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Active participation of solvent molecules in photo-induced enol-keto tautomerisation of 7-hydroxyquinoline with a mobile proton carrier as substituent

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Abstract

Evidence is provided that transformation of the electronically excited enol form E* of 7-hydroxy,8-(*N*-morpholinomethyl)quinoline (HMMQ) into the excited state K* of its keto form requires formation of a hydrogen bonded complex of E* with a solvent molecule. The excited zwitterionic form Z* generated after a first intramolecular proton transfer has the mobile proton carrier (morpholino group) initially locked in position by an intramolecular hydrogen bond with the deprotonated O atom. It is concluded that participation of the proton in an additional hydrogen bond, involving a solvent molecule, is the main reason why the proton carrier can get into motion to deliver the proton at the remote site. The conclusion has been achieved by studying the spectral variations in the fluorescence spectra of HMMQ in various binary solvent mixtures, containing at least one component able to form hydrogen bonds with a proton donor. In the case of solutions in *n*-hexane/THF there is clear evidence of 1 : 1 complex formation between Z* and THF, as has been also obtained previously in the case of solutions of HMMQ in *n*-hexane/1,4-dioxane. Evidence is obtained that dichloromethane is causing conversion of Z* into K* through H-bonding with Z*, but that it quenches the fluorescence from K* completely.

Keywords: Long distance proton transfer; Ultra-fast proton transfer; Solvent assisted proton transfer

1. Introduction

An important class of reactions, encountered in all areas of chemistry and biochemistry, involves the transfer of a proton from one atom to another. These reactions, which are often a key step in the functioning of enzymes and proteins [1–4], have been studied extensively, both from experimental [5,6] and from theoretical points of view [7]. Often proton transfer reactions consist of a sequence of elementary chemical reactions of which some may take less than a picosecond to be completed. A number of proton transfer reactions do not proceed at ordinary temperatures by thermal activation, but have to be triggered by optical excitation of the system to an electronically excited state. When the excited state proton transfer (ESIPT) proceeds adiabatically, fluorescence of both the initial and final product can be observed after absorption of the single photon triggering the process. Then the most suitable means to study mechanism and kinetics of the process are fluorescence spectroscopic methods.

In biological processes protons may be transferred between sites which are far apart. The actual transport mechanism is not known in full detail in those cases [1]. Model systems, in which an overall intramolecular proton transfer can be induced, have been studied in order to discover elementary steps and mechanisms involved. When the proton donor and proton acceptor sites are sufficiently close, they are often linked by an intramolecular hydrogen bond which enables direct tunneling of the proton between them. A striking example of this is provided by the rate constant of the thermally induced reverse tautomerization of the photo-tautomer of ortho-hydroxybenzaldehyde [8], which increases when the temperature is lowered. This is caused by an equilibrium between an open form and an intramolecularly hydrogen bonded form, which shifts upon lowering of the temperature towards the side of the latter. In the photo-induced enol-keto tautomerization of 7-hydroxyquinoline, the proton donor and acceptor sites are too far apart to achieve direct tunneling of the proton between them. However,when alcohol molecules are available in the solution they may catalyse the process by forming hydrogen bonds with both the donor and the acceptor. Then the donor may be deprotonated

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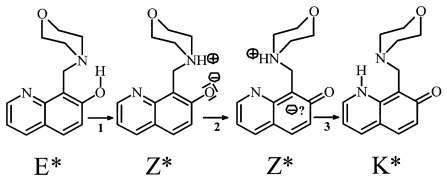

Fig. 1. Excited state intramolecular proton transfer (ESIPT) in 7-hydroxy,8-(*N*-morpholinomethyl)quinoline through the action of the side group.

while the acceptor gets protonated by action of the two alcohol molecules [9]. In order to avoid the participation of alcohol molecules in the enol-keto tautomerization of 7-hydroxyquinoline, the molecule has been provided with a mobile proton carrier. The substituted molecule is 7-hydroxy,8-(*N*-morpholinomethyl)quinoline (HMMQ). It serves to study several aspects of great importance in liquid state chemical reactivity, as for instance the effects of friction imposed by the solvent on the motion of the proton carrier [10–14]. The theoretical explanation of these effects require rather detailed knowledge about the solute-solvent interactions involved. This paper reports new discoveries concerning the manner in which solvent molecules act in promoting the photo-induced enol-keto tautomerisation of HMMQ.

The fluorescence of solutions of HMMQ in polar solvents reveals an overall excited state intramolecular proton transfer (ESIPT) consisting of three steps in which the excited enol form (E*) is converted into an excited intermediate zwitterionic form (Z*) which yields the excited keto form (K*) after internal rotation of the protonated side group in Z* [10–14]. This is illustrated in Fig. 1. Despite the strongly polar character of Z*, the conversion of E* into Z* is also encountered in solutions of HMMQ in non-polar solvents such as alkanes, benzene and *p*-xylene. However, K* is not formed in those cases, presumably because the required rotation of the side group is inhibited by a rather stable intramolecular hydrogen bond (H-bond) between the deprotonated O atom and the protonated morpholino group in Z*. The mechanism in which the polar solvent enables the transformation of Z* into K* is not known. There are two realistic mechanisms to consider in this respect. The first one is that the reaction field (depending on the relative permittivity) is causing a redistribution of electrons in Z* resulting in weakening of the intramolecular H-bond. The other one is that the proton participates in an H-bond involving a solvent molecule, while the intramolecular H-bond is retained. Reduction of the Coulombic attraction between the proton and the negatively charged O atom in Z* by the relative permittivity may be disregarded as an option in the explanation, because there is no possibility to have a sufficiently large number of solvent molecules between these charges to cause an essentially macroscopic effect. At any rate, the required explanation must be based on a mechanism allowing the side group to get into motion.

Although the relative permittivity (ε) of liquid 1,4-dioxane is merely equal to 2.2, the solution of HMMQ in this solvent exhibits the formation of K*, in contrast to the solutions in the non-polar solvents just mentioned [14]. Previously we have shown that a 1 : 1 complex of 1,4-dioxane and Z* is an intermediate in the conversion of Z* into K* in the solution of HMMQ in liquid dioxane. The 1,4-dioxane in the complex may be involved in an additional H-bond of the proton in the intramolecular H-bond in Z* (simultaneous interaction of the proton with two sites) which weakens the original intramolecular H-bond. The question arises whether a large value of ε or a complex of a solvent molecule with Z* is the more important requirement to obtain a conversion of Z* into K*. This question has been addressed by studying variations in the fluorescence spectra of HMMQ in various binary solvent mixtures as a function of solvent composition. The selected solvent mixtures contain at least one component whose molecules may make an H-bond with HMMQ. These components are 1,4-dioxane, tetrahydrofuran (THF), diethylether, 1-propanol, acetonitrile, dichloromethane and *p*-xylene.

2. Experimental

Synthesis and purification of 7-hydroxy,8-(*N*-morpholinomethyl)quinoline (HMMQ) have been described previously [1]. All solvents were of spectrograde quality and were used as supplied. Fluorescence of solutions of HMMQ in various binary solvent mixtures were recorded for different mixing ratios. The solvent mixtures were *n*-hexane/diethylether, *n*-hexane/THF, *n*-hexane/1-propanol, *n*-hexane/acetonitrile, *p*-xylene/acetonitrile, and dichloromethane/THF. Mixtures of *n*-hexane and acetonitrile are poorly miscible and the achievable range of compositions of the *n*-hexane/acetonitrile mixtures is limited to concentrations of acetonitrile lower than 0.28 M and larger than 16.64 M. Therefore, the series *n*-hexane/acetonitrile is not very suitable for a verification of the composition dependence of the fluorescence of the solute. The concentration of HMMQ in the solutions was less than 10^{-4} M and the absorbance at the excitation wavelength was kept constant in each of the series of solvent mixtures. The fluorescence spectra were recorded on a Perkin-Elmer MPF-66 fluorescence spectrophotometer and are corrected for instrumental distortions.

3. Results

The spectra of the series of solutions of HMMQ in *n*-hexane/diethylether are presented in Fig. 2. It shows that the major fluorescence band (at 24 100 cm^{-1}) shifts to 23 000 cm^{-1} and decreases substantially in intensity when the concentration diethylether changes from the minimum to the maximum value, while a weak band at 17 500 cm^{-1} is increasing gradually in intensity. The relative growth of the weak band is smaller than the relative attenuation of the main band. Another weak band is visible as a shoulder at

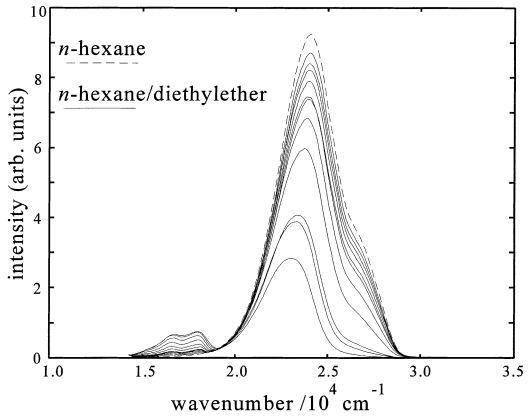

Fig. 2. Fluorescence spectra of HMMQ in *n*-hexane with increasing concentration of diethylether and constant concentration HMMQ.

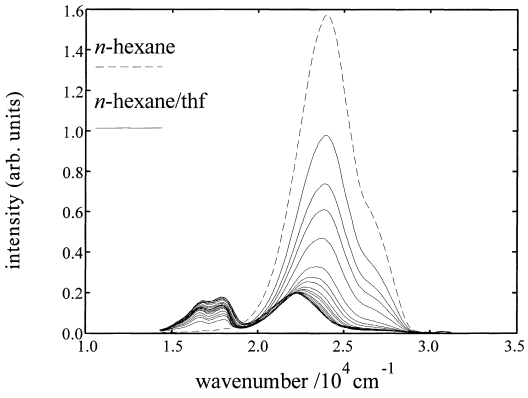

Fig. 3. Fluorescence spectra of HMMQ in *n*-hexane with increasing concentration of THF and constant concentration HMMQ.

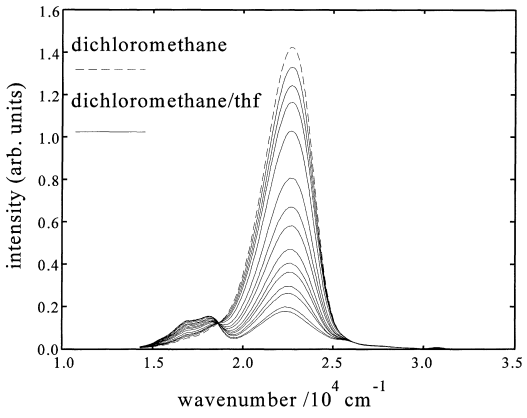

Fig. 4. Fluorescence spectra of HMMQ in dichloromethane with increasing concentration of THF and constant concentration HMMQ.

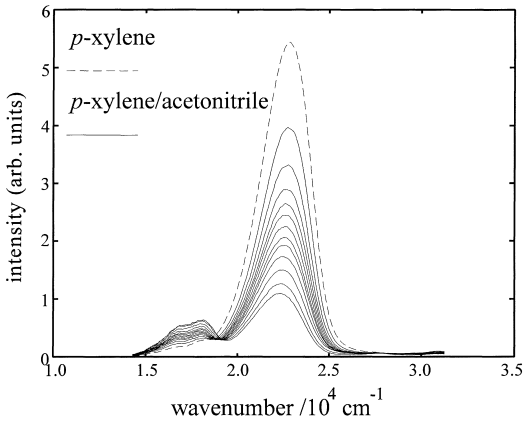

Fig. 5. Fluorescence spectra of HMMQ in *p*-xylene with increasing concentration of acetonitrile and constant concentration HMMQ.

27 000 cm^{-1}. It does not shift in the course of these changes in solvent composition.

A similar behaviour can be observed in Fig. 3 which presents the spectra of HMMQ in the mixtures *n*-hexane/THF. The main band located at 24 100 cm^{-1} shifts to a final position at 22 100 cm^{-1} and loses intensity, while a band at 17 500 cm^{-1} gains intensity with increasing concentration THF. These spectral changes are also encountered in the case of the series of solutions in *n*-hexane/1-propanol and the series of solutions in *n*-hexane/acetonitrile, when the concentration of the polar component increases.

The solutions of HMMQ in dichloromethane/THF differ in certain aspects from the previous cases. In the dichloromethane/THF series the weak band at 17 500 cm^{-1} is growing at the expense of the main band, but the latter does not shift noticeably and remains close to 22 700 cm^{-1} when the THF content increases (see Fig. 4). An isoemmisive point appears in Fig. 4 at 14 000 cm^{-1}, because the bands practically do not shift with solvent composition.

In the series of solutions in *p*-xylene/acetonitrile the major band is also attenuated and shifts from 22 900 cm^{-1} to 22 100 cm^{-1}, while a weak band at 17 500 cm^{-1} is growing with increasing concentration acetonitrile (Fig. 5).

The weak band (shoulder) appearing in the spectra of the series *n*-hexane/diethylether, *n*-hexane/THF, *n*-hexane/1-propanol and *n*-hexane/acetonitrile around 27500 cm^{-1} can not be seen in the spectra of the series dichloromethane/THF and *p*-xylene/acetonitrile.

4. Discussion

The bands which appear in the fluorescence spectra presented in Figs. 2–5 are also encountered in the case of solutions of HMMQ in polar solvents and in neat 1,4-dioxane. They have already been assigned to various excited species [1,5]. The band around 27 000 cm^{-1} arises from emission by E* and the band between 22 500 cm^{-1} and 25 000 cm^{-1} and the band at 17 000 cm^{-1} are coming from Z* and K*, respectively. These bands attributed to E*, Z* and K* are named F_E, F_Z and F_K, respectively.

The band F_K does not appear in the spectra of solutions of HMMQ in either *n*-hexane, *p*-xylene or dichloromethane.

The solvatochromic shifts of the band F_Z given in Table 1 do not seem to be governed by polarization of the solvent (considered as dielectric continuum) alone. A very

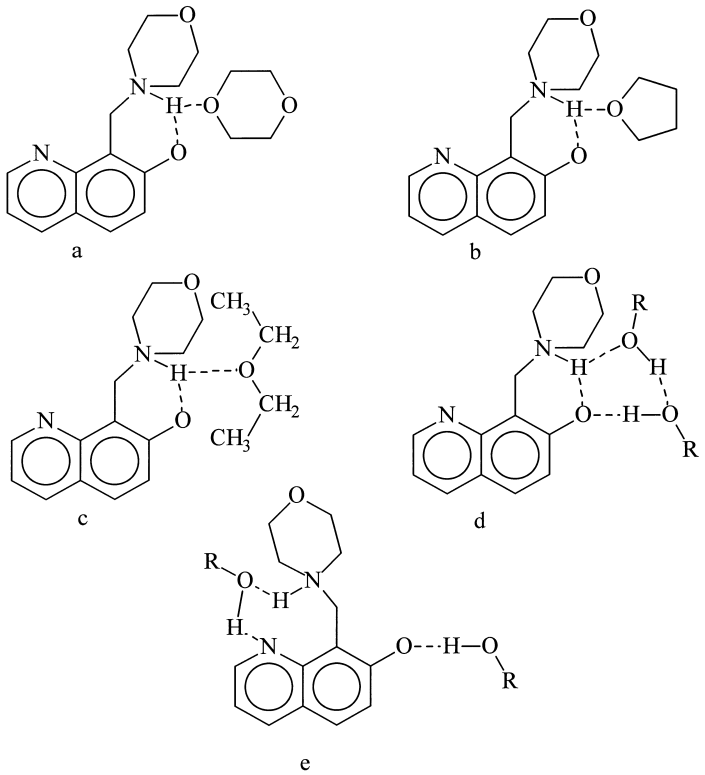

Fig. 6. Schematical presentation of the Z* form of HMMQ H-bonded to different sorts of solvent molecules: (a) HMMQ-1,4-dioxane complex; (b) HMMQ-THF complex; (c) HMMQ-diethylether complex; (d–e) two complexes between HMMQ and two alcohol molecules.

Table 1
Position and shift of the band F_Z in the fluorescence spectrum of HMMQ in various solvents with different relative permittivity ε. The shift is defined with respect to the position of the band in the case of *n*-hexane

Solvent	ε [16]	F_Z (cm^{-1})	Shift of F_Z (cm^{-1})
n-Hexane	1.89	24 100	0
p-Xylene	2.27	22 900	1200
Dichloromethane	9.08	22 700	1400
1,4-Dioxane	2.22	22 100	2000
Diethylether	4.34	23 000	1100
Tetrahydrofuran	7.39	22 100	2000
1-Propanol	20.1	21 800	2300
Acetonitrile	37.5	22 100	2000

clear example is the larger shift (2000 cm^{-1}) caused by neat 1,4-dioxane, compared to that (1100 cm^{-1}) arising from interaction with neat diethylether. If the shifts are attributed to complex formation between Z* and the solvent, one has to conclude that diethylether is more weakly bound to Z* than 1,4-dioxane as to be expected from the steric hindrance involved when a H-bond has to be formed between diethylether and the proton on the morpholino group which is already bonded to the deprotonated O atom (Fig. 6c). Other examples of uncorrelated shifts and solvent polarization are found by comparing the shifts for the following pairs of solvents: dichloromethane and THF, diethylether and *p*-xylene, 1-propanol and acetonitrile. Each pair shows an ordering of the shifts which is opposite to that expected on the basis of solvent polarization. This may be interpreted as evidence for the involvement of specific interaction (*i.e.* complex formation) between Z* and the solvent.

The ratio R_{ZK} of the quantum yields Φ_{fZ} and Φ_{fK} of the emision in the bands F_Z and F_K, respectively, has previously been found to vary linearly as a function of the inverse concentration of 1,4-dioxane in the case of the solvent mixtures *n*-hexane/1,4-dioxane. This behaviour has been explained on the basis of a kinetic scheme [14]. This scheme has to be modified slightly, because recent molecular dynamics studies revealed that a 1,4-dioxane attached to the proton on the morpholino group in Z* is dragged by the rotating side group along the path leading to K* [15]. The modified version of this scheme, presented in Fig. 7, takes the complex formation explicitly into account. A complex formed by reaction of bare Z* with a reactant P is represented by {Z*P} and this is converted into a complex {K*P} after internal rotation of the side group. The scheme implies that the band F_Z is the superposition of the fluorescence bands of bare Z* and {Z*P}. Quenching of fluorescence in the bands F_Z and F_K by P is controlled in this scheme by intersystem crossing and internal conversion in {Z*P} and {K*P}, respectively. The present scheme yields a similar relation for R_{ZK} as the one obtained previously [14]:

$$R_{ZK} \equiv \frac{\Phi_{fZ}}{\Phi_{fK}} = \alpha + \beta \frac{1}{C_p} \quad (1)$$

with the constants α and β defined by

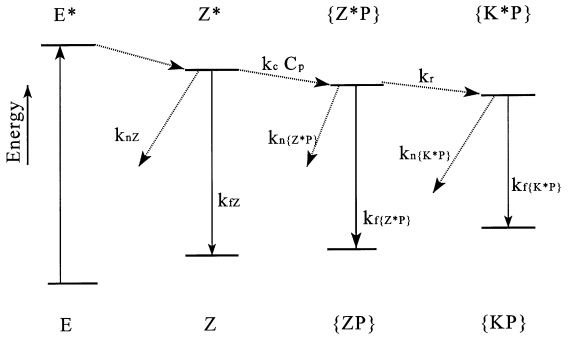

Fig. 7. Kinetic scheme for the evolution of E* into K*. Complex formation between Z* and a solvent molecule, {Z*P}, is considered, and this complex is converted into the complex {K*P}. The radiative rate constants for fluorescence from Z*, {Z*P}, and {K*P} are k_{fZ}, $k_{f\{Z^*P\}}$ and $k_{f\{K^*P\}}$, respectively. The rate constants for non-radiative decay of Z*, {Z*P} and {K*P} are k_{nZ}, $k_{n\{Z^*P\}}$, and $k_{n\{K^*P\}}$, respectively. The rate constant for the formation of the intermediate state {Z*P} is k_cC_P, where C_P is the concentration of 1,4-dioxane (or polar solvent). The rate constant for the rotation of the morpholino group, which lead to the formation of {K*P} is k_r.

$$\alpha \equiv \frac{Dk_{f\{Z^*P\}}}{k_{f\{K^*P\}}k_r}$$

$$\beta \equiv \frac{BDk_{fZ}}{k_{f\{K^*P\}}k_ck_r}$$

with

$$\begin{aligned} A &\equiv k_{fZ} + k_{nZ} + k_cC_p \\ B &\equiv k_{f\{Z^*P\}} + k_{n\{Z^*P\}} + k_r \\ D &\equiv k_{f\{K^*P\}} + k_{n\{K^*P\}} \end{aligned} \quad (2)$$

where k_{fZ}, $k_{f\{K^*P\}}$ and $k_{f\{K^*P\}}$ are the rate constants for the fluorescence from Z*, {K*P} and {Z*P}, respectively; k_{nZ}, k_{nK} and $k_{n\{Z^*P\}}$ are the rate constants for the non-radiative decay of Z*, {K*P} and {Z*P}, respectively. Further, k_cC_P is the rate constant for the formation of {Z*P}, where C_P is the concentration of solvent P, and k_r is the rate of the rotation of the protonated side group in {Z*P} leading to the formation of {K*P}. When this kinetic scheme is used for the series of mixtures, C_P is the concentration of the polar solvent in the solutions or the concentration of the solvent that is involved in the formation of K*. The fluorescence quantum yields Φ_{fZ} and Φ_{fK} of the F_Z band and the F_K band, respectively, are defined by

$$\Phi_{fZ} = \frac{k_{fZ}}{A}\Phi_Z + \frac{k_{f\{Z^*P\}}}{B}\Phi_{\{Z^*P\}}$$

$$\Phi_{fK} = \frac{k_{fK}k_r}{BD}\Phi_{\{Z^*P\}}$$

with

$$\Phi_{\{Z^*P\}} = \frac{k_cC_P}{A}\Phi_Z \quad (3)$$

where Φ_Z and $\Phi_{\{Z^*P\}}$ are the quantum yields of the formation of the species Z* and {Z*P}. A similar linearity as in the case of the *n*-hexane/1,4-dioxane mixtures is observed in the present case of the mixtures *n*-hexane/THF when R_{ZK} is plotted as a function of the inverse concentration THF (see Fig. 8). This is evidence for 1 : 1 complex formation between HMMQ and THF in these mixtures.

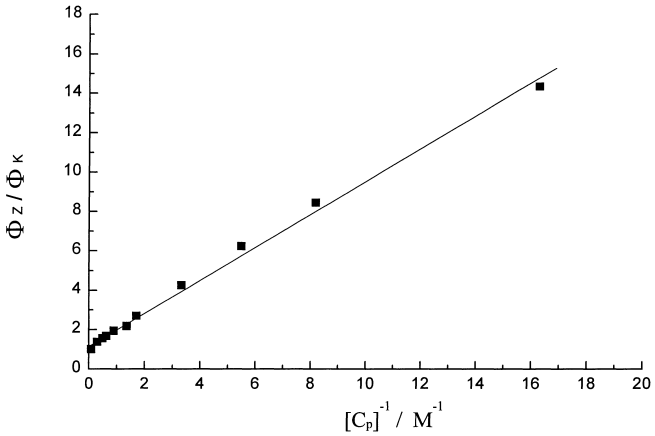

Fig. 8. The ratio of the quantum yields of fluorescence from Z* and K*, denoted by Φ_{fZ} and Φ_{fK} respectively, as a function of $1/C_P$, with C_P equal to the concentration of THF in *n*-hexane.

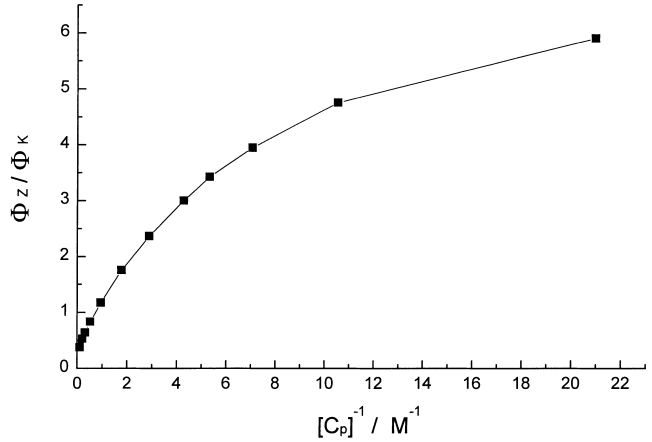

Fig. 9. The ratio of the quantum yields of fluorescence from Z* and K*, denoted by Φ_{fZ} and Φ_{fK} respectively, as a function of $1/C_P$, with C_P equal to the concentration of diethylether in *n*-hexane.

The series of solutions in *n*-hexane/diethylether do not show a linear dependence of R_{ZK} on $1/C_P$ (Fig. 9). This may mean either that interaction between Z* and solvent polarization is important or that the mechanism is different. In the former case, the radiationless electronic relaxation rates may be modified as a result of modified energy gaps between electronic states. This possibility may be disregarded, because linear dependence on $1/C_P$ is observed in the case of THF which has a larger relative dielectric permittivity then diethyl ether. A mechanism which could be responsible for the nonlinear behaviour is dissociation of the {Z*P} complex, at the site where the proton is to be delivered. In order to make this clear, a distinction has to be introduced between the forms of {Z*P} which enable intramolecular H-bonding to the O atom or to the N atom of the aromatic system. These forms will be referred to as $\{Z_i^*P\}$ and $\{Z_f^*P\}$, respectively.

These metastable forms differ substantially in the distribution of electrons in the aromatic system, as revealed by quantum chemical calculations. As mentioned before, diethyl ether suffers steric hindrance in its complex formation with the intramolecularly H-bonded Z*. This is more severe in the case of $\{Z_i^*P\}$ than in the case of $\{Z_f^*P\}$. Therefore, the diethyl ether may be released easily from $\{Z_f^*P\}$. The forward reactions Z*{Z*P} 6 {K*P} in the scheme should then be extended with an equilibrium. The sheme becomes then $Z_i^* \rightarrow \{Z_f^*P\} \rightarrow \{Z_f^*P\}$.

The solutions in mixtures of *n*-hexane/1-propanol do not exhibit a linear relation between R_{ZK} and $1/C_P$. The plot exhibits a curvature as in Fig. 9. This non-linearity may have several reasons, namely complex formation with two alcohol molecules as in Fig. 6d, additional H-bonding of an alcohol molecule to the N atom in the quinoline ring (Fig. 6e) and strong effect of solvent polarization (very large g) on rate constants for internal conversion and intersystem crossing in Z* and K*. There is no way to disentangle these contributions. The important conclusion is that the effects of solvent polarization can not be ruled out when ε about 20 or larger. In this respect, a series of solutions in *n*-hexane/dichloromethane would be interesting to study the case of intermediate magnitude of solvent polarization. Unfortunately, this is not possible, because the fluorescence from K* gets quenched completely by dichloromethane. Intermediate magnitude of solvent polarization is also expected in solutions in dichloromethane/THF. These solutions do not satisfy the linear relation in Eq. (1). The nonlinearity appears as a curvature in the plot as in Fig. 9. The most probable reason why the equation does not apply is, that THF and dichloromethane are competing in complex formation with Z* and this is not taken into account in the scheme. Competition in complex formation between the constituents of the solvent mixture may also explain the non-linearity in the case for the series of solutions in *p*-xylene/acetonitrile.

It is remarkable that no clear sign of K* is observed in the latter case, since dichloromethane is a rather polar solvent (Table 1). The solvatochromic shift of the fluorescence band of Z* caused by dichloromethane, which is smaller than that caused by THF, indicates that complex formation rather than solvent polarization is involved in the solute-solvent interaction. The smaller shift is in accordance with a weaker H-bond to Z*. This bond involves a link with a Cl atom and the proton in the intramolecular H-bond, resembling the bonding of THF in Fig. 6b. The additional H-bond should coexist with the intramolecular bond for a non-vanishing period. If this situation lasts for a time comparable to the radiative lifetime of Z*, the fluorescence would be quenched substantially by enhanced intersystem crossing. Since there is practically no quenching of the band F_Z by dichloromethane, the intramolecular H-bond must be broken within a period of say 500 ps, which is the time elapsed between formation of Z* and K* in H-bonding solvent. The fluorescence from Z* is not quenched, because dichloromethane is then only H-bonded to the protonated morpholino group, which is not strongly coupled to the excited chromophoric system. In this picture, the absence of fluorescence of K* must be attributed to complete quenching of its fluorescence by enhanced intersystem crossing (heavy atom effect). It is very likely that a Cl atom of dichloromethane is H-bonded to the proton on the N atom in the quinoline ring in a complex with K* and causes then a much larger perturbation of the chromophoric system than when it is bonded to the mobile morpholino group.

Although the π-electron system of benzene is known to be able to form H-bonds, the interaction of Z* with *p*-xylene does not lead to conversion of Z* into K* as in the case of interaction with 1,4-dioxane. The formation of an additional H-bond with the proton involved in the intramolecular H-bond in Z*, may be inhibited by steric hindrance in the case of *p*-xylene.

5. Conclusions

Solutions of HMMQ in alkanes reveal ESIPT leading from the excited enol form E* to a zwitterionic form Z* in which the protonated potentially mobile side group is fixed in position by an intramolecular H-bond. When HMMQ is dissolved in solvents whose constituent molecules are able to make H-bonds with a proton donor, the photo-excited enol form E* can be transformed into the excited keto form K* even if the relative permittivity has a value as low as 2.2. Complex formation of Z* involving an additional H-bond of the proton with a solvent molecule provokes breaking of the intramolecular bond which enables the side group to get into rotational motion and to deliver the proton at the site of the N atom in the quinoline ring. The series of solutions of HMMQ in *n*-hexane/THF provide evidence for the formation of a 1 : 1 complex between Z* and THF in much the same way as found previously in the case of the series of solutions in *n*-hexane/1,4-dioxane. Surprisingly diethyl ether does not form such complexes with Z*, presumably due to steric hindrance. Clear evidence for 1 : 1 H-bonded complexes is also lacking in the series of solutions in *n*-hexane/1-propanol, dichloromethane/THF and *p*-xylene/acetonitrile, although solvatochromic spectral shifts indicate complex formation of Z*. This can be attributed to the existence of several types of complexes involving Z* in the solutions in the latter mixtures. Dichloromethane causes the transformation of Z* into K* through formation of an H-bonded complex with Z* and quenches the fluorescence of K* completely by enhancement of intersystem crossing.

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