Two Distinct Solvated Structures of *p*-Nitroaniline in Acetonitrile

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The presence of two distinct forms of p-nitroaniline (pNA) associated with solvent acetonitrile (AN) molecules is shown by using an SVD (Singular Value Decomposition) analysis of the UV-VIS spectra of pNA in AN/CCl_4 mixed solvents. All the three species (including the unassociated form in pure CCl_4) observed have varying degrees of intramolecular charge transfer due to the association.

The molecular and electronic structure of conjugated systems having an electron donor and an acceptor has been studied extensively, as they are ideal systems to probe intramolecular charge-transfer interactions[1]. The absorption spectra of these molecules exhibit spectral shifts depending upon the polarity of the medium. These spectral shifts are usually correlated with the varying degrees of charge transfer character as the polarity of the medium is varied; a polar structure is stabilized by a polar solvent[2]. In this letter, using an SVD analysis of the observed spectra of pNA in AN/CCl_4 mixed solvents, we show that the shifts are due to the presence of three distinct species in varying proportions.

The sample of pNA (Wako Chemicals) was purified by vacuum sublimation. The solvents used were of HPLC grade (Wako Chemicals) and were used as received. The absorption spectra were recorded on a Hitachi U-3500 spectrophotometer making use of freshly prepared solutions (10^{-4}-10^{-5} mol dm^{-3}).

The absorption spectrum of pNA exhibits a bathochromic shift as the solvent polarity is increased. The overall red shift upon going from CCl_4 (λ_{max}=329 nm) to AN (364 nm) is large. In order to examine the solvent polarity dependence in more detail, the absorption spectra of pNA were measured in solvent mixtures containing varying proportions of CCl_4 and AN so as to cover the entire range of dielectric constant ε between 2.2 (pure CCl_4) and 37.5 (pure AN). The results are shown in Figure 1, where the six representative spectra (0, 0.4, 4, 10, 40 and 100% AN) are included. The observed spectra exhibit large bathochromic shifts indicating increased charge transfer between the donor and acceptor groups as the concentration of AN increases. However, when the concentration of AN exceeds 40%, the spectra is nearly the same as that in 100% AN.

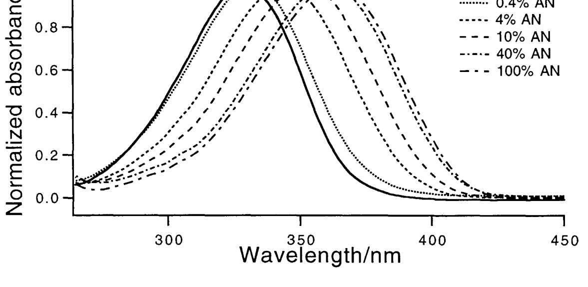


Figure 1. UV-VIS absorption spectra of pNA in AN/CCl_4 at different volume percents of acetonitrile.

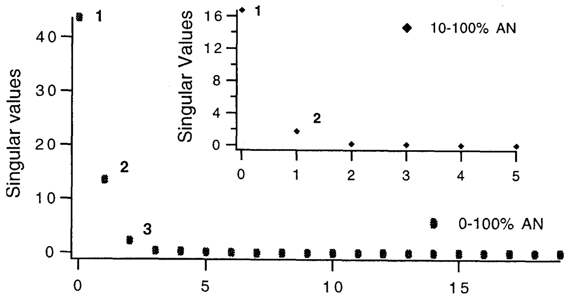


Figure 2. Singular values derived from an SVD analysis of 20 spectra obtained at 20 different AN concentrations (0-100% AN). Inset shows the singular values obtained with spectra only between 10-100% AN.

Although the spectral shifts observed seem to be continuous, an SVD analysis[3] performed using 20 absorption spectra obtained at 20 different AN concentrations indicate the presence of 3 distinct components as shown in Figure 2.

In order to extract the three individual spectral components, we have assumed a basis set containing 3 spectral components obtained through a general inspection of the observed spectra. Theabsorption spectrum of pNA in pure CCl_4 was taken as one of the components (basis spectrum 1). The second component (basis spectrum 2) was obtained by subtracting the basis spectrum 1 from the 2% AN spectrum with a constant factor. The third component (basis spectrum 3) was obtained by subtracting the basis spectrum 2 from the spectrum in pure AN with another constant factor. The constant factors were chosen in such a way that the basis spectra derived were of similar shape to that of the observed spectra.

Each of the observed spectra were then fitted as a linear combination of the three basis spectra (only the amplitudes are varied, keeping the position and width constant). Representative examples of the fitting analysis along with the observed and resolved spectra are shown in Figure 3 for five different AN concentrations, namely 0 (100% CCl_4), 0.4, 4.0, 10 and 100%. The spectrally resolved components are shown in Figure 3 as comp_1 representing the contribution of basis spectrum 1, comp_2 the basis spectrum 2 and comp_3 the basis spectrum 3 respectively. The agreement is excellent in the fitting and it is very difficult to distinguish between the observed spectra (dots) and the fitted spectra (solid line) in Figure 3.

The amplitudes thus obtained are shown in Figure 4 as a function of the volume % of AN. The figure illustrates that the first component (which is represented by the basis spectrum 1) decreases in amplitude as the AN proportion in the mixture increases and vanishes completely above 10% of the AN concentration. This is clearly shown by a separate SVD analysis of the spectra above 10% of AN proportion given as an inset in Figure 2, which shows that there are only two components in the solution. The second component (basis spectrum 2) increases rapidly in amplitude as

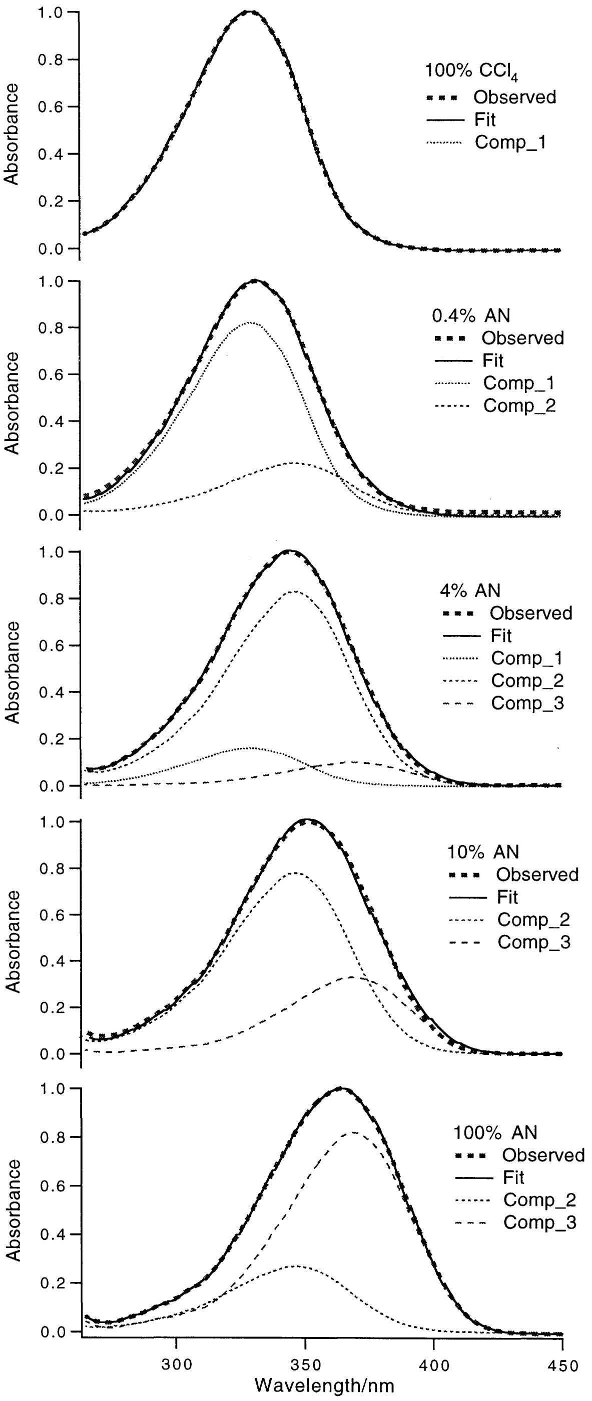


Figure 3. Representative examples of curve fitting of the UV-VIS absorption spectra of pNA in AN/CCl_4.

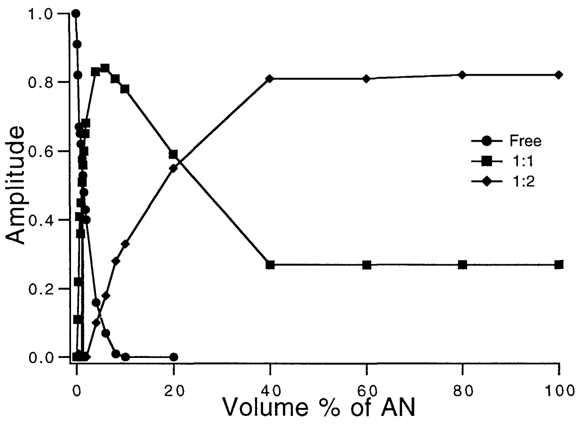
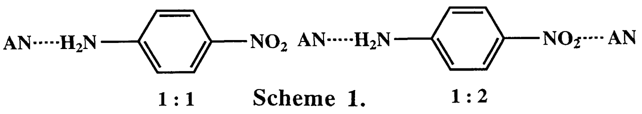


Figure 4. A plot illustrating the amplitude of the three (free,1:1 and 1:2 associated pNA) species vs the volume percent of AN.

AN proportion in the mixture is increased, then decreases and thereafter reaches a nearly constant value above 40% volume percent of AN. At the same time the 3rd component (basis spectrum 3) starts appearing above 5% of AN and the amplitude increases up to 40% and stays nearly constant at still higher concentrations of AN. Even in 100% AN solution both the second and third components coexist indicating that there are two distinct solvated structures of pNA in AN. On the basis of this AN concentration dependence, we assign the first component to the free pNA molecule, the second component to the 1:1 pNA/AN associated species, and the third component to the 1:2 pNA/AN associated species observed. The possible structures of the two associated species are shown in Scheme I. These structures are deduced from



Scheme 1.

Raman studies in the mixed solvents carried out both in the nitro and the amino symmetric stretching vibration regions[4]. The details of the Raman studies will be the subject of a forthcoming publication.

References and Notes

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