Influence of the Bulk and Donor-Acceptor Properties of Solvent on Ligand Field Spectra

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INFLUENCE OF THE BULK AND DONOR-ACCEPTOR PROPERTIES
OF SOLVENT ON LIGAND FIELD SPECTRA

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ABSTRACT

The influence of solvents on the electronic
absorption spectra of chromium (III) complexes was
investigated. The dependence of the crystal field
parameter Dq on dielectric constant as well as Gutmann
donor number DN of solvent was found and described. By
using the proposed model, unknown in the literature
donor numbers for a few alcohols were estimated.

INTRODUCTION

The influence of solvent on solute molecule has
been intensively studied but the problem is yet far
from being completely understood. At present, there are
two approches to quantitative description of this
effect. The theoretical approach describes solvent as
an isotropic environment of dissolved particles and

characterizes it by its bulk properties. Unfortunately, this approach involves only the influence of the nonspecific interactions. The other approach is based on description of the solvent effect by suitably chosen empirical parameters measuring specific and nonspecific interactions. The drawback of this approach is that such parameters are not universal and depend on each other.

The interactions between solvent and solute molecule are separated in the literature into specific and nonspecific . As a result, linear functions with few parameters for description of the solvent effect are proposed[1-5]. One of the most interesting is that proposed by Svoboda and coworkers[5]:

$$A = A^o + a*f(\varepsilon) + b*f(n) + c*DN + d*AN \qquad\qquad 1$$

where:

A	– a symbol for the physicochemical property dependent on solvent effect,
A^o	– value of the same property in gas phase,
$f(\varepsilon)$	– function of dielectric constant ε,
$f(n)$	– function of refractive index n,
DN	– donor number of solvent[6],
AN	– acceptor number of solvent[7],
a,b,c,d	– the regression coefficients characterizing sensitivity of the property A to the individual parameters.

Originally, in function 1, instead of DN, Kagiya Δ_D value[8] was taken into consideration but because of high correlation of these two empirical parameters (corr. coeff. = 0.984 [9]) and because the donor number is much more often used, we decided to take into account the

latter one. In the relation presented above dielectric
constant and refractive index correspond to the
nonspecific interactions while donor and acceptor
number to the specific ones. This four-parameter
function was determined on the basis of factor analysis
of data matrices containing 35 empirical and
nonempirical parameters for 85 solvents[5]. The chosen
parameters being the most ortogonal to each other
appear to be the most suitable for description of the
effects discussed.

   The solvent effect on d-d transitions of complex
compounds has been usually assumed to be insignificant.
However, one can observe that solvent affects the shift
of d-d absorption bands as well as changes of their
oscillator strengths[10-12]. The formula for description
of the influence of the nonspecific interactions on
crystal field parameter Dq [10] (O_h symmetry) is as
follows:

$$Dq = Dq^0 + Dq^0 (r/r_0)^9 \, [(5(\varepsilon-1)/(5\varepsilon+4)]$$

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where:

   Dq^0 - extrapolated value of Dq parameter   for
          complex molecule in vacuum,

   r   - distance between the central ion and ligand,

   r_0 - radius of cavity in which   the   solute
          molecule is supposed to lie,

   ε - dielectric constant of solvent.

   The relation was succesfully applied in the study
of the nonspecific interactions between protic solvents
(water and alcohols) and Cr(III) as well as Ni(II)
complexes[10-12]. It is shown in this paper that to
extend the class of solvents described by the model, it

is necessary to take into account additionally donor
number of solvent.

EXPERIMENTAL

 Electronic absorption spectra of $[Cr(H_2O)_6](NO_3)_3$
and $K_3[Cr(NCS)_6] \cdot 4H_2O$ in water (W), dimethyl sulfoxide
(DMSO), N,N-dimethylformamide (DMF), methanol (M),
ethanol (E), acetone (A), tetrahydrofurane (THF) and
next in hexyl (H), n-amyl (NA), isoamyl (IA), isobutyl
(IB), isopropyl (IP), benzyl (BE), and t-butyl (B)
alcohols were recorded in the range of 12000-28000 cm^{-1}
with a Hitachi 356 UV/VIS spectrophotometer.

 Due to slight changes of the complex band
parameters in solvents studied, it was necessary to use
the computer resolution technique for analysis of the
measured spectra[13]. The bands corresponding to the
spin-allowed as well as spin-forbidden transitions were
taken into account in the computer resolution process.
All the calculations were carried out on a
microcomputer compatible with IBM PC/XT.

 The following values of dielectric constants ε,
donor numbers DN, and acceptor numbers AN were used in
the analysis of the solvent effect:

ε: W – 78.5, DMSO – 46.4, DMF – 38.3, M – 32.6,
   E – 24.3, A – 20.7, THF – 7.6, H – 13.3,
   NA – 13.9, IA – 14.7, IB – 17.7, IP – 18.3,
   BE – 13.1, B – 12.5

DN: W – 18.0, DMSO – 29.8, DMF – 26.6, M – 19.0,
   E – 20.0, A – 17.0, THF – 20.0

AN: W – 54.8, DMSO – 19.3, DMF – 16.0, M – 41.3,
   E – 37.1, A – 12.5, THF – 18.3

RESULTS AND DISCUSSION

The analysis based on the model 2 had given good results only for protic solvents[10-12] such as alcohols and water. As one can notice, this approach involves only the influence of the nonspecific interactions. The question was if taking into consideration the specific interactions would extend the class of solvents described by the model. Seven solvents (water, DMSO, DMF, methanol, ethanol, acetone, THF) and two chromium (III) compounds ($[Cr(H_2O)_6](NO_3)_3$, $K_3[Cr(NCS)_6] \cdot 4H_2O$) were taken into account in this test. All the measured spectra were resolved into component bands and the crystal field parameters were calculated. On the basis of the equation 1 two additional linear terms (c*DN and d*AN) were taken into consideration in the model 2 and the regression analysis was carried out. The coefficient d for aquo as well as for thiocyanine complex turned out to be practically equal to zero (-0.154 ± 0.129 and -0.050 ± 0.025 respectively) and was rejected. This result was surprising since for thiocyanine complex, as an anion, one could rather expect dependence on acceptor number. This effect is probably connected with the specific interactions solvent - central ion (which is cation for both complexes) where donor properties of solvent appear to be important. Finally, the following semiempirical relationship was tested:

$$Dq = Dq^0 + a[(5(\varepsilon-1)/(5\varepsilon+4)] + c*DN \qquad 3$$

The results of the regression analysis, according to the equation 3, for complexes and solvents studied, are listed in Table 1. The analysis gave very good results and confirmed the significance of influence of

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TABLE 1

The Results of the Regression Analysis According to the
Eq. 3 for the Following Complexes: 1: $[Cr(H_2O)_6](NO_3)_3$,
2: $K_3[Cr(NCS)_6] \cdot 4H_2O$.

Solvent	ε	DN	$Dq \ [cm^{-1}]$	
			1	2
Water	78.5	18.0	1739	
DMSO	46.4	29.8	1687	1773
DMF	38.3	26.6	1700	1776
Methanol	32.6	19.0	1731	1783
Ethanol	24.3	20.0	1724	1777
Acetone	20.7	17.0		1780
THF	7.6	20.0	1695	1748
$Dq^o \ [cm^{-1}]$			1630($\pm$8)	1607($\pm$5)
a			190.7($\pm$8.5)	211.0($\pm$6.3)
c			-4.24($\pm$0.12)	-1.22($\pm$0.08)
$Dq^{max \ a} \ [cm^{-1}]$			1821($\pm$16)	1818($\pm$11)
corr. coeff.[b]			0.998	0.997

[a] $Dq^{max} = \lim Dq$ when $\varepsilon \rightarrow \infty$, $DN \rightarrow 0$

[b] correlation between theoretical and experimental
values of the function 3

the donor properties of solvent on ligand field
spectra. Due to the negative value of the regression
coefficient c such properties cause the red shift of
d-d bands contrary to the bulk properties. Such a
direction of shifts indicates that value of Dq^o
parameter is not the lowest possible one of the Dq
parameter. It is visible, for instance, for small
dielectric constant and high donor number of solvent.

TABLE 2

Donor   Numbers   and   Values   of   the   Other
Electron-Donating Scales for a Few Alcohols (Estimated
on the Basis of Relation 3).   1: Data   Calculated   from
Spectrum of $[Cr(H_2O)_6](NO_3)_3$, 2: Data   Calculated   from
Spectrum of $K_3[Cr(NCS)_6] \cdot 4H_2O$.

| Solvent | Dq $[cm^{-1}]$ | | DN | | DN^a | Δ_D | D(II,I) |
	1	2	1	2			
H	1723		17.2		17.2	70.8	2.9
NA	1730	1773	15.8	15.6	15.7	63.3	2.8
IA	1728		16.8		16.8	68.8	2.9
IZ	1724	1775	18.4	18.9	18.6	77.8	3.0
IP	1720	1774	19.6	19.7	19.6	82.8	3.1
BE	1729		15.8		15.8	63.8	2.8
B	1698	1762	22.7	22.4	22.5	97.3	3.4

^{a} proposed value for the solvent

It is interesting that Dq^o as well as Dq^{max} values are
very similar for the complexes investigated.

    The   relation   3   also   gives   a   possibility   to
calculate   unknown   values   of   donor   numbers.   As   an
example,   the   alcohols   were   chosen.   In   this   group   of
solvents DN is known only for ethanol and methanol. In
Table   2,   values   of   donor   numbers   calculated   from
relation 3 for a few alcohols are listed. Additionally,
on the basis of the high correlation of Kagiya Δ_D[8] as
well as Selbin D(II,I)[14] solvent scale with DN value[9]
the values of Δ_D and D(II,I) for alcohols studied were
calculated (Table 2). In the literature, the values of
DN were determined also from Δ_D or D(II,I)[9]. In the

case of alcohols these values (from DCII,I): ethanol –
30.9, methanol 32.5 $^\circ$; true values: 19.0 and 20.0
respectively) are too high. The values calculated in
this paper appear to be more reasonable.

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