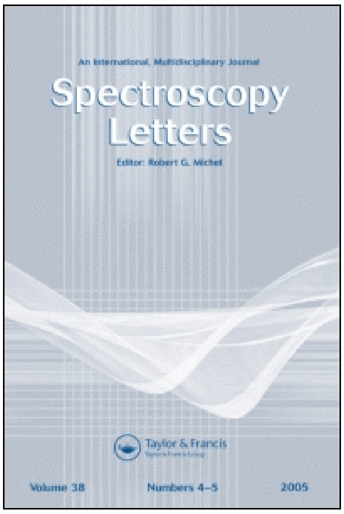

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A SPECTROSCOPIC STUDY OF PREFERENTIAL SOLVATION OF $Fe(bipy)_2(CN)_2$ IN BINARY AQUEOUS 2-ETHOXY ETHANOL MIXTURES

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ABSTRACT

Preferential Solvation of bis-(2,2'-bipyridyl) biscyanoiron(II) was investigated in 2-ethoxy ethanol water binary aqueous mixtures . The treatment showed that preferential solvation by 2-ethoxy ethanol occurs . The preferential solvation constant at 298.15 °K was found to be equal to (4.96 ± 0.06) and the free energy of preferential solvations ΔG° has a value of 3.97 KJ mol^{-1} .

INTRODUCTION

The term solvatochromism refers to the shift of an electronic absorption band when varying the electrophilic properties of the medium . Intermolecular

solute-solvent interaction forces lead to these solvatochromic shifts . These interactions usually involve alterations in the electronic ground state or may also involve the excited state of the absorbing species(1-2).

Pronounced and strong solvatochromism have been reported for compounds of the type $Fe(II)(LL)_2(CN)_2$ where LL = 2,2' bipyridine , 1,10 phenanthroline or bidentate schiff bases(3-6).

Because many chemical reactions are carried out in solvent mixtures , preferential solvation has received much attention in the literature(7-9). The aim of this work is thus to study preferential solvation of our title complex $Fe(bipy)_2(CN)_2$ in the binary 2-ethoxy ethanol water system .

A suitable thermodynamic model which is developed by Frankel et al(10) is used in this work . This method is based upon the hypothesis that if preferential solvation occurs , then the solvent is distributed between two phases , the bulk solvent and the solvation shell of the solute . Furthermore it is assumed that the solvation shell is made up of independent sites which are always occupied . Frankel et al deduced the following equation in his derivation

$$\frac{y_A}{y_B} = K \frac{Y_A}{Y_B} \quad \text{.........} (1)$$

Where K is the preferential solvation constant and y_A and y_B refer to the mole fractions of A and B in the solvation shell and Y_A and Y_B to the bulk solvent .

The plot of y_A/y_B vs. Y_A/Y_B is expected to yield a straight line of slope K . The composition of the solvation shell Y_A/Y_B can be determined as the intercept of the horizontal line with the diagonal straight line from $Y_A = 0$ to $Y_A = 1$, as in a typical phase diagram procedure . This method proved to be feasible and gave good results in our study .

EXPERIMENTAL

The schiff base complex $Fe(bipy)_2(CN)_2$ was prepared by published methods(11) and characterized by its distinguished spectra . 2-ethoxyethanol was of analar grade and doubly distilled water was used in the various aqueous mixtures . Visible absorption spectra were run on a unicam SP 800A recording spectrophotometer equipped with thermostatic attachments and by using a cell of path length 1 cm . All the spectra were made at the equilibrium temperature of 298.15° K . After properly thermostating the solvent mixture to achieve the equilibrium temperature of 298.15° K a very minute crystal of the solute was added to it to yield an absorbance of nearly unity . To ensure equilibrium , the solvent mixture was kept for an additional five minutes in the thermostated cell at 298.15° K and then the spectrum was run , and the wavelength of maximum absorption was recorded . The same experiment was repeated for the various solvent mixtures with varying mole fractions .

RESULTS AND DISCUSSION

The title complex exhibits intense charge - transfer (M L C T) bands in the visible spectrum . This can be assigned to charge transfer from iron to the schiff base ligand ($t_{2g} \dashrightarrow \pi^*$) .

Table (1)

Wavelengths of maximum absorption for the lowest energy - transfer band of $Fe(bipy)_2(CN)_2$ in the binary 2-ethoxyethanol water mixtures at 298.15°K .

$Y^{\dagger}$(2-ethoxyethanol)	λ (nm)	ν_{max} (cm^{-1})
0	521	19194
0.02	528	18939
0.04	531	18832
0.07	540	18519
0.12	544	18382
0.16	549	18215
0.21	553	18083
0.30	558	17921
0.43	564	17730
0.63	571	17513
1.00	579	17271

$\dagger$ = mole fraction .

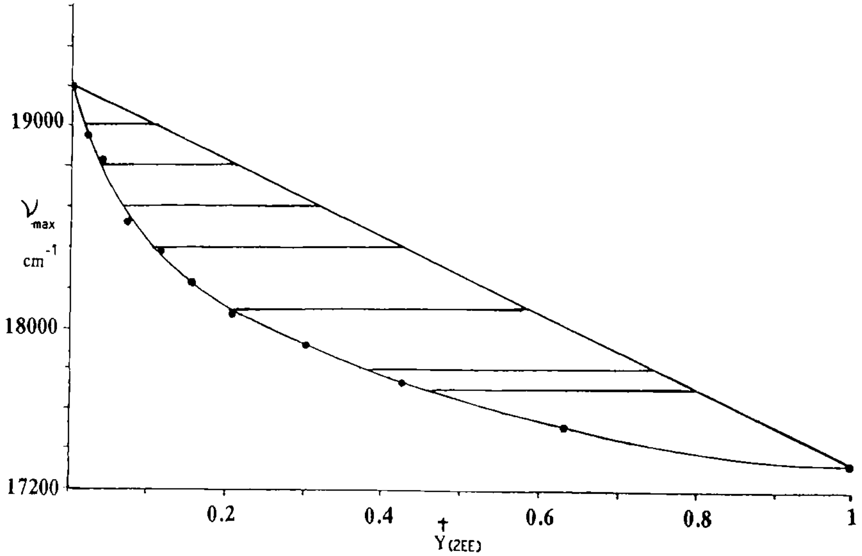

Figure 1 : Tie lines construction from the frequency plot for equilibrium between bulk and solvation phases at 298.15°K for the solvatochromic behaviour of $Fe(bipy)_2(CN)_2$ in the binary 2-ethoxyethanol water system .

Table (2)

Ratio of mole fractions of bulk (Y) and solvation (y) phases at equilibrium at 298.15°K for the solvatochromic behaviour of $Fe(bipy)_2(CN)_2$ in the binary 2-ethoxyethanol water system .

$Y_{(2EE)}/Y_{(H_2O)}$	$y_{(2EE)}/y_{(H_2O)}$
0.02	0.12
0.05	0.27
0.08	0.47
0.14	0.75
0.26	1.38
0.60	3.00
0.82	4.13

Table 1 shows the variation of the maximum wavelengths (λmax) and frequencies (ν) with composition of the solvent mixtures . Consulting this table , it could be seen that as the proportion of the organic cosolvent increases , the frequencies shift to lower energies .

2-ethoxyethanol being much more nucleophilic than water channels electron density onto the metal atom through the cyanide ligands . This will effectively decrease the Fe ---> CN back bonding of electrons from filled metal d orbitals into vacant π^* . This effect will stabilize the ground state energy of the t_{2g} electronic level , and the frequencies consequently shift to lower energy . It is to be noted in this respect that solvent effects on the charge - transfer band of $[Fe(bipy)_3]^{2+}$ are negligibly small whereas there is a marked effect on cyanide complexes as seen above . This evidence suggests that the cyanide ligand is a specific site of solvation and that direct solvent interaction with bipy ligand is unlikely to be the cause of solvent effects on the frequency of maximum absorption .

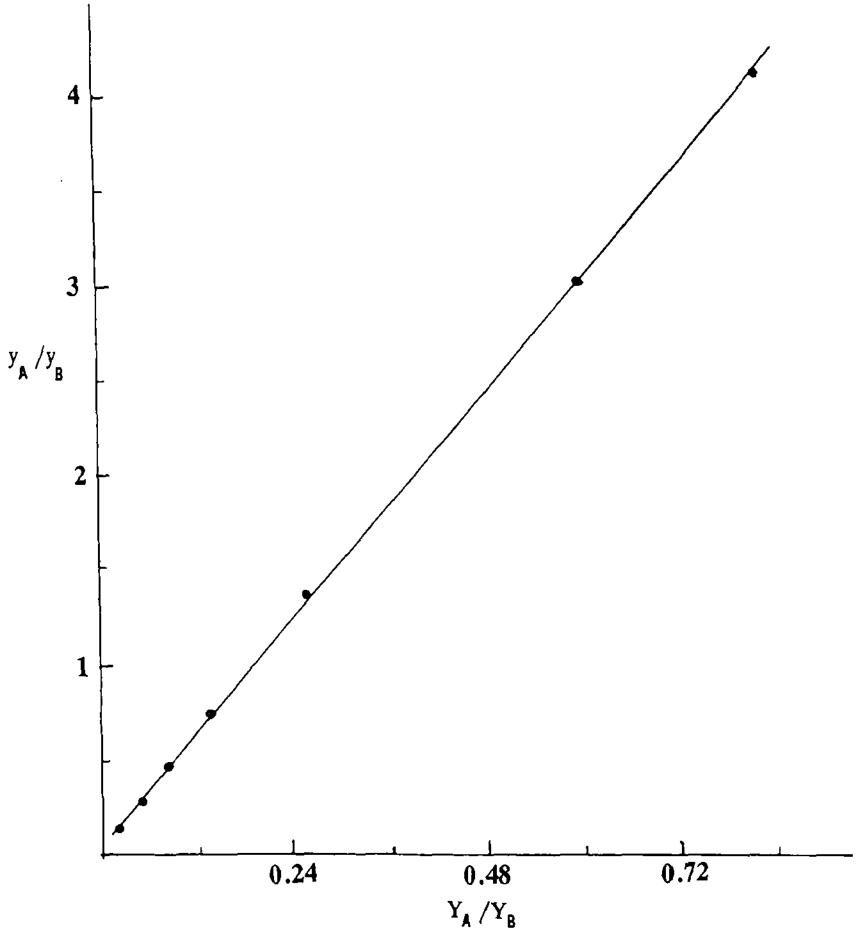

Figure 2 : Preferential solvation plot of solvation phase ratio y_{2EE}/y_{H_2O} vs bulk phase ratio Y_{2EE}/Y_{H_2O} for the solvatochromic behaviour of $Fe(bipy)_2(CN)_2$ at 298.15 °K in the binary 2-ethoxyethanol water system .

In general the plots of charge transfer energies vs bulk solvent composition are very similar to partial vapour pressure plots of binary mixed solvents . Noting that the spectra of the complexes reflect the solvation shell instead of the bulk solvent composition , it is possible to estimate y_A /y_B directly from the plot of figure 1 . For a given solvent composition Y_A , the measured frequency corresponds to an effective concentration y_A to be determined at the intercept of the horizontal line with the diagonal straight line from $Y_A = 0$ to $Y_A = 1$ as in a typical phase diagram procedure . These tie lines are manifested in figure 1 , Table 2 lists all the solvent compositions in the bulk and solvation shell determined as in the above procedure .

According to the model described , the plot of y_A /y_B vs Y_A /Y_B is expected to be linear , as is found experimentally (Figure 2) .

The preferential solvation constant K is found from the slope of this linear plot to be

$$K = (4.96 + 0.06)$$

This corresponds to a free energy of preferential solvation of 3.97 KJ mol^{-1} at 298.15°K .

According to $\Delta G^\circ = RT \ln K$.

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