

Charge transfer band of N-alkyl pyridinium iodide in a mixed binary solvent system

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Abstract. The charge transfer (CT) band of N-alkyl pyridinium iodides has been studied in a binary solvent system (polar + nonpolar). The observed band shift has been explained in terms of a chemical model involving a stepwise solvation by the polar component. The band position has been found to be a linear function of the mole fraction of the polar component indicating that the solvent composition in the immediate neighbourhood of the solute is the same as that in the bulk. Specific solvation effects appear to play a role in some mixed solvents, where the percentage of the nonpolar part is high. An idea of the energy change in the stepwise solvation process can be obtained from nonspecific solvation effects.

Keywords. CT band; ion pairs; mixed solvents; N-alkyl pyridinium iodide.

1. Introduction

It is well known that N-alkyl pyridinium iodides exist either partly or wholly in the associated or ion pair form in solvents of low dielectric constant. The longest wavelength absorption band of these compounds in a solution is supposed to be due to a transfer of charge within the solvated ion pair:



The position of the band depends to a great extent on solvents and temperature. A complete theoretical elucidation of the effect of the medium on the absorption spectra of such a transition requires a detailed knowledge of the dielectric medium in the immediate neighbourhood of the ion pair. Due to the lack of such information a microscopic model has been proposed to explain the characteristic solvatochromism. Kosower (1958), has introduced *Z* values which provide an empirical measure of the strength of interaction of the ion pair with its local environment. Although much work has been done on the dependence of the *Z* values on solvent and temperature (Bagchi and Chowdhury 1976; Brinen *et al* 1965), very little systematic study has been made regarding the variation of *Z* values with the composition of a binary solvent system. In fact a binary solvent system of varying composition may provide information concerning specific solvent solute interaction. With this idea in mind, we have studied the spectral characteristics of alkyl pyridinium iodides in a binary solvent system with ethanol as one polar component as reported in this paper. For the second component we have used a nonpolar solvent having a low dielectric constant, *e.g.* carbon-tetrachloride, 1,4-dioxane, ethylacetate and 1,2-dichloroethane.

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2. Materials and methods

4-Cyano-pyridine (Koch Light) and pyrazine (Fluka, AG) were used without further purification. Ethiodides of 4-cyano-pyridine and pyrazine were prepared by methods described earlier (Bagchi and Chowdhury 1976; Mackay and Poziomek 1970).

The solvents were purified by standard procedures (Weissberger 1955; Coetzee and Ritcher 1969) and were distilled just before the experiment, as also the solutions with mixed solvents having different compositions. Necessary precautions were taken during the transfer of solutions to minimise contamination by moisture and/or air.

3. Spectrophotometric measurements

Spectrophotometric measurements were carried out on a Beckman model 26 spectrophotometer using stoppered cells (1 cm) placed in a thermostatted cell holder. To ensure that temperature equilibrium had been established, data were taken only when the optical density at a particular wavelength did not change with time. Necessary precautions were taken during transfer of the solution to minimise contact with moisture. Concentrations were of the order of 10^{-3} (M).

Triiodide may be formed in some of the mixed solvents and detected by its characteristic absorption bands. Only those solutions which did not show absorption due to I_3^- were used for the experiment.

4. Results

The longest wavelength absorption band of N-ethyl-4-cyano-pyridinium iodide as a function of the molefraction of ethanol (the polar component) is shown in figure 1. It

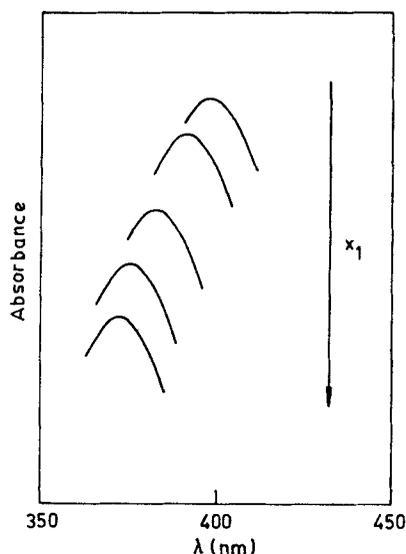


Figure 1. CT band of N-ethyl-4-cyano-pyridinium iodide as a function of the mole fraction (X_1) of a polar component (ethanol) in a mixed binary solvent system.

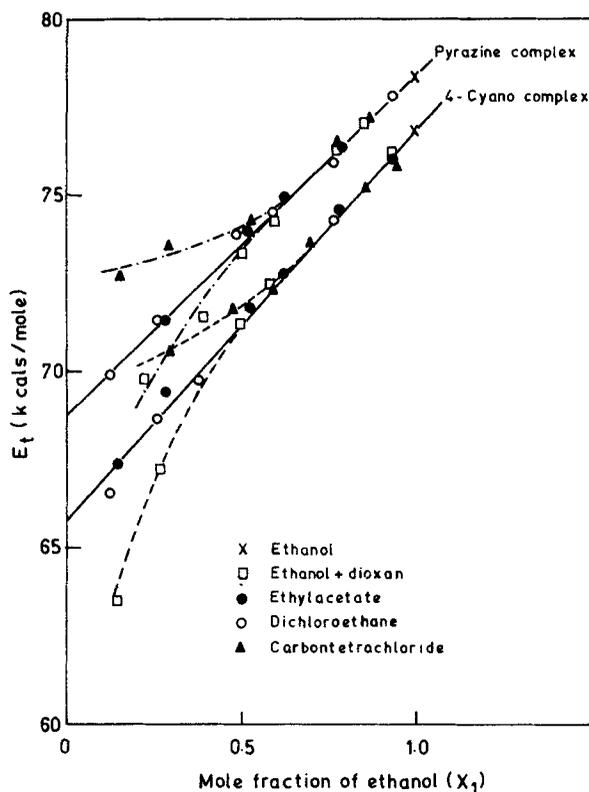


Figure 2. A plot of E_T^{\max} vs X_1 the mole fraction of ethanol in different mixed binary solvent systems.

can be seen that the λ_{\max} shifts continuously to lower energy regions as the molefraction of ethanol decreases. Bandwidth and shape remain unaffected by the presence of nonpolar component. Moreover, the extent of shift does not depend on the concentration of the solute as long as the solvent composition is fixed.

A plot of the transition energy, E_T^{\max} vs the molefraction (X_1) of ethanol is shown in figure 2. It can be seen from the plot that within experimental error, there exists a linear relationship between E_T^{\max} and X_1 . A deviation from linearity is observed in the ethanol-carbontetrachloride and ethanol-dioxane systems in the region of low ethanol molefraction values. Moreover, linearity appears to be independent of the nature of the nonpolar component in the binary solvent system.

5. Discussion

In the concentration ranges presently employed there are possibilities of solute-solute and solute-solvent interactions in solution. The fact that the band shifts depend only on the solvent composition and not on the concentration of the solute indicates that no specific interaction between solute molecules themselves takes place. The solute exists in a solution of low dielectric constant as three distinctly different species in equilibrium

viz the contact ion pairs, the solvent-separated ion pairs and free ions as shown below:



The continuous nature of the shift (absence of any isobestic point) and the insensitivity of the bandwidth and shape towards the variation of solvent composition indicate that the band shift is not due to a change in concentration of the different species caused by a modification of the above equilibria. Of these the contact ion pair contributes to the characteristic CT band and as such the spectral shift is determined by the solvation characteristics of the contact ion pair.

It has been shown by Kosower (1958) that stabilisation of the ground state and the simultaneous destabilisation of the Franck Condon (FC) excited state due to interactions with solvent molecules in the cybotactic region leads to the characteristic solvent sensitivity of the CT band in this type of complex. To explain the change of the band maximum with external perturbation e.g. temperature and pressure, Bagchi and Chowdhury (1976), suggested a stepwise solvation model,



where DAS_i is a solvated species with $i = 0, 1, 2, \dots$ and S is a polar solvent molecule. According to this model, one can speak of an average solvated species with average solvation number (\bar{n}).

Since nonpolar solvents do not significantly interact with ion pairs, their presence will merely modify the stepwise solvation process according to the law of mass action by changing the molefraction of S . Thus more and more desolvation will take place leading to relative destabilisation of the ground state. In other words the cybotactic region around an ion pair will contain lesser and lesser polar solvent molecules as one goes from the polar end to the nonpolar end of the solvent system. Thus reactions due to the solvent molecules around the ion pair would decrease leading to lesser stabilisation of the ground state. Thus the band will be shifted towards longer wavelengths.

The linear relationship between E_T^{max} and X_1 , the molefraction of ethanol, indicates that the composition in the cybotactic region around the ion pair is the same as that in the bulk. Moreover, according to this model, the polar part only effectively solvates the ion pair and as such the observed linear relation between E_T^{max} and X_1 would not depend on the nature of the solvent.

In our experiment deviation from linearity has been observed at the nonpolar end in ethanol-carbontetrachloride and ethanol-dioxane systems. This can be explained in terms of the specificities of interaction at the nonpolar end as follows.

In ethanol-carbontetrachloride systems the value of E_T^{max} at higher percentages of carbontetrachloride is found to be higher than that expected from the linear relationship. It might be that the ion pair is solvated preferentially by ethanol molecules even though the percentage of carbontetrachloride in the bulk is high. Thus the mole fraction of ethanol in the cybotactic region around the ion pair becomes greater than that in the bulk. Consequently the reaction field near the ion pair becomes stronger than in the case where the molefraction in the cybotactic region is the same as that in the bulk. This extra stabilisation of the ground state of the ion pair in turn, shifts E_T^{max} to a higher value than that expected. Similar specific interactions have been observed by other workers (Hyne and Levy 1962).

In the case of ethanol-dioxane mixtures the deviation is in the reverse direction. It has been observed that when the percentage of dioxane is increased in a water-dioxane system there is an enhanced tendency to form 1-1 H-bonded complexes between water and dioxane (Atkinson and Yoshihiro 1966). In our case it might be expected that at a higher percentage of dioxane, it forms hydrogen bonds with ethanol molecules in the bulk, thus reducing the number of free ethanol molecules which solvate the ion pair. This means that the availability of free ethanol molecules in the cybotactic region is lower than expected, which leads to a lesser contribution towards the stabilisation of the ground state of the solute than expected in terms of bulk composition thus making the E_T^{\max} value lower.

We have calculated dE_T^{\max}/dn_1 from the slope of the plot of E_T^{\max} vs X_1 using,

$$\frac{dE_T^{\max}}{dn_1} = \frac{dE_T^{\max}}{dX_1} \left(\frac{dX_1}{dn_1} \right) \quad (5)$$

The resulting values have been plotted against the molefraction of the nonpolar component. This is shown in figure 3. Now dE_T^{\max}/dn_1 may be looked upon as the change in the energy of the solvated ion pair due to a change of one molecule of ethanol thus giving an estimate of $\Delta E_{i,i-1}$, the energy change associated with the stepwise solvation process in our model. Physically the energy change associated with the stepwise solvation process should depend on the extent of solvation already present. It can be observed from the graph that the value of $\Delta E_{i,i-1}$ increases as the molefraction (X_2) of the nonpolar component is increased. The higher value of X_2 means, according to our model, a lower value of the ethanol solvation number. Thus the results are consistent with the general physical principle. The results are also in conformity with Kebarle's experimental data (1977) on the enthalpy of dissociation of ion hydrates in the gaseous phase. Similar work with other mixed solvents is in progress.

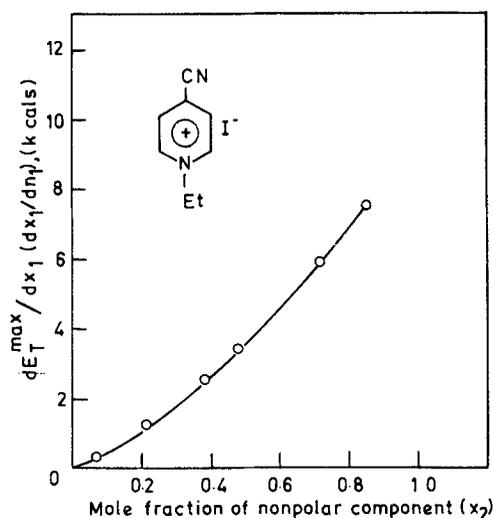


Figure 3. A plot of $\frac{dE_T^{\max}}{dX_1} \left(\frac{dX_1}{dn_1} \right)$ vs X_2 , the mole fraction of a nonpolar component in a mixed binary solvent system.

6. Conclusion

The band shift is a linear function of the molefraction of the polar solvent and independent of the nature of the nonpolar component in cases where specific solvation effects are absent. The specific solvation effect, however, plays a role in ethanol-carbon-tetrachloride and ethanol-dioxane systems.

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