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Donor and Acceptor Number Effects for the Solvatochromic Behaviour of *bis*-(2,2′-bipyridyl)-*bis*-cyanoiron(II) in Binary Aqueous Mixtures

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Summary. Correlation with acceptor numbers was made for the solvatochromic behaviour of *bis*-(2,2′-bipyridyl)-*bis*-cyanoiron(II) in binary aqueous mixtures of acetonitrile and *DMF*. The relationship between isosolvation point and donor number of the organic cosolvent was proved to be linear. Preferential solvation occurs by water in the case of the binary acetonitrile mixtures and by *DMF* in the case of the binary *DMF*, aqueous mixtures.

Keywords. Acceptor Number; Donor number; Acetonitrile; N,N-Dimethylformamide; Solvation; *Bis*-(2,2′-bipyridyl)-*bis*-cyanoiron(II); Isosolvation point.

Effekte von Donor- und Akzeptor-Zahlen auf die Solvatochromie von *bis*-(2,2′-Bipyridyl)-*bis*-cyanoeisen-(II) in binären wäßrigen Lösungen

Zusammenfassung. Es wurde eine Korrelation zwischen Akzeptorzahl und dem solvatochromen Verhalten von *bis*-(2,2′-bipyridyl)-*bis*-cyanoeisen(II) in binären wäßrigen Mischungen von Acetonitril und *DMF* durchgeführt. Die Beziehung zwischen Isosolvatisierungspunkt und Donorzahl der organischen Kosolventien erwies sich als linear. Bevorzugte Solvatisierung durch Wasser tritt im Fall der binären Acetonitrilmischungen auf, bei den wäßrigen *DMF*-Mischungen hingegen wird das Substrat bevorzugt durch *DMF* Solvatisiert.

Introduction

"Donor number" (DN) is known to be a quantitative measure for the nucleophilic properties of Solvents [1, 2]. On the other hand, to characterize the electrophilic properties of solvents, "Acceptor numbers", (AN) have been introduced [3, 4]. The acceptor number (AN) is a dimensionless number based on the ^{31}P chemical shifts of triethylphosphine oxide (Et_3PO) measured in solution [3]. By applying acceptor numbers, predictions may be made concerning the courses of many reactions which are predominantly influenced by the electrophilic properties of solvents. In fact, the nature of the solvent can have a pronounced effect on many properties such as solubilities [5], reactivities [6], redox potentials [7] and kinetics [8]. To probe the solvent environment, solvatochromism can be used. This can be defined as the solvent dependence of the frequency of an electronic transition. Solvatochromism of ternary low spin iron(II) complexes of the $Fe(CN)_2(diimine)_2$ type have been recently described by a variety of authors [9–11]. In a recent paper [12], solvent effects and correlation with Reichardt's E_T values on charge transfer spectra of the title complex have been made. However, no correlation with acceptor numbers or discussion of preferential solvation have been attempted. In the present work, correlation with acceptor numbers (AN) for the solvatochromic behaviour of the title complex in acetonitrile and *DMF*, aqueous mixtures will be presented. Since a great deal of inorganic reactions takes place in binary aqueous solvent mixtures, preferential solvation will be discussed in the same two solvents and the effect of the donor number on isosolvation points will be illustrated.

Experimental

DMF and acetonitrile were of Analar grade and doubly distilled water was used in the preparation of the various mixtures. The title complex was prepared by published methods [13] and characterized by its distinguished spectra. The spectra were run on a Unicam SP-800A recording spectrophotometer.

Results and Discussion

Table 1 lists the wave numbers, mole fractions and acceptor numbers (AN) for binary aqueous mixtures of acetonitrile and *DMF*. Acceptor numbers were obtained for each solvent mixture from Ref. [15]. Table 1 shows clearly that with increasing acceptor numbers the energy increases as well. This indicates that the solvent attack occurs electrophilically at the cyanide ligands. A solvent of large AN decrease the electron density at the cyanide ligands and increases π-backbonding with the

Table 1. Acceptance number and wave numbers of maximum absorption (ν_{max}) for the lowest energy-transfer band of $Fe(brpy)_2(CN)_2$ in various binary aqueous mole fractions (X) of acetonitrile (A) and *DMF* (D)

$X(A)$	$\nu_{max}(cm^{-1})$	AN	$X(D)$	$\nu_{max}(cm^{-1})$	AN
0.00	19194	54.8	0.00	19194	54.8
0.04	18939	53.7	0.03	18868	53.0
0.08	18727	52.5	0.06	18657	51.6
0.13	18519	51.0	0.09	18416	50.2
0.19	18382	49.5	0.14	18182	48.2
0.26	18282	47.7	0.19	17953	46.2
0.33	18182	46.3	0.25	17825	44.0
0.45	18051	44.3	0.35	17483	40.3
0.55	17986	42.6	0.48	17182	35.6
0.76	17668	38.1	0.56	17007	33.2
0.85	17452	34.5	0.68	16779	30.0
0.90	17271	30.9	0.80	16540	26.0
0.95	16978	25.5	0.90	16380	21.8
1.00	16667	18.9	1.00	16234	16.0

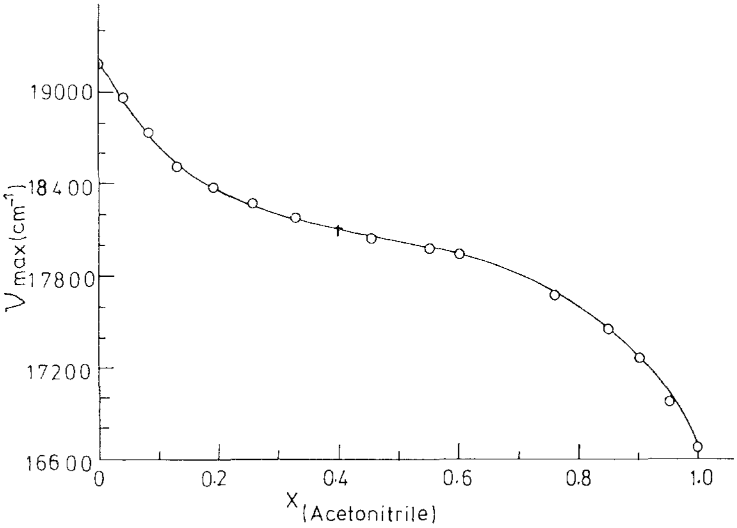

Fig. 1. Relation between ν(MLCT) values for Fe(*bipy*)$_2$(CN)$_2$ and mole fraction of acetonitrile in various binary aqueous mixtures; † = isosolvation point

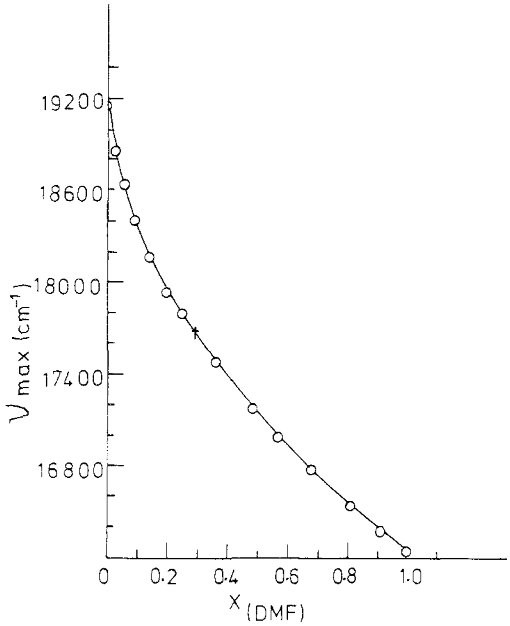

Fig. 2. Relation between ν(MLCT) values for Fe(*bipy*)$_2$(CN)$_2$ and mole fraction of *DMF* in various binary aqueous mixtures; † = isosolvation point

metal ion. This effect will increase the energy separation between the metal ion and the ligand bipyridine. Consequently hypsochromic shifts in the energies occur as a function of AN. The plots of frequency in cm^{-1} vs. mole fractions of acetonitrile and *DMF* are shown graphically in Figs. 1 and 2. From these figures it can be seen that the plots of energy vs. bulk solvent composition are not linear. This pronounced deviation from linearity indicates strongly preferential solvation. The extent of preferential solvation may be described by the position of the isosolvation point. The latter point is defined as the bulk solvent composition at which the spectral properties of the mixture towards a given solute lie midway between those of the pure solvent components [14]. Applying this definition to our system the isosolvation point for the acetonitrile aqueous system occurs at 0.6 mole fraction of the organic solvent or $X_{H_2O}^{iso} = 0.4$. For the *DMF* aqueous mixtures, the point at which energy lies midway between the values for the pure solvents is at 0.27 mole fraction of *DMF* or $X_{H_2O}^{iso} = 0.73$. These isosolvation points suggest that a linear relationship should exist between the position of the isosolvation point and DN of the aprotic cosolvent rather that the acceptor number. The donor numbers of acetonitrile and *DMF* are 14.1 and 26.6, respectively. The isosolvation point for the acetonitrile aqueous mixture is 0.4 molar fraction of water as stated in the text above (Fig. 1). Then, if the linear relationship discussed above is true, the isosolvation point for *DMF* aqueous mixture is expected to occur at 0.75 molar fraction of water. This compares favourably well with the experimental value obtained which is 0.73 (Fig. 2). This indicates that specific solvent–solute interactions between water and the cosolvent are mainly determined by the donor properties of the solvent. Addition of a small amount of water to a pure organic solvent of high donor number will produce a smaller increase in acceptor number than in a solvent of low donor number. In our system, at 0.95 molar fractions of acetonitrile (DN = 14.1) and *DMF* (DN = 26.6), which correspond to minute addition of water, will produce a corresponding change in the acceptor number of 6.6 and 3.3, respectively. This shows that with increasing donor number (DN) of the cosolvent, there would be a decrease in acceptor properties and the solvent mixture will possess new structural features which are absent in the pure solvents. This linear relationship between isosolvation points and DN of the aprotic solvent finds favourable support in the work of Mayer et al. [15] on the ^{31}P chemical shift of triethylphosphine oxide which serves as a reference base. The values of the isosolvation points obtained in this work, indicate that in the case of acetonitrile ($X_{H_2O}^{iso} = 0.4$) preferential solvation by water occurs and that water should predominate in the solvation shell of the complex. On the other hand, the result for *DMF* shows that preferential solvation occurs by *DMF* predominating in the solvation shell rather than water ($X_{H_2O}^{iso} = 0.73$). For both solvents acetonitrile

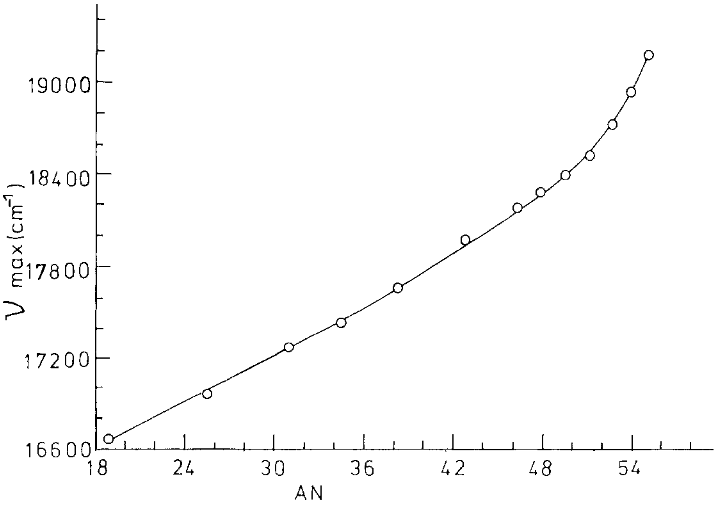

Fig. 3. Relation between ν(MLCT) values for Fe(*bipy*)$_2$(CN)$_2$ and acceptance number (AN) for various binary aqueous mixtures of acetonitrile

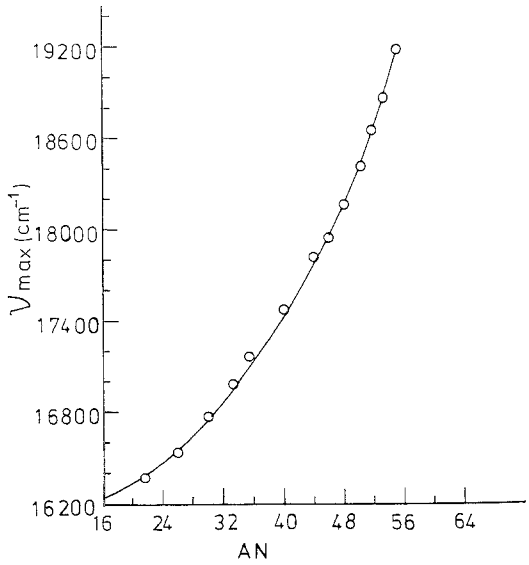

Fig. 4. Relation between ν(MLCT) values for Fe(*bipy*)$_2$(CN)$_2$ and acceptance number (AN) for various binary aqueous mixtures of *DMF*

and *DMF*, the change of energy vs. AN is not linear especially at high water contents. This is manifested in Figs. 3 and 4 for acetonitrile and *DMF*, respectively. The rate of increase of energy is different at high and low AN values. This may be due to the fact that at high water concentrations the water molecules form polymeric structures and therefore acetonitrile and *DMF* become more available to enter the solvation shell. Since the spectra of complexes reflect the solvation shell rather than the bulk solvent, the variation of energy vs. AN exhibits a curvature and is nonlinear.

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