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UV Spectral Study of Ion–Ligand Interactions: Alkali and Alkaline Earth Cation Binding to *N*-Methyl-8-quinolone

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Abstract

The electronic absorption spectra of *N*-methyl-8-quinolone in acetonitrile and in acetonitrile containing Li(I) and Mg(II) ions (from perchlorates) provide evidences for the base–hard acids interaction and the consequent perturbations induced by the ion binding to the electronic structure of the ligand itself. More than one chromophore has been detected in the studied systems; the direct cation–ligand binding seems to involve a significant amount of charge-transfer from the ligand to the ion. The role of water, generally present in the used systems, is also discussed in relation to the structure of the associates.

Introduction

Hard acids like protons, alkali and alkaline earth cations induce remarkable modifications on the electronic absorption spectra of organic N- and/or O-ligands (bases) in solution. Such spectral perturbations are generally recognized to arise from proton– or cation–ligand binding. The associated interaction energy is commonly described on the basis of an energy-partitioning scheme whose dominant components are [1]: (i) an electrostatic term due to ion–dipole interaction; (ii) a polarization term arising from ion-induced dipole interaction, and (iii) a charge-transfer term. It has been found [2] that the charge-transfer term is the most important contribution involved in the proton–base interaction (protonation process); in the metal ion–base association the electrostatic term predominates [2], the contribution of the charge-transfer term being, inter alia, directly related to the cation charge-density.

We have previously investigated the interaction of N- and O-methylated forms of hydroxypyridines [3] and hydroxypyridine-1-oxides with magnesium ions in an aprotic solvent (MeCN). Most of the observed Mg(II) induced spectral shifts have been found similar to those caused by protic solvent–ligand interaction (*i.e.* blue shift via solvent–ligand hydrogen bonding); vice versa the electronic absorption spectra of systems having a *β*-pyridone as ligand (*i.e.* *N*-methyl-3-pyridone) reveal an equilibrium involving a cation–ligand complex in which the electronic structure of the ligand seems to be identical to that of the protonated ligand itself (protonation-type interaction); the amount of this last species increases with the increasing of ion concentration. These findings imply that in some cases the cation–ligand binding involves a significant amount of charge-transfer from the ligand to the ion. With the aim of providing further experimental evidence on the characteristics of the hard acids–bases interactions in solution, we have studied the perturbations induced by the presence of $LiClO_4$ and $Mg(ClO_4)_2$ on the electronic absorption spectra of *N*-methyl-8-quinoline, a ligand having a *β*-pyridonic structure.

Experimental

Anhydrous *N*-methyl-8-quinolone (**1**) was obtained [4] by drying under vacuum (60 °C) *N*-methyl-8-quinolone·$2H_2O$. This hydrated compound was isolated by passing an aqueous solution of its iodide [5] through a column filled up with Amberlite IRA-400 (OH^-) followed by freeze-drying of the eluate.

Commercial (analytical grade) lithium and magnesium perchlorate (Merck) were dried (120 °C) *in vacuo* for several hours. Spectroquality acetonitrile (MeCN), containing 0.1% of water, was used without any further purification. MeCN 0.1 M in HCl was prepared by adding to the solvent the appropriate amount of concentrated aqueous solution of the acid.

All absorption spectra were recorded at room temperature with a Cary 2100 spectrophotometer using 1 cm cells.

Results and Discussion

Spectra of N-Methyl-8-quinolone in Aprotic and Protic Solvents

The UV absorption spectra of **1** in various solvents have been previously described [4, 6]. In order to better evaluate the effects induced on the transition energies of **1** by its binding to Li(I) and Mg(II) we have systematically recorded the absorption spectra

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TABLE 1. UV Data for *N*-Methyl-8-quinolone in Acetonitrile and Aqueous Solutions

Solvent	Species[a]	λ_{max}	ϵ
MeCN	N	530	1.3×10^3
		374	3.7×10^3
		287	2.7×10^4
		258	shoulder
MeCN 0.1 HCl	C	368	2.2×10^3
		256	4.1×10^4
H_2O (pH = 1)	C	368	2×10^3
		256	4×10^4
H_2O (pH = 11)	N	444	7.6×10^2
		346	6.7×10^2
		334	6.6×10^2
		272	2×10^4
H_2O unbuffered	$N \rightleftarrows C$	446	b
		348	b
		274	b
		256	b

[a] N = neutral; C = cationic (see eqn. (1)). [b] The relative intensities are pH dependent; the 256 and 348 nm bands intensities increase with increasing solution acidity.

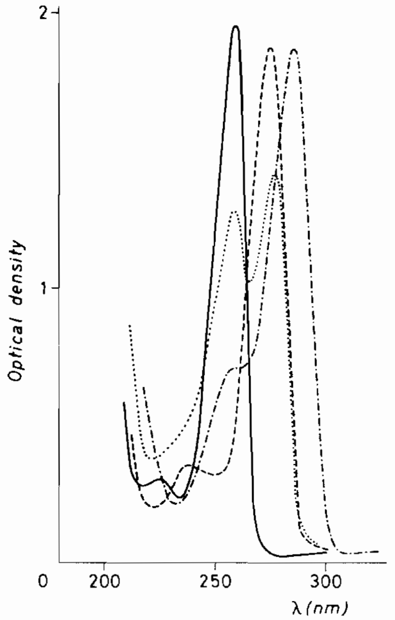
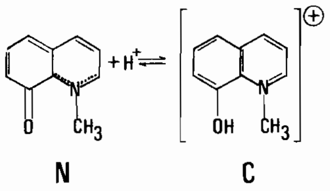


Fig. 1. UV absorption spectra (range 200–300 nm) of *N*-methyl-8-quinolone in: (– · – ·) spectroquality acetonitrile, (——) acidic acetonitrile (0.1 M HCl), (– – –) water (pH ~ 12), (·······) water (unbuffered).

of the ligand itself in MeCN, in acidic MeCN (0.1 M HCl) and in aqueous solution at different pH values.

The positions of the observed maxima are reported in Table I while Fig. 1 shows the spectral range more significantly affected by the complexation processes.

The absorption bands observed in MeCN and acidic MeCN as solvent are ascribed, respectively, to the neutral, **N**, and cationic, **C**, chromophores of **1** according to the protonation process schematized in eqn. (1)



(1)

In going from MeCN to an alkaline aqueous solution (where **1** exists essentially as a neutral species) blue-shifts are observed independently of the n–π* or π–π* character of the transitions themselves; these shifts are explained in terms of water–ligand interactions; in fact: (a) n–π* transitions are blue-shifted when the n-electrons of the ligand are involved in a hydrogen bond; (b) π–π* transitions are blue-shifted when the ground state is more stabilized by dipole–dipole (solvent–solute) interaction than the low lying excited states (as it should be between **1** and water molecules). The interpretation of the spectra of **1** in acidic and unbuffered water is also feasible on the basis of the protonation equilibrium (eqn. (1)); in fact: (i) in acidic water solution the **C** species predominates (as in MeCN 0.1 M HCl) and the absorption bands at 256 and 368 nm are to be attributed to this chromophore; (ii) in unbuffered aqueous solution both species **N** and **C** are present; the intensity of the relative absorption bands depends on the pH whose value in our experimental condition should be around the p*K* value of the ligand itself.

Spectra of 1 in Aprotic Solvent Containing the Hard Acids Li(I) and Mg(II)

UV absorption spectra of **1** in MeCN containing a fixed amount of Li(I) and Mg(II) ions are shown in Fig. 2. In a way similar to that described for aqueous solution at different pH values, complexation of **1** with Li(I) and Mg(II) results in the formation of two chromophores having absorption bands respectively at 256 and 274 nm; the 256 nm absorbing species resembles the 'protonated ligand' while the transition at 274 nm is proper of the ligand involved in a 'hydrogen bond type interaction'. The ratio between the two chromophores is a function of the ion concentration and its charge-density (Mg(II) ions at 1 M conc. induce essentially the 'protonated species'). An analysis of the 300–800 nm spectral region modifications (see Fig. 2) provide similar inferences.

The Role of Water and the Structure of the Complex Species

MeCN and magnesium perchlorate are highly hygroscopic; this means that a certain amount of

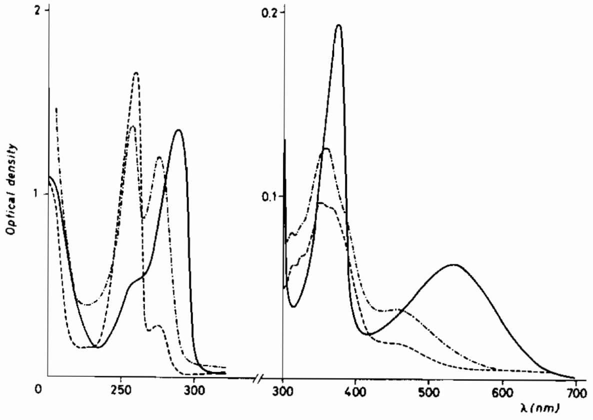


Fig. 2. UV absorption spectra of *N*-methyl-8-quinolone in (——) spectroquality acetonitrile, (—·—) acetonitrile + $LiClO_4$ 1 M, (– – –) acetonitrile + $Mg(ClO_4)_2$ 1 M.

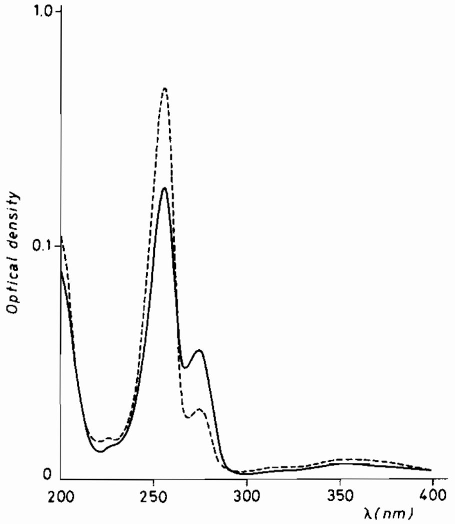


Fig. 3. UV absorption spectra of *N*-methyl-8-quinolone in: (– – –) spectroquality acetonitrile + $Mg(ClO_4)_2$ 1 M and water (0.1 M), (——) spectroquality acetonitrile + $Mg(ClO_4)_2$ 1 M and water (10 M).

water is contained in our systems used to study the spectral behaviour of cation–ligand complexes, *i.e.* we are dealing with a binary mixture of MeCN and water as solvent. In this experimental condition the two solvent components will compete to occupy the cation first solvation sphere whose composition can differ markedly from that of the bulk solvent and preferentially contain one component with respect to the other. Indeed it has been shown that: (i) alkali cations are preferentially solvated [7] by water in a MeCN–H_2O binary mixture; (ii) no MeCN seems bound to a cation when the $[H_2O]/[\text{cation}]$ ratio in a MeCN–H_2O mixture exceeds the solvation number of the cation itself [8]. A ligand present in such a system will be able to antagonize effectively with MeCN molecules for direct coordination to the metal cation only when the $[H_2O]/[\text{cation}]$ ratio is lower than the cation coordination number and if its 'donicity' [9] is stronger than that of acetonitrile. We have previously established [3] that a water content up to 1 M does not preclude to an appropriate ligand a direct binding with Mg(II); when the water content increases the direct cation–ligand interaction is perturbed or even forbidden as a result of cation full-hydration processes (for Mg(II) this should be accomplished when the ratio $[H_2O]/[Mg(II)]$ exceeds the value of 6). We have confirmed these findings in the present study: Fig. 3 shows the spectra of **1** in MeCN–Mg(II) (1 M) solution containing different amounts of added water. The observed reduction of the optical density at 256 nm supports indeed the assumption that high concentration of water prevents the direct ion–ligand binding*. The structure of the several complex species formed in our experimental conditions might be presumed by taking into account: (i) the results of a neutron diffraction study of $Mg(ClO_4)_2$–MeCN in solution [10] pointing out the presence of a mixture of tetrahedral and octahedral surrounding of Mg(II) by MeCN molecules and a not well defined arrangement of the solvent around the perchlorate anion; (ii) the cation preferential solvation for H_2O; (iii) the moderately weak interaction between the cation–ligand complexes and the perchlorate counterions.

Conclusions

Our present findings have to be considered as further experimental evidence in support of direct interactions between IA and IIA group cations and O- or N-ligands; the role these interactions play in biological systems [3, 4] is fundamental especially with regard to biomolecules whose environment is commonly described as 'non-aqueous'. Mg(II) binding to DNA bases, for instance, induces a strong ligand

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*Our experimental evidence seems to contrast with a recent proposal [13] that magnesium ions, in MeCN, mediate protonation processes of imines via the water present in the solvent. Derived from an IR spectroscopic study of imines (like *N*-benzyliden-1-aminobutane) dissolved in wet MeCN, this assumption is based on the appearance of an absorption band induced by the presence of solvated magnesium ions and ascribed to the iminium ($>C{=}N^{+}\overset{H}{<}$) stretching vibration whose intensity increases by a deliberated addition of water to the solution itself. This mechanism has been emphasized by the same authors [14] in a recent discussion of the reduction process of monodentate imines by NAD(P)H models, but a possible direct complexation of the substrate with Mg(II) ions has also been considered. A dependence of the cation role on the different chemical properties of the ligands might be a factor which can match different experimental findings; further investigations in this direction are required in order to draw definitive conclusions.

polarization and consequently perturbs: (i) the hydrogen bonds between complementary base pairs [11]; (ii) the $\pi-\pi$ heteroassociation (stacking) between bases [12].

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