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N. J. Gould [a] & D. J. Morantz [a]

[a] Division of Materials and Moleclular Science Thames Polytecnic, Wellington Street, London, S.E., 18

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The Influence of the Matrix on the Phosphorescence Properties of 2-Amino-Pyridine in Acetonitrile/Water Mixtures at 77 °K

N. J. GOULD and D. J. MORANTZ

Division of Materials and Molecular Science
Thames Polytechnic, Wellington Street,
London, S.E.18

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Abstract—The phosphorescence lifetimes and intensities are reported for 10^{-3} M solutions of 2-amino-pyridine in a series of mixtures of acetonitrile and water, cooled to 77 °K. These phosphorescence properties are shown to be dependent on the matrix composition and are minimal at a stoichiometric ratio of 2 moles acetonitrile : 1 mole water. Evidence is presented for the existence of a molecular complex, $MeCN.2H_2O$, at this ratio.

1. Introduction

The effect of the matrix on the triplet → singlet decay of aromatic molecules in solid solution is not well understood, although examples of the influence of the matrix on the phosphorescence spectra, lifetimes, and intensities are known. Shpol'skii and coworkers(1) have shown that where geometrical similarities exist between solute and solvent, quasi-linear spectra can be observed. Morantz and Martin(2) showed that the lifetime of various aromatic hydrocarbons, dissolved in a range of solidified *n*-alcohols, varied with the chain length of the solvent.

Very little work has been carried out on the lifetimes of phosphors in mixed matrices. Richtol and Klappmeier(3) showed that the addition of less than 1% ethanol to a hydrocarbon matrix gave a dramatic increase in the phosphorescence intensity of biacetyl. Morantz and Wysocki(4) have carried out an extensive study of the phosphorescence parameters of amino-pyridines in frozen ethanol/water matrices at 77 °K. They have shown that these parameters are dependent on the matrix structure and conclude that the variation can be accounted for on the basis of the solubility of the phosphor in the various possible structures. A related study is reported by Morantz and James(5) who used ethanol/3-methyl pentane mixtures as matrices.

We considered that the effect of the composition of a binary matrix should be further investigated, using a binary mixture which has been well characterised. Acetonitrile/water mixtures have received considerable attention, a number of physical properties being well characterized and we therefore selected this system. A suitable phosphor is 2-amino-pyridine as this dissolves readily and is one of a group of pyridines previously studied in this laboratory.(4) We will see that similar changes occur in these matrices as for alcohol systems.(4,5)

2. Experimental

MATERIALS

Acetonitrile was purified in two stages; the first stage was an azeotropic distillation with benzene to remove water. The ternary azeotrope (acetonitrile-benzene-water) was distilled off first, the acetonitrile fraction was then collected, refluxed with molecular sieves and fractionally distilled through a 4-ft column packed with glass helices.

Conductivity water was used without further purification.

2-amino-pyridine, (2AP), was repeatedly recrystallised from an ethanol–ether mixture until a sample giving a consistent melting point and characteristic ultra-violet absorption spectrum was obtained.

A solute concentration of 10^{-3} molar was made up in each of the solvents and the mixtures were obtained by thoroughly mixing the appropriate proportions of each of the solutions.

APPARATUS

The apparatus has been described by Morantz and Martin.(2) This was modified by the incorporation of two teflon spacers inside the Dewar to facilitate the measurement of relative intensity.

PROCEDURE

Each lifetime reported is the mean lifetime of 20 individual measurements. A set of ten measurements was obtained for two samples prepared with solvents from different purification runs. The lifetimes reported are the mean lifetimes (τ_m) or first order decay-times to base e, evaluated from plots of the natural logarithms of relative phosphorescence intensity against time. These plots were linear over the time period studied. The standard error of the mean was less than ± 1% for the reported lifetimes.

The relative phosphorescence intensities were obtained by recording a series of decay curves under identical conditions. The linear graph obtained, as above, was extrapolated to the $T = 0$ axis and the value of the intensity (I_0) estimated. Each relative intensity reported is the mean value of at least ten experiments and the standard error of the mean is not more than ± 5%.

3. Results

(1) *The phosphorescence properties of 2-amino-pyridine*

The mean phosphorescence lifetimes and relative intensities of 2-amino-pyridine (2AP) have been measured in a series of mixed acetonitrile-water matrices at 77 °K. The variation of mean lifetimes and of relative intensities with the composition of the matrix is shown in Fig. 1 and Fig. 2 respectively.

These graphs have several features in common:

(i) Both the mean lifetime and relative intensity show only a small variation with composition between the limits $x_{H_2O} = 0.00$ and $x_{H_2O} = 0.63$, region (i),

(ii) In the region of $x_{H_2O} = 0.66$, region (ii), there are sharp minima in both graphs,

(iii) At $x_{H_2O} > 0.66$, region (iii), maxima are obtained in both graphs.

(2) *The binary system acetonitrile/water*

Some data is available on the physical properties of liquid binary mixtures of acetonitrile and water, however, data on the solid mixtures is sparse.

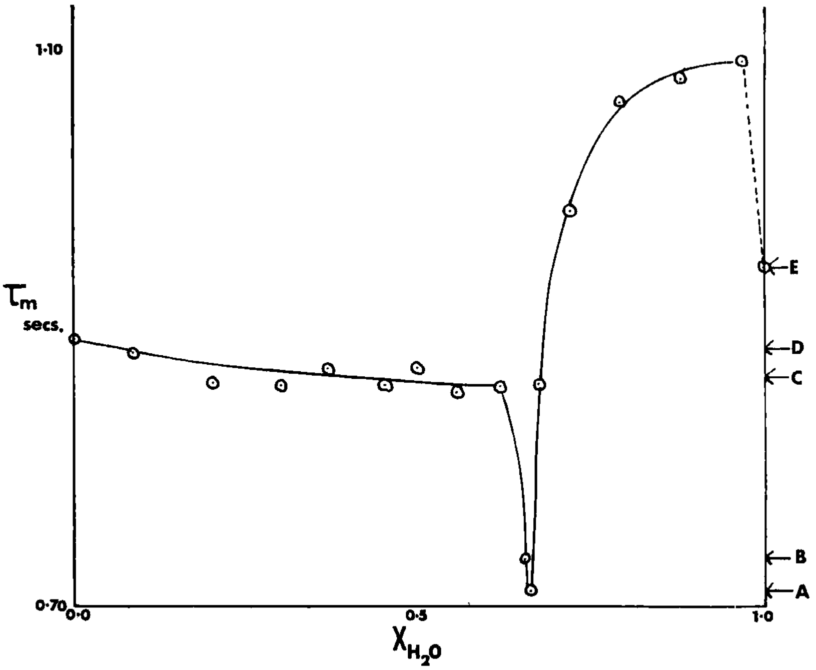

Figure 1. Phosphorescence lifetimes of 10^{-3} M 2-amino-pyridine in various acetonitrile/water mixtures at 77 °K. *A* is τ_m in MeCN.2H$_2$O complex matrix; *B* is τ_m in pure MCH matrix; *C* is τ_m in MCH matrix with 10^{-3} M MeCN added; *D* is τ_m in pure MeCN matrix; *E* is τ_m in pure ice matrix.

Cunningham, Vidulich and Kay[6] reported comprehensive measurements of the dielectric constants, viscosities and densities for a series of binary mixtures at 25 °C. Addison and Smith[7] have shown that the presence of molecular complexes in solution can be detected by analysing the volume changes which occur on mixing two liquids. The density data[6] for the water/acetonitrile system was therefore analysed using this approach and the existence of a molecular complex with composition 2 moles water : 1 mole acetonitrile is indicated. Similar results were also given by Armitage *et al.*[8]

Other methods of investigation such as an analysis based on fluidity of the mixtures,[9] or on the dielectric constant[10] also gave evidence for the existence of a 2 : 1 molecular complex. Finally, Blandamer, Foster and Waddington[11] have measured the ultrasonic

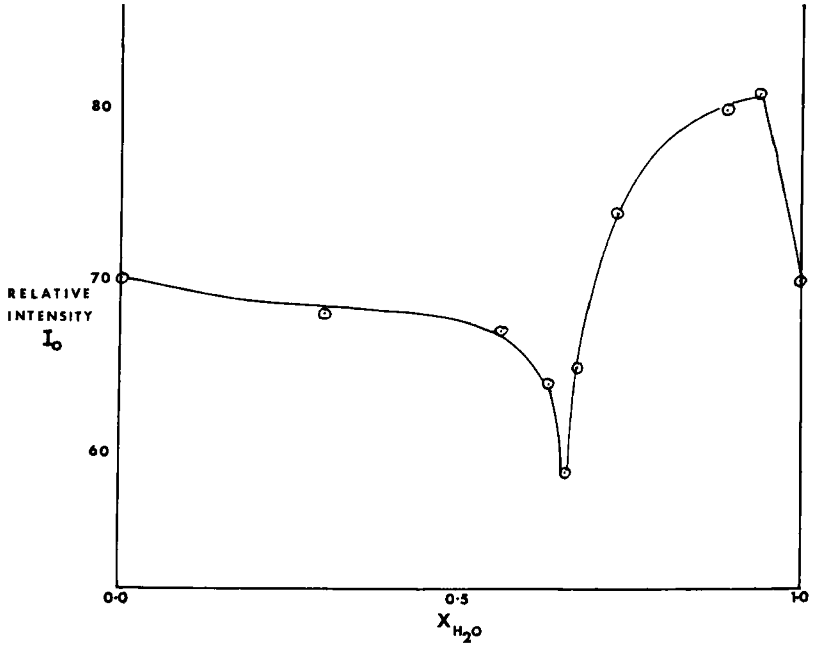

Figure 2. Relative phosphorescence intensities of 10^{-3} M 2-amino-pyridine in various acetonitrile/water mixtures at 77 °K.

absorption of this system and have shown that a maximum absorption is obtained at $x_{H_2O} = 0.66$ (2 : 1 ratio).

The full phase-diagram has not apparently been reported, although Ewert(12) has measured some melting points for various mixtures of the two solvents. This data was insufficient to construct the phase diagram, thus a more complete set of melting points was determined and the phase diagram was derived. This is shown in Fig. 3. The diagram indicates the presence of a molecular complex at $x_{H_2O} = 0.66$, which supports the conclusion derived from a consideration of other physical properties of the liquid mixtures.

(3) *The effect of acetonitrile added to 2AP in an inert solvent*

The possible interaction of the phosphor with the matrix components has been investigated by a study of the phosphorescence lifetime of 2AP dissolved in a methyl cyclohexane (MCH) matrix in the presence of small quantities of MeCN. The results are given in

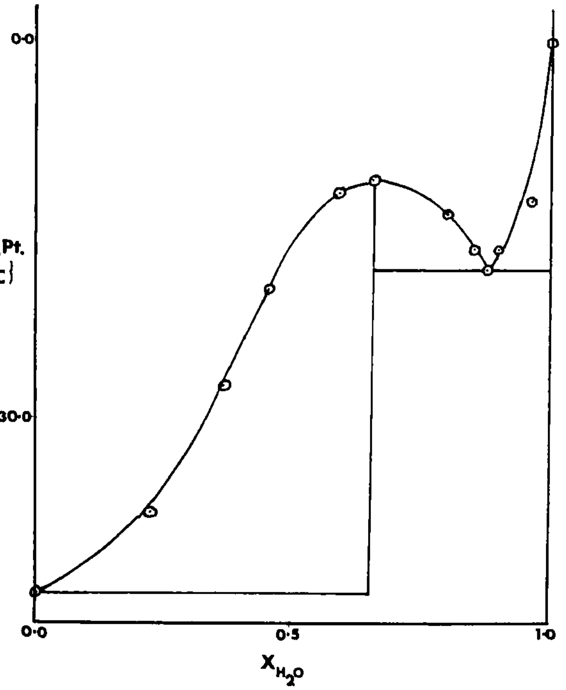

Figure 3. The phase diagram for the acetonitrile/water system indicating the existence of a molecular complex $MeCN.2H_2O$.

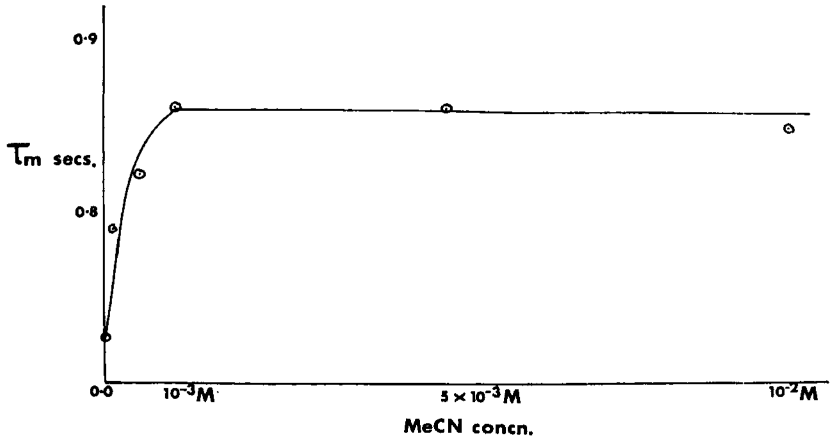

Figure 4. Phosphorescence lifetimes of 10^{-3} M 2-amino-pyridine in a methylcyclohexane matrix containing various concentrations of acetonitrile at 77 °K.

Fig. 4. It can be seen that the lifetime shows an increase with increasing MeCN concentration until the concentration of phosphor and additive are equivalent, after this point further addition of MeCN has little effect on the lifetime. Furthermore, the lifetime of 2AP in MCH solutions containing small concentrations of MeCN ($\tau_m = 0.86$ secs) is similar to that in pure MeCN (0.89 secs); and the lifetime in pure MCH (0.73 secs) is very close to that in a matrix corresponding to MeCN.2H_2O complexes (0.71 secs).

4. Discussion

Our results and related published data indicate the existence of strong molecular complexes. We can consider three regions corresponding to the different possible molecular species which can occur in these mixtures.

Region	*Species Present*
(i) $0 < x_{H_2O} < 0.63$	MeCN; MeCN.2H_2O
(ii) $0.63 < x_{H_2O} < 0.67$	Mainly MeCN.2H_2O
(iii) $0.67 < x_{H_2O} < 1.00$	MeCN.2H_2O; H_2O

Direct measurement of the position of the acetonitrile/water/complex equilibrium may be difficult as this requires an inert solvent which is non-interacting with both components and in which both components are soluble. The relative insensitivity of the phosphorescence parameters to added water in region (i) indicates that the complex is favoured and that there is little free water present.

Thus, it appears that any water molecules which are added to the mixture in region (i) will complex to the MeCN molecules and the immediate surroundings of the 2AP will probably remain composed of MeCN molecules. The addition of water, in this matrix composition region will be expected to have only a small effect on the lifetimes and intensities of the phosphor up to the composition where all the MeCN is in the form of the complex.

To confirm that the effective environment of 2AP is composed of MeCN molecules in region (i), we consider the case of 2AP dissolved in an inert solvent to which various amounts of MeCN are added. These results, shown in Fig. 4, demonstrate that the lifetime in the inert solvent (0.73 secs) rises to a maximum of 0.86 secs which is very close to the value in pure MeCN. Thus, the postulate that in the inert solvent 2AP phosphorescence is determined by MeCN is reasonable. Moreover the maximum value of the lifetime is reached at equimolar MeCN/2AP concentrations and so we conclude that 2AP is solvated by MeCN in a one to one ratio. It is reasonable, therefore, to conclude that in region (i) the 2AP is solvated by MeCN until all of the MeCN is removed by complexing.

Region (ii) is characterised by low values of lifetime and intensity. Here, we consider that the solvation of 2AP is minimal, there being no free MeCN available as a result of complex formation. Indeed the lifetime (0.71 secs) at this concentration compares with the value of 2AP in an inert solvent (0.73 secs in methylcyclohexane).

In region (iii) the lifetime and intensity is more than restored and indeed rises from the " inert solvent value " to above the " acetonitrile value ". The rate of increase appears to level off at 1.1 secs. However the nature of the system (iii) is not easily resolved. It is probable that water is in some way associated with the MeCN/water complex, providing a water-like environment for the 2AP phosphor. The value in pure water, however, lies well below the maximum in region (iii). We believe that this may be a solubility effect with the 2AP being aggregated in pure ice in a manner similar to that described by Morantz and Wysocki.(4)

The substantial increase in lifetime from 0.7 secs to 1.1 secs between an " inert solvent " and an " aqueous solvent " appears to be analogous to that found by Morantz and Martin(2) for the increases in lifetime between inert paraffin solvents and various *n*-alcohol solvents. The phenomenon may be quite general and the increase in lifetime in the polar matrices above that of the inert matrices can be explained by a mechanism where the excited state interacts with the polar matrix to a higher degree than the ground state in the same matrix. Such an interaction differential is known, for example, in the case of enhanced acidity of certain aromatic amines and phenols.(13)

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