Spectrophotometric Studies on the Solvatochromism of the $Fe(CN)_2(phen)_2$ Complex

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Summary. The solvatochromic behaviour of bis-(cyano)-bis-(9,10-phenanthroline)-iron(II) has been reexamined spectrophotometrically in a series of 19 solvents including water, alcohols and dipolar. aprotic media. Satisfactory correlations between the wave numbers of the long-wavelength band and solvent acceptor numbers are obtained in all media; only values, for carboxylic acids deviate from the regression line.

Keywords. Bis-(cyano)-bis-(9,10-phenanthroline)-iron(II); Solvatochromism; Acceptor numbers.

Spektrophotometrische Untersuchungen über die Solvatochromie der Komplexverbindung $Fe(CN)_2(phen)_2$

Zusammenfassung. Das solvatochrome Verhalten von bis-(Cyano)-bis-(9,10-phenanthrolin)-eisen(II) wurde in 19 Lösungsmitteln, darunter Wasser, Alkohole und dipolare aprotische Medien, spektrophotometrisch überprüft. In allen Medien wurden zufriedenstellende Korrelationen zwischen den Wellenzahlen der langwelligen Bande und den Akzeptorzahlen der Lösungsmittel erhalten; lediglich die Werte für Carbonsäuren weichen von der Ausgleichgeraden ab.

Introduction

Bis-(cyano)-bis-(9,10-phenanthroline)-iron(II) is known as a strongly solvatochromic complex. It exibits intense charge-transfer bands in the visible region; the frequencies of absorption maxima and extinction coefficients vary considerably with the nature of the solvent. The position of the band corresponding to the $t_{2g} \rightarrow \pi^*$ transition can be correlated with some success [1, 2] with Reichard's E_T solvent parameter [3]. Several years age, Soukup and Schmid [4] have reported a correlation between ν_{max} and AN, the solvent acceptor number [5, 6]. For a set of 12 solvents (hexamethylphosphoric triamide, propylene carbonate, N,N-dimethylformamide, acetonitrile, dimethylsulfoxide, nitromethane, formamide, acetic acid, water, ethanol, formic acid, and trifluoroacetic acid), the authors obtained a linear plot with a correlation coefficient of $r = 0.980$ and a standard deviation of $\sigma = 4.58$ [4]. This relationship was subsequently depicted and discussed by Gutmann and Resch [7].

On the other hand, Al-Alousy and Burgess [2] have suggested that the plot of ν_{max} vs. AN consists of two separated lines for dipolar aprotic solvents and for alcohols plus formamide, respectively. Points for water and for carboxylic acids fit

to none of these lines. Note, however, that ν_{max} values considered in Ref. [2] were taken from various literature sources. Hence, it was of interest to us to reexamine the overall picture of the solvatochromism of $Fe(CN)_2(phen)_2$.

Results and Discussion

Wavelengths of maximum absorption for the lowest energy metal to ligand charge-transfer band of $Fe(CN)_2(phen)_2$ in 19 solvents are reported in Table 1.

Treatment of the results for the alcohols and formamide by the least squares procedure gave the following correlation equation

$$AN = (0.007 \pm 0.004)\nu_{max} - (87.8 \pm 77.1) \qquad 1$$

with $r = 0.9146$ and $\sigma = 0.99$ (errors of regression coefficients were determined on the basis of the Student distribution with a confidence level of 0.95). On the contrary to the suggestion made in Ref. [2], addition of the point for water improves correlation 1 considerably. For solvents no. 13–19 (Table 1), the resulting regression is

$$AN = (0.010 \pm 0.002)\nu_{max} - (135.3 \pm 41.0) \qquad 2$$

($r = 0.9800$, $\sigma = 1.28$, Exner function $\psi = 0.24$).

When 12 aprotic solvents are considered, the correlation equation has the form:

$$AN = (0.011 \pm 0.003)\nu_{max} - (155.8 \pm 47.7) \qquad 3$$

with $r = 0.9483$, $\sigma = 1.11$, and $\psi = 0.35$.

Table 1. Wave numbers of the long-wavelength band of $Fe(CN)_2(phen)_2$ in various solvents

No	Solvent	AN	λ_{max} (nm)	ν_{max} (cm^{-1})
1	Hexamethylphosphoric triamide	10.6	634	15770
2	Acetone	12.6	625	16000
3	N-Methylpyrrolidinone	13.3	619	16160
4	N,N-Dimethylacetamide	13.6	617	16210
5	Benzonitrile	15.5	607	16470
6	N,N-Dimethylformamide	16.0	614	16280
7	1,2-Dichloroethane	16.7	606	16500
8	Propylene carbonate	18.3	600	16670
9	Acetonitrile	18.9	597	16750
10	Dimethylsulfoxide	19.3	603	16580
11	Dichloromethane	20.4	597	16750
12	Chloroform	23.1	595	16810
13	2-Propanol	33.5	572	17480
14	1-Butanol	36.8	569	17570
15	Ethanol	37.1	557	17950
16	1-Propanol	37.3	565	17700
17	Formamide	39.8	548	18240
18	Methanol	41.3	546	18320
19	Water	54.8	512	19530

Now, let us compare the correlations presented for both groups of solvents. Obviously, they constitute two separated almost parallel lines, as it was postulated by *Al-Alousy* and *Burgess* [2]. Considering the errors of regression coefficients, we can say that the separation of the lines is not justified from the statistical point of view. Furthermore, one may expect that an overall relationship between AN and v_{max} should exist for all solvents studied. Indeed, for all solvents listed in Table 1, eqn. 4 holds with $r = 0.9868$, $\sigma = 2.00$, and $\psi = 0.17$ (Fig. 1).

$$AN = (0.013 \pm 0.001)v_{max} - (194.4 \pm 18.4) \qquad 4$$

Comparison of AN_{calc} with AN_{exp} indicates that the most serious deviation occurs with 1-butanol; in this case, the deviation is greater than 2σ. When this value is excluded, the correlation is somewhat improved. The results of the regression

$$AN = (0.013 \pm 0.001)v_{max} - (192.1 \pm 15.9) \qquad 5$$

are then $r = 0.9906$, $\sigma = 1.69$, and $\psi = 0.14$.

Thus, we assume that eqn. 5 offers a suitable method for the estimation of the acceptor numbers of solvents for which the AN values are still unknown (cf. Ref. [4]). However, it is worth mentioning that this conclusion is not valid for carboxylic acids. Our measurements with HCOOH, CH$_3$COOH, and CF$_3$COOH, for which appropriate acceptor numbers were determined [5], indicated great deviations from regression lines expressed by eqs. 4 and 5 (see also Ref. [2]).

At present, little can be said about the reason of these deviations, but it is interesting to recall that "original" acceptor numbers were derived from ^{31}P NMR measurements of triethylphosphine oxide dissolved in the respective solvent. One should remember that Et$_3$PO is partially protonated by carboxylic acids and the NMR signals reflect a rapid exchange [5]:

$$Et_3PO + HOOCR \rightleftharpoons Et_3POH^+ + RCOO^- \qquad 6$$
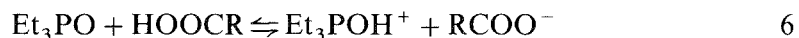
On the other hand, it may be assumed that for Fe(CN)$_2$(phen)$_2$ the protonation does

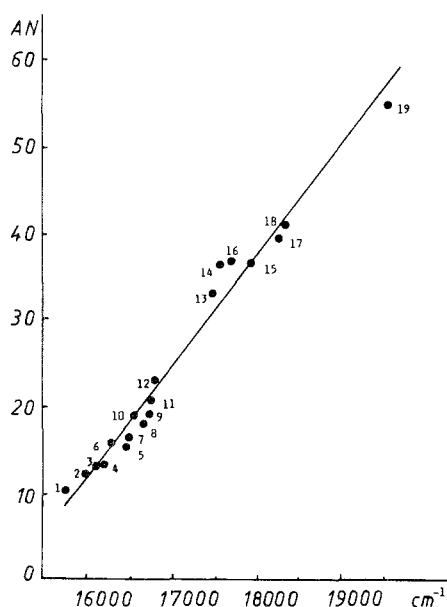Fig. 1. Relation between the wave number of the long-wavelength band of Fe(CN)$_2$(phen)$_2$ and solvent acceptor numbers; for numbers, cf. Table 1

not occur, and this may explain the reason for the deviation of the acidic solvents from the correlations described above.

Finally, taking into account the foregoing statements, we have reconsidered the solvent effect on the visible spectrum of bis-(cyano)-bis-(4,7-dimethyl-9,10-phenanthroline)-iron(II) [8, 9]. For a set of 6 hydroxylic solvents (alcohols and water) the correlation equation

$$AN = (0.010 \pm 0.003)v_{max} - (145.2 \pm 48.7) \qquad 7$$

with $r = 0.9826$, $\sigma = 1.29$, and $\psi = 0.23$ can be written. For a group of 11 aprotic solvents, eqn. 8 is obtained ($r = 0.9473$, $\sigma = 1.67$, $\psi = 0.35$).

$$AN = (0.008 \pm 0.002)v_{max} - (113.7 \pm 32.5) \qquad 8$$

The data for 17 solvents (hydroxylic and aprotic together) can be correlated as

$$AN = (0.012 \pm 0.002)v_{max} - (175.1 \pm 23.4) \qquad 9$$

($r = 0.9778$, $\sigma = 2.86$, $\psi = 0.22$). If the deviating value for nitromethane is excluded (AN_{calc} and AN_{exp} differ by more than 2σ), the correlation is somewhat improved ($r = 0.9876$, $\sigma = 2.20$, $\psi = 0.17$).

$$AN = (0.012 \pm 0.001)v_{max} - (177.0 \pm 18.3) \qquad 10$$

Considering these results, the statement "wavenumbers for protic solvents lie on a separate line and are lower than expected from the acceptor numbers" [10] seems not to be reasonable. It can rather be concluded that the complexes considered in this communication are almost universal indicators for the acceptor properties of aprotic and hydroxylic solvents. Note also that the use of so-called Individual Acceptor Numbers, which characterize the acceptor properties of protic solvents as a function of solvation numbers and solvation shell structure [10], instead of original AN, does not improve correlations 4 and 10.

Experimental

Solvents used in our experiments were of spectral grade or were dried and purified according to standard procedures. $Fe(CN)_2(phen)_2$ (Alfa Ventron) was used as purchased. Visible spectra were recroded at a temperature of $23 \pm 0.2\,^{\circ}C$ by means of a Philips PU 8730 spectrophotometer, using a cell with a pathlength of 1.0 cm. The accuracy of the assignment of the wavelength of the maximum absorption and the reproducibility of the values determined in different experiments were in the range of ± 1 nm.

Acknowledgements

References

[1] Burgess J., Chambers J. G., Heines R. I. (1981) Transition Met. Chem. 6: 145
[2] Al-Alousy A., Burgess J. (1990) Inorg. Chim. Acta 169: 167

[3] Reichard C. (1988) Solvents and solvent effects in organic chemistry. Verlag Chemie, Weinheim

[4] Soukup R. W., Schmid R. (1985) J. Chem. Educ. **62**: 459

[5] Mayer U., Gutmann V., Gerger W. (1975) Monatsch. Chem. **106**: 1235

[6] Mayer U. (1983) Ions and molecules in solution. In: Tanaka N. (ed.) Studies in physical and theoretical chemistry, vol. 27. Elsevier, Amsterdam, p 219

[7] Gutmann V., Resch C. (1988) Monatsh. Chem. **119**: 1251

[8] Burgess J. (1970) Spectrochim. Acta A **26**: 1369

[9] Mayer U. (1979) Pure Appl. Chem. **51**: 1697

[10] Mayer U., Hoffmann H., Kellner R. (1988) Monatsh. Chem. **119**: 1223