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Preferential Solvation of Fe(*phen*)$_2$(CN)$_2$ in Binary Aqueous Acetone and 2-Methoxyethanol Mixtures

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Summary. Preferential solvation of *bis*-1,10-phenanthroline-*bis*-cyanoiron(II) was investigated in aqueous acetone and 2-methoxyethanol binary mixtures. The solvatochromic behaviour is discussed in terms of donor and acceptor numbers. The thermodynamic model of *Frankel* was used to treat preferential solvation in the binary aqueous 2-methoxyethanol mixtures and reveals that preferential solvation by the organic solvent occurs. The preferential solvation constant at 298.15 K was found to be equal to 3.30 ± 0.039, and the free energy of preferential solvation amounts to $2.96\,kJ \cdot mole^{-1}$.

Keywords. Acceptor number; Acetone; Donor number; 2-Methoxyethanol; *bis*-1,10-Phenanthroline-*bis*-cyanoiron(II); Preferential solvation; Solvent mixtures.

Bevorzugte Solvatation von Fe(*phen*)$_2$(CN)$_2$ in binären Mischungen aus Wasser und Aceton bzw. 2-Methoxyethanol

Zusammenfassung. Die bevorzugte Solvatation von *bis*-1,10-Phenanthrolin-*bis*-cyanoeisen(II) wurde in binären wäßrigen Mischungen mit Aceton bzw. 2-Methoxyethanol als organischer Komponente untersucht. Das solvatochrome Verhalten wird in Zusammenhang mit Donor- und Akzeptorzahlen diskutiert. Die theoretische Behandlung erfolgte mit Hilfe des thermodynamischen Modells von *Frankel* und zeigt, daß das organische Lösungsmittel bevorzugt solvatisiert. Die entsprechende Konstante bei 298.15 K wurde zu 3.30 ± 0.039 ermmittelt. Die freie Energie der bevorzugten Solvatation beträgt $2.96\,kJ \cdot mol^{-1}$.

Introduction

The acceptor number (AN) has been introduced to scale the electron pair accepting properties of solvents [1, 2]. Solvatochromism of ternary low spin iron(II) complexes of the Fe(CN)$_2$(diimine)$_2$ type have been recently described by various authors [3–7]. In a previous work, donor and acceptor number effects for the solvatochromism of Fe(*bipy*)$_2$(CN)$_2$ in binary aqueous acetonitrile and *DMF* have been discussed [6]. In this investigation, these effects are discussed for the solvatochromism of the title complex in binary aqueous acetone and 2-methoxyethanol mixtures. Furthermore and to highlight preferential solvation effects, the thermodynamic model of *Frankel* [8] was applied for the 2-methoxyethanol-water mixtures. This model is based upon the hypothesis that if the solvation shell is made up of

independent sites which are always occupied, then the solvent molecules will be distributed between the bulk solvent and the solvation shell of the solute according to equation 1.

$$K = \frac{x_A/x_B}{y_A/y_B} \qquad 1$$

Here, x_A and x_B represent the mole fractions of components A and B in the solvation shell, and y_A and y_B refer to the same quantity in the bulk solvent. According to this equation, the plot of x_A/x_B *vs.* y_A/y_B will give a straight line of slope K which represents the preferential solvation constant. The composition of the solvation shell (x_A/x_B) can be determined from the intercept of the horizontal line with the diagonal from $y_A = 0$ to $y_B = 1$ as in a typical phase diagram procedure. This method proved to be satisfactory and was thus applied in our study.

Results and Discussion

Table 1 lists the wave numbers, mole fractions, and acceptor numbers (AN) for binary aqueous mixtures of acetone and 2-methoxyethanol. The acceptor numbers for the acetone mixtures were obtained from Ref. [9]. Table 1 demonstrates that the energy increases with increasing AN and that the cyanide ligand is a specific site of solvation. A solvent of large AN decreases the electron density at the cyanide ligands and increases π-back bonding with the metal ion. Consequently, the energy separation between the metal ion and the ligand phenanthroline is increased. Figs. 1 and 3 show that the plots of energy *vs.* bulk solvent compositions are non-linear

Table 1. Acceptor number and wave numbers of maximum absorption (ν_{max}) for the lowest energy transfer band of Fe(*phen*)$_2$(CN)$_2$ at various mole fractions of acetone (x_A)

x_A	ν_{max}(cm^{-1})	AN
0.00	19305	54.8
0.03	19084	53.6
0.06	18904	52.6
0.10	18762	50.6
0.14	18519	48.6
0.20	18315	46.7
0.27	18182	44.3
0.31	18116	42.4
0.36	18050	42.3
0.49	17521	39.2
0.69	17606	33.4
0.77	17422	31.0
0.87	17123	27.3
0.93	16778	22.8
1.00	16026	12.5

Table 2. Wave numbers of maximum absorption (ν_{max}) for the lowest energy transfer band of Fe(*phen*)$_2$(CN)$_2$ at various mole fractions of 2-methoxyethanol (x_M)

x_M	ν_{max}(cm^{-1})
0.00	19305
0.02	19157
0.05	19939
0.10	18757
0.13	18657
0.19	18484
0.25	18315
0.35	18149
0.48	17986
0.68	17762
0.76	17699
0.86	17606
0.93	17575
1.00	17544

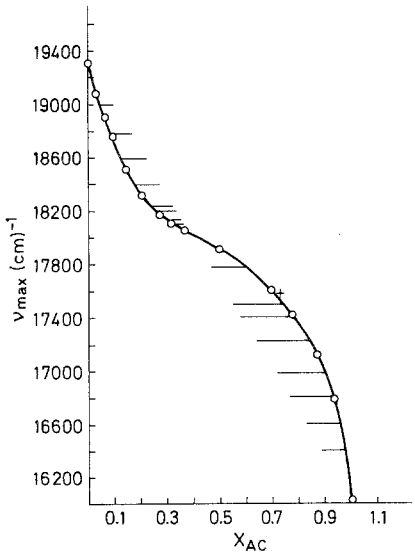

Fig. 1. Relation between ν(MLCT) values for Fe(*phen*)$_2$-(CN)$_2$ and mole fraction of acetone in various binary mixtures; † = isosolvation point

for both solvents, suggesting preferential solvation. The extent of preferential solvation may be described by the position of the isosolvation point [10]. These points occur at a mole fraction of 0.73 for acetone ($x^{iso}_{H_2O} = 0.27$) and at a mole fraction of 0.23 for 2-methoxyethanol ($x^{iso}_{H_2O} = 0.77$). The values indicate that preferential solvation occurs by water in the case of acetone and by the organic solvent in the case of 2-methoxyethanol. Also, in water-acetone the frequency plot (Fig. 1) shows two distinct regions. The nonlinearity of the plot of energy *vs.* AN (Fig. 2) indicates that the spectra of complexes reflect the solvation shell rather than the bulk solvent. Water should be more easily transferred from the bulk solvent to the complex

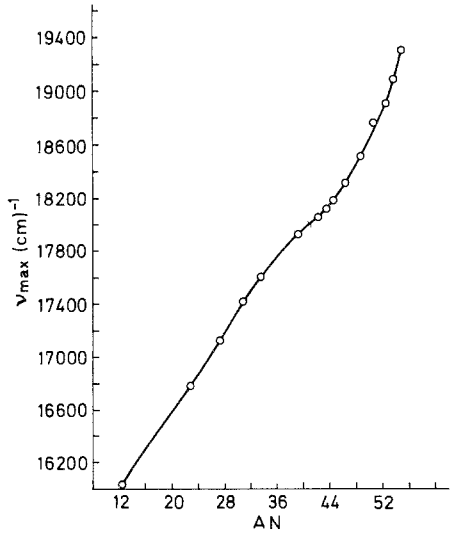

Fig. 2. Relation between ν(MLCT) values for Fe(*phen*)$_2$-(CN)$_2$ and acceptor number for various binary aqueous mixtures of acetone

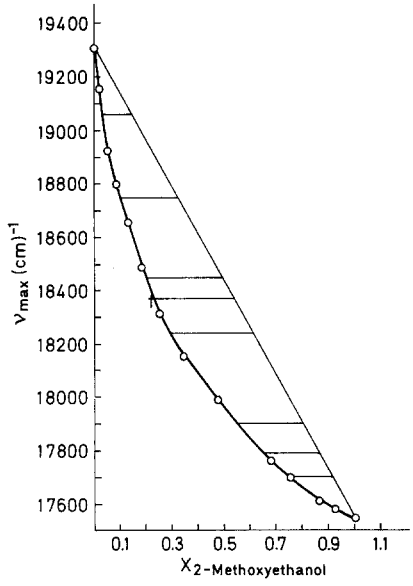

Fig. 3. Tie lines construction from the frequency plot for equilibrium between bulk and solvation phases at 298.15 K for Fe(*phen*)$_2$(CN)$_2$ in the 2-methoxyethanol-water system; † = isosolvation point

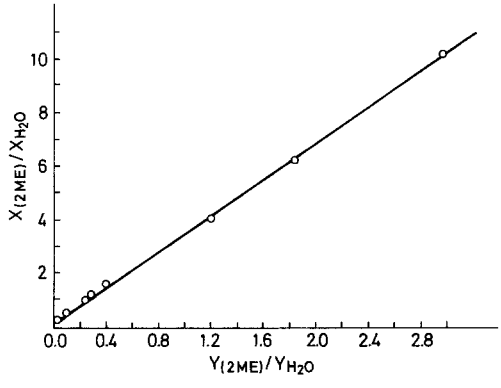

Fig. 4. Preferential solvation plot (phase ratio x_M/x_{H_2O} *vs.* bulk phase ratio y_M/y_{H_2O}) for Fe(*phen*)$_2$-(CN)$_2$ at 298.15 K in the 2-methoxyethanol-water system

solvation shell at low molar fractions of water. However, at high water concentrations, acetone becomes more available to enter the solvation shell because of the possibility that water molecules form polymeric structures. 2-methoxyethanol, having a relatively high isosolvation point ($x^{iso}_{H_2O} = 0.77$), is expected to be a solvent of high donicity (DN). This can be seen from the linear relationship between isosolvation points and donicity [9]. Thus, 2-methoxyethanol being much more nucleophilic than water, channels electron density onto the metal atom through the cyanide ligands. This effect will stabilize the ground state energy of the t_{2g} electronic level and the frequencies shift to lower energies (Table 2). To elaborate and characterize preferential solvation in the case of 2-methoxyethanol, the model of

Table 3. Ratio of mole fractions of bulk (y) and solvation (x) phases at equilibrium at 298.15 K for the solvatochromic behaviour of Fe(*phen*)$_2$(CN)$_2$ in the binary 2-methoxyethanol-water system

y_M/y_{H_2O}	x_M/x_{H_2O}
0.03	0.16
0.11	0.47
0.25	0.96
0.30	1.13
0.41	1.56
1.22	4.00
1.86	6.14
3.00	10.11

Frankel [8] was used. As stated in the introduction, for a given solvent composition y_A, the measured frequency corresponds to an effective concentration x_A to be determined at the intercept of the horizontal line with the diagonal from $y_A = 0$ to $y_A = 1$ as in a typical phase diagram procedure. Table 3 lists all the solvent compositions in the bulk and solvation shells, determined as in the above procedure. Figure 4 shows that the plot of x_A/x_B *vs.* y_A/y_B is linear and the preferential solvation constant is found from the slope of this linear plot to be $K = 3.30 \pm 0.039$. This corresponds to a free energy of preferential solvation of 2.96 kJ·mole^{-1} at 298.15 K.

Experimental

The solvents acetone and 2-methoxyethanol were of analytical grade, doubly distilled water was used in the preparation of the various mixtures. The title complex Fe(CN)$_2$(*phen*)$_2$ (Aldrich) was used as purchased. Visible absorption spectra were run on a Univam SP 800 A spectrophotometer, equipped with a thermostatic attachment and using a cell of path length 1 cm.

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