, relation (7) can be also written as resulted from the regression equation established statistically:

\[
\nu = (3512 \pm 56) f(\varepsilon) + (14845 \pm 52)
\]

For \( \delta_1 < 0 \) (\( P_1 < x_1 \)), the water concentration in the first solvation shell of iQCEM is smaller than its concentration in the rest of solution, while for \( x_1 \) values for which \( \delta_1 > 0 \) (\( P_1 > x_1 \)), the iQCEM first solvation shell is enriched in water molecules, compared with the rest of solution.

The prevalence of the active solvent in the first solvation shell of iQCEM, \( K_{12} \), gives also information about the solvent molecules distribution in the vicinity of the spectrally active molecule. When \( K_{12} < 12 \), it results \( P_1 \leq x_1 \) and the molar concentration of the active solvent is smaller in the first solvation shell compared with the rest of the solution. When \( K_{12} > 12 \), it results \( P_1 \geq x_1 \) and the active solvent is in a higher concentration in the first solvation shell, compared with the rest of the solution. The dependence of \( K_{12} \) vs. \( x_1 \) is illustrated in figure 6.

The obtained information from figures 5 and 6 are better discredited than those from figure 4 in which does not result in significant differences between the compositions of the first solvation shell of iQCEM and the rest of the ternary solution.

The excess function, \( \delta_1 \), and the preferential solvation constant, \( K_{12} \), give similar information about the molecular
composition of the first solvation shell of the complexes realized by hydrogen bonds: the ethanol molecules are predominant for $x_1 < 0.1$, while at $0.1 < x_1 < 0.34$ water molecules are dominant in the first iQCEM-complexes solvation shell. For $0.34 < x_1 < 0.65$, ethanol molecules are prevalent in the iQCEM-complexes solvation shell; as for $0.65 < x_1 < 0.8$, water molecules are dominant in the first solvation shell and at higher molar concentrations of water in the binary solvent, ethanol molecules being isolated in the first solvation shell of iQCEM-complexes. The interpretations are similar for figure 6.

One can conclude that for $\delta > 0$ it results that $K_{12} > 1\left(p_1 > x_1\right)$, which indicates the prevalence of water molecules in the first solvation shell of the iQCEM complexes developed by hydrogen bonds. When $\delta < 0$ and $K_{12} < 1$, the ethanol molecules are predominant in the vicinity of these complexes. For $x_1 = 0.2$ and also for $x_1 > 0.8$, the water content in the first solvation shell of iQCEM is smaller than in the rest of the solution. The large aggregates formed by hydrogen bonds between the water molecules cannot penetrate the first solvation shell of the ylid complex, even at high concentrations of water molecules in the binary solvent water + ethanol.

Conclusions

For some concentrations of the binary solvent, the water molecules are predominant in the first solvation shell of iQCEM. For $0.35 < x_1 < 0.70$ the average statistical weights of water molecules (considered as being more active than the ethanol molecules from the orientation-interaction point of view) in the first solvation shell are smaller than its molar concentrations in the rest of the ternary system. These non-homogeneities are also due to the abnormal solvation of ethanol in water at some molar concentrations.

References


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