Pure Appl. Chem., Vol. 73, No. 3, pp. 405–409, 2001.

Dynamic solvatochromism in solvent mixtures*

Diana E. Wetzler[1], Carlos Chesta[2], Roberto Fernández-Prini[1,3], and Pedro F. Aramendía[1,†]

[1]INQUIMAE, DQIAQF, FCEN, Universidad de Buenos Aires, C. Universitaria, 1428 Buenos Aires, Argentina; [2]Dept de Química, Universidad Nacional de Río Cuarto, 5800 Río Cuarto, Argentina; [3]Unidad de Actividad Química, CNEA, Libertador 8250 1428 Buenos Aires, Argentina

Abstract: Solvatochromism and thermochromism of 4-aminophthalimide and 4-amino-*N*-methylphthalimide were studied by absorption and steady-state and time-resolved emission spectroscopy in solvent mixtures of toluene–ethanol and toluene–acetonitrile at different temperatures. Emission spectra shift to the red upon addition of a polar solvent (PS) to toluene. Solvent mixtures show a much greater thermochromic shift to the blue in emission than the neat solvents. This is explained by the decrease in temperature of the exothermic association of the polar solvent to the excited state. Emission spectra are time dependent in solvent mixtures in the ns timescale. The time evolution of this emission is interpreted on the basis of the different solvation of the ground state and the emitting excited state. Stern–Volmer plots are obtained for the dependence of the spectral-shift characteristic time with [PS].

INTRODUCTION

Aminophthalimides have been extensively used as strong fluorescent probes [1–6]. Their fluorescence is considered a typical example of the involvement of many excited states [7]. The maximum of emission is very sensitive to the polarity and hydrogen bond donating (HBD) ability of the medium. A time-dependent fluorescence spectrum was observed in neat solvents [1,3,5] and in solvent mixtures [1,6,7]

After a polarity increase upon excitation, preferential solvation of the more polar component of the mixture is enhanced in the excited state [8]. The change is achieved by diffusion-controlled exchange of solvent molecules. The dynamics and extent of this effect is dependent on temperature and on solvent composition. Due to their great spectral shift in solvent mixtures, 4-aminophthalimide (AP) and its *N*-methyl derivative (AMP) are ideal for monitoring solvation changes. In this work, we present absorption, and steady-state and time-resolved emission spectroscopic studies of AP and AMP in mixtures of ethanol–toluene (eth–tol), and acetonitrile–toluene (acn–tol) as a function of composition and temperature.

RESULTS

Solvatochromism

Absorption and emission spectra shift to the red as solvent polarity increases. The Stokes shift shows a good linear correlation with $E_T(30)$ in neat solvents, as shown in Fig. 1. It also shows the Stokes shift in tol–eth mixtures.

---

*Lecture presented at the XVIII[th] IUPAC Symposium on Photochemistry, Dresden, Germany, 22–27 July 2000. Other presentations are published in this issue, pp. 395–548.
†Corresponding author

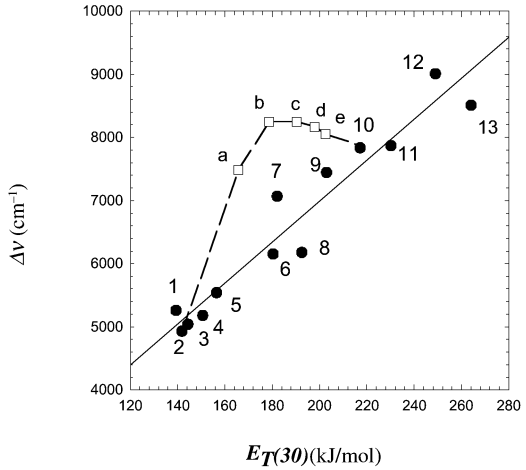

Fig. 1 Stokes shift of AP vs. $E_T(30)$ in neat solvents (dark circles, values from ref. 4): 1: triethylamine (this work); 2: toluene; 3: diethylether; 4: dioxane; 5: tetrahydrofurane; 6: acetone; 7: *ter*-butanol; 8: acetonitrile; 9: 2-propanol; 10: ethanol; 11: methanol; 12: trifluoroethanol (this work); 13: water. Squares: mixtures of toluene–ethanol at 27 °C, [ethanol] / M = a: 0.146; b: 0.429; c: 1.36; d: 4.40; e: 7.04. $E_T(30)$ for the mixtures measured in this work.

Thermochromism

Emission and absorption spectra shift to the blue upon temperature increase in all cases. The magnitude of this shift is much greater for emission than for absorption, and it is also greater in solvent mixtures than in neat solvents, as shown in Fig. 2 for AP. Similar results are obtained for AMP.

Semiempirical calculations

Semiempirical calculations were performed under the AM1 approximation with the AMPAC program (version 6.55, Semichem, Inc., Shawnee, Kansas). Only calculations for AMP were carried out. They predict an absorption maximum in vacuum of 396 nm and an emission maximum at 435 nm. The predicted Stokes shift in vacuum is half the value measured in toluene. In the relaxed excited state, the amino group lies in the plane of the aromatic ring. A charge transfer (as measured by the Mulliken charge on each atom) from the amino nitrogen to the *para* carbonyl group takes place, as found for similar donor–acceptor compounds [9].

Ethanol hydrogen bonds to ground-state AMP in three different positions: the two carbonyls and the amino groups. The interaction energy in these three sites is very similar: 18 ± 2 kJ/mol. The association enhances the negative charge in the ground state of the oxygen atom where ethanol is bonded. Nevertheless, in the relaxed excited state the negative charge increase locates always at the oxygen atom of the carbonyl which is *para* to the amino group. Calculations predict that acn binds preferentially to the amino group, with an interaction energy of 8 kJ/mol.

Kinetics of fluorescence decay

Emission spectra shift to the red as a function of time in all solvent mixtures. The rate of this shift increases with temperature and concentration of the polar solvent (PS). AP and AMP behave in the same way. The spectral shift with time obtained in solvent mixtures is much greater than the one observed in neat solvents. This effect is therefore assigned to the diffusion of polar solvent molecules to the excited state [8].

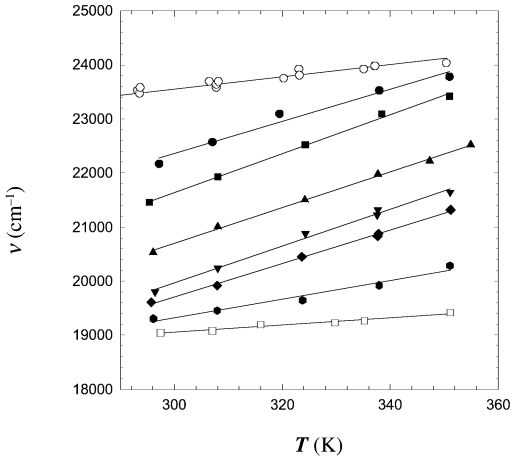

Fig. 2 Plot of the frequency of the maximum of the fluorescence emission spectrum as a function of temperature for AP in toluene–ethanol mixtures. The curves, from top to bottom correspond to: pure toluene, [ethanol] / M = 0.029; 0.059; 0.146; 0.289; 0.429; 1.36; pure ethanol.

Depending on the temperature, for [eth] = 0.146 M in toluene, the shift of the spectrum is practically completed in 3 to 10 ns. The total fluorescence decay takes place with a characteristic lifetime of ca. 15 ns, which is temperature independent. The decay kinetics of the fluorescence, monitored at a fixed wavelength, is not single exponential. In the blue side of the spectrum the decay is mainly due to spectral shift. On the red side of the spectrum there is a build-up component from spectral shift and a longer decay due to the total depopulation of the excited state.

The most elemental kinetic scheme to explain this behavior is the following:

$$AP^* \xrightarrow{k_0} AP$$

$$AP^* + PS \xrightarrow{k_d.[PS]} (AP - PS)^*$$

$$(AP - PS)^* \xrightarrow{k_{-d}} AP^* + PS$$

$$(AP - PS)^* \xrightarrow{k_0} AP - PS$$

Where AP is a solute molecule with a ground-state equilibrated solvation sphere. AP–PS represents the association of AP to an additional PS. We assume that AP* and (AP–PS)* decay with the same probability. This assumption is supported by the fact that the larger decay time is practically independent of solvent composition in the range of interest for the kinetic measurements ([PS] < 1.5 M). The two relaxation times of the mechanism, under the assumptions that k_{-d} and k_d.[PS] >> k_0, are: $1/\tau_1 = k_0$; $1/\tau_2 = k_{-d} + k_d.[PS]$; $\tau_2 < \tau_1$.

The Stern–Volmer type behavior found for τ_2 with solvent composition is consistent with the mechanism. The value of the ordinate and the intercept of these representations are summarized in Table 1, together with its Arrhenius parameters.

DISCUSSION

The good correlation of the Stokes shift with $E_T(30)$ indicate that AP and AMP are sensitive to polarity and HBD capability of the medium. The influence of HBD is more evident in a plot of Stokes shift vs. the solvent parameter α, that gives also a good linear correlation.

The dynamics of excited state relaxation and decay can also explain the solvatochromic and thermochromic properties. The kinetic scheme presented above is an oversimplification. A more realistic

picture of the situation must include an ensemble of ground-state molecules, differing in the composition of the solvation sphere. If the total number of solvating molecules is a constant *m*, we can characterize the solvation state of the solute by the number *n* of PS molecules. As absorption spectra have a small red shift in the range [PS] < 1.5 M, we can assume a constant absorption coefficient, so that the initially excited molecules have a solvation state equal to the ground state. After excitation, solvent exchange takes place. This process is not limited to a single molecule. This model leads to a time-dependent distribution of excited states. Such a kinetic scheme can be solved taking as a basis the model developed by Tachiya [10]. It yields a Langmuir-type dependence of the mean number of solvating PS molecules with the bulk [PS]. We are currently developing the equations of this mechanism [11]. Similar models were used for dynamics [12] and equilibrium [13] in analogous cases.

The difference in solvatochromism shown in Fig. 1 is due to the mentioned change in composition of the environment in the excited state. A single value of $E_T(30)$ cannot account for the solvent effect. At [eth] > 1M in tol the Stokes shift is similar to neat eth: at such concentrations, diffusion equilibration is fast compared to excited-state decay, and all molecules emit from environments that are saturated with respect to eth. At [eth] < 1 M diffusion-controlled equilibration of solvation competes with excited-state deactivation, and a great proportion of the emission originates in nonequilibrated states.

Table 1 Values of the ordinate and slope of Stern–Volmer plots of τ_2 (see text) in mixtures of a polar solvent with toluene. Arrhenius parameters for ordinate and slope for AP in ethanol.

Compound	**Polar solvent**	**Temperature (°C)**	**Ordinate (10^8 s^{-1})**	**Slope (10^9 M^{-1} s^{-1})**
AP	Ethanol	6	1.77	0.90
AP	Ethanol	27	2.6	1.32
AP	Ethanol	61	5.9	3.2
AMP	Ethanol	27	3.1	1.16
AP	Acetonitrile	27	3.3	0.65
AMP	Acetonitrile	27	3.7	0.48
Compound	**Polar solvent**	**Arrhenius parameters**	**Ordinate**	**Slope**
AP	Ethanol	A	$2.7\ 10^{11}$ s^{-1}	$2.1\ 10^{12}$ M^{-1} s^{-1}
		Ea / kJ.mol^{-1}	17	18

The thermochromic shift to the blue upon temperature increase in neat solvents is due to the polarity increase in the excited state, which causes a negative entropy change in the system [14]. This shifts the free energy of the emission to higher absolute values. The slopes of the plots in Fig. 2 are 137 J/Kmol in tol and 80 J/Kmol in eth, normal values for solvent plus probe reorganization. In solvent mixtures the values increase up to 400 J/Kmol. This is due to the fact that the emitting ensemble changes with temperature. The association of eth with the excited state is exothermic. Increasing the temperature turns the average environment of the emitting state less polar, and this shifts the spectra to the blue. This effect is superimposed to the polarity increase to yield a steeper variation of the emission free energy with temperature.

REFERENCES

1. W. R. Ware, S. K. Lee, G. J. Brant, P. P. Chow. *J. Chem. Phys.* **54**, 4729 (1971).
2. C. Reichardt. *Chem. Rev.* **94**, 2319 (1994).
3. E. Laitinen, K. Salonen, T. Harju. *J. Chem. Phys.* **105**, 9771 (1996).
4. T. Soujanya, T. S. R. Krishna, A. Samanta. *J. Phys. Chem.* **96**, 8544 (1992); T. Soujanya, R. W. Fessenden, A. Samanta. *J. Phys. Chem.* **100**, 3507 (1996).
5. C. F. Chapman, R. S. Fee, M. Maroncelli. *J. Phys. Chem.* **99**, 4811 (1995).

6. T. A. Betts, F. V. Bright. *Appl. Spectrosc.* **44**, 1203 (1990).
7. J. R. Lakowicz. *Principles of Fluorescence Spectroscopy,* Ch. 8, Plenum, New York (1983).
8. P. Suppan. *J. Photochem. Photobiol. A: Chem.* **50**, 293 (1990).
9. Y. V. Il'chev, W. Kuehnle, K. A. Zachariasse. *J. Phys Chem A* **102**, 5670 (1997).
10. M. Tachiya. *J. Chem. Phys.* **76**, 340 (1982).
11. D. E. Wetzler, C. Chesta, R. Fernández-Prini, P. F. Aramendía. To be published.
12. R. A. Moore, J. Lee, G. W. Robinson. *J. Phys. Chem.* **89**, 3648 (1985).
13. L. W. Flanagin, P. B. Balbuena, K. P. Johnston, P. J. Rossky. *J. Phys. Chem. B* **101**, 7998 (1997).
14. J. Cortés, H. Heitele, J. Jortner. *J. Phys. Chem.* **98**, 2527 (1994).