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Solvent—Solute Interaction. Solvation of Vanadyl Acetyl-Acetonate in Non-Aqueous Media

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The electronic absorption spectrum of vanadyl acetylacetonate has been studied in 15 organic solvents. It has been found that wavenumbers and molar absorptivities of the long-wavelength bands (d-d transitions) can be well described by a complementary *Lewis* acid—base model including *Gutmann*'s donor number [*Gutmann V.*, *Wychera E.*, Inorg. Nucl. Chem. Letters **2**, 257 (1966)] and acceptor number [*Mayer U.*, *Gutmann V.*, *Gerger W.*, Monatsh. Chem. **106**, 1235 (1975)] of a solvent. This model describes also the solvent effect of the hyperfine splitting constant, A_{iso} (^{51}V), from e.s.r. spectra of VO *acac*$_2$. These observations are discussed in terms of the donor—acceptor concept for solvent—solute interactions.

(Keywords: Correlation analysis; Solvent effect; Vanadyl acetylacetonate)

Lösungsmittel-Substrat-Wechselwirkungen. Solvatation von Vanadyl-Acetylacetonat in nichtwäßrigen Lösungsmitteln

Elektronenabsorptionsspektren von Vanadyl-acetylacetonat wurden in 15 organischen Lösungsmitteln gemessen. Sowohl die Wellenzahlen als auch die molaren Extinktionen der langwelligen Bande (d-d-Übergang) können mit einem Lewis-Säuren-Basen-Modell, das sowohl die *Gutmann*-Donornummern [*Gutmann V.*, *Wychera E.*, Inorg. Nucl. Chem. Letters **2**, 257 (1966)] als auch die Acceptornummern [*Mayer U.*, *Gutmann V.*, *Gerger W.*, Monatsh. Chem. **106**, 1235 (1975)] beinhaltet, beschrieben werden. Dieses Modell beschreibt auch den Lösungsmitteleffekt der Hyperfeinspaltung, A_{iso} (^{51}V), in den e.s.r. Spektren von VO *acac*$_2$. Diese Beobachtungen werden auf Basis eines Donor-Acceptor-Modells für die Lösungsmittel-Substrat-Wechselwirkungen diskutiert.

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Introduction

In two previous communications[1,2] we reported the solvent effects on the spectrophotometric, polarographic and e.s.r. behavior of copper(II) acetylacetonate. These studies indicated that the value of the molar absorptivity for the long-wavelength band (d-d transition) and the value of the hyperfine splitting constant for the Cu nucleus are linearly dependent on the *Lewis* basicity of solvents expressed by corresponding *Gutmann*'s donor numbers[3,4]. As a consequence, we suggested that in sufficiently donating solvents the square molecules of Cu *acac*$_2$ are transformed into square pyramidal molecules of Cu *acac*$_2$ · *solv*. We have now extended this study to include the pyramidal complex VO *acac*$_2$.

Solvent effects on the optical[5–13], e.s.r.[13–15] and n.m.r.[16,17] spectra of vanadyl acetylacetonate have been observed by many workers. It was convincingly demonstrated that all these spectra are strongly solvent-dependent and experimental results have been interpreted in terms of the solvation of the vanadyl oxygen atom. On other hand, *Gutmann* and *Mayer*[18] postulated that strong neutral and anionic *Lewis* bases can coordinate to the vanadium atom. In our opinion, however, the problem is more complicated. The reasons for this assumption are presented in this communication.

Materials and Methods

VO *acac*$_2$ was prepared and purified by a well known method[19]. All solvents were dried and purified by established procedures[20] immediately before use. Optical spectra were recorded at 25 °C on a Specord (Jena) or on a Varian-635 spectrophotometer.

Results and Discussion

The purpose of this work is to formulate an empirical but quantitative description of the solvent effect on the optical spectrum of VO *acac*$_2$. A series of organic solvents differing markedly in their polarities and *Lewis* acid—base properties was chosen. In general, three low intensity absorption bands were observed in the spectral region 12 000-30 000 cm^{-1} but the short-wavelength band was often registered as a shoulder so that its maximum position is known with the least accuracy among the three bands. Taking this into account we will discuss the solvent effects on the properties of the bands in the visible region only.

Table 1 lists the optical data for two long-wavelength bands of VO *acac*$_2$ and some solvent parameters. In the last column of this table,

Table 1. *Optical and e.s.r. data for vanadyl acetylacetonate and solvent characteristics*

					Optical spectrum				
No.	Solvent	D[a]	DN[b]	AN[c]	ν_1/cm^{-1}	ε_1[d]	ν_2/cm^{-1}	ε_2[d]	$A_{\mathrm{iso}}(^{51}\mathrm{V})$[e]
1	Benzene	2.3	0.1	8.2	16360	60	14640	56	106.55
2	Nitromethane	35.8	2.7	20.5	16200	41	14080	51	
3	Nitrobenzene	34.8	4.4	14.8	17000	38	14940	40.7	105.75
4	Benzonitrile	25.2	11.9	15.5	16600	47	14280	51.5	
5	Acetonitrile	37.5	14.1	18.9	16520	64	13840	81	104.6
6	1,4-Dioxane	2.2	14.8	10.8	16800	56	14100	67	105.2
7	Propylene carbonate	64.4	15.1	18.3	16560	38.5	14000	47.5	103.8
8	Acetone	20.7	17.0	12.5	16640	49	13860	62	105.7
9	Water	78.3	18.0	54.8					101.2
10	Methanol	32.6	19	41.3	17420	20	12900	42	102.35
11	Ethanol	24.6	20	37.1	17120	13.3	12740	28	102.7
12	Tetrahydrofuran	7.4	20.0	8.0	16800	54	13470	68	105.5
13	N,N-Dimethylformamide	36.7	26.6	16.0	17000	37	12960	61	104.4
14	N,N-Dimethylacetamide	37.8	27.8	13.6	16620	25	12720	49.8	
15	Dimethylsulfoxide	46.7	29.8	19.3	16250	22.8	12400	49.5	104.25
16	Pyridine	13.2	33.1	14.2	16840	25	12640	41	104.25
17	Hexamethylphosphoramide	30	38.8	10.6					104.1

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[a] Dielectric permittivity at 25 °C.

[b] *Gutmann*'s donor number taken from Ref.[4].

[c] AN = acceptor number (Ref.[24]).

[d] Molar absorptivity in $\mathrm{l\,mol^{-1}\,cm^{-1}}$.

[e] Hyperfine splitting constant taken from Ref.[13]. $A_{\mathrm{iso}}(^{51}\mathrm{V})$ values are given in Gauss; $1\,\mathrm{G} = 10^{-4}\,\mathrm{T}$.

there are also presented $A_{\rm iso}$ (^{51}V) values from e.s.r. spectra reported by *Guzy* et al.[13]. As can be seen, the positions of the absorption maxima and the molar absorptivities are strongly influenced by different solvents.

Since the molecule of VO *acac*$_2$ has a C_{2v} symmetry, which predicts complete removal of d-orbital degeneracy, four d-d transitions are possible, although not all are allowed by formal symmetry rules. Therefore it is possible to assign two bands observed between 12000 and 18000 cm^{-1} to the d-d origin[21–23]. As a consequence, we have analysed the solvent effect on the difference ($\nu_1 - \nu_2$) and on the ratio $\varepsilon_1/\varepsilon_2$. The first totally empirical parameter was proposed by *Selbin*[8] as a measure of VO *acac*$_2$—solvent interaction. We assume that the ratio $\varepsilon_1/\varepsilon_2$ is also sensitive for ranking solvents.

First of all, ($\nu_1 - \nu_2$) and $\varepsilon_1/\varepsilon_2$ values were the subject of linear regression analysis. We have started with correlations of these values against *DN* and *AN*, respectively. Treating the problem with the least-squares method we have obtained expressions of the following form:

$$(\nu_1 - \nu_2) = 81\,DN + 1\,740 \tag{1}$$

with a correlation coefficient of $r = 0.850$;

$$(\nu_1 - \nu_2) = 55.9\,AN + 2\,124,\ r = 0.565; \tag{2}$$

$$\varepsilon_1/\varepsilon_2 = -0.0156\,DN + 0.991,\ r = 0.802; \tag{3}$$

$$\varepsilon_1/\varepsilon_2 = -0.0123\,AN + 0.945,\ r = 0.609. \tag{4}$$

It is clear that neither donor numbers nor acceptor numbers can be directly used to interpret VO *acac*$_2$—solvent interaction. Similarly, the plots of ($\nu_1 - \nu_2$) and $\varepsilon_1/\varepsilon_2$ versus the dielectric permittivity showed no correlations.

It has been suggested many times in the literature (for review see Refs.[25–26]) that solvent-dependent physicochemical properties can be analysed in terms of regression analysis using various complementary solvent parameters. *Koppel* and *Palm*[27] have summarized this concept and have introduced a four-parameter equation which includes apart from *Lewis* acidity and basicity parameters, contributions due also to nonspecific interactions using functions of dielectric permittivity and refraction index. Another semiempirical multiparametric equation for calculating the solvent dependence of chemical reactions using the donor numbers and the acceptor numbers was published more recently by *Mayer*[28]. It was found, however, that in many cases already a two-parameter regresssion analysis[29,30] including only *Lewis* acidity and basicity parameters fits the solvent-dependent experimental data quite

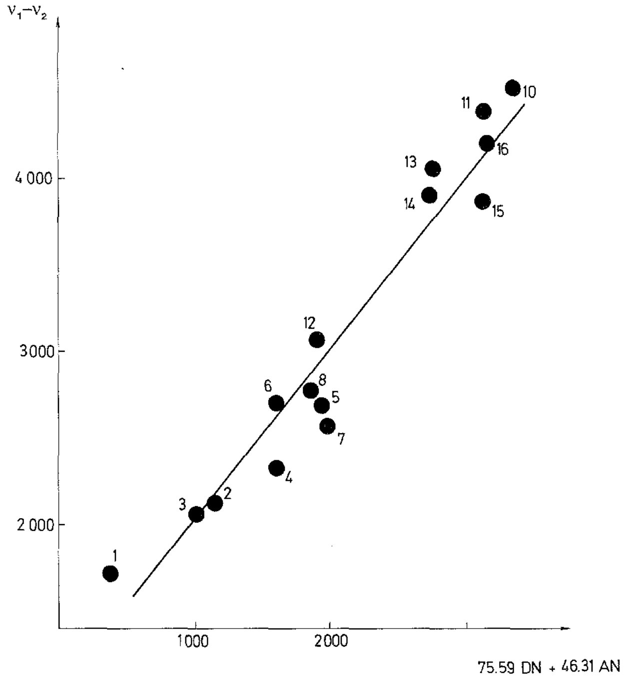

Fig. 1. Two-parameter correlation between ($\nu_1 - \nu_2$) values for the optical spectrum of vanadyl acetylacetonate and *Gutmann*'s donor and acceptor numbers for 15 solvents according to eqn. (6) (for solvent numbers cf. Table 1)

well, and an addition of other solvent parameters is not statistically significant. Therefore in our regression analysis we have used a two-parameter approach (cf. also Refs.[29,30]) in the following form:

$$Q = \alpha DN + \beta DN + \gamma \qquad (5)$$

where Q is solvent-dependent physicochemical property, whereas α and β describe the sensitivity of Q to change of solvent basicity and acidity, respectively. The correlation equations are then as follows (errors are standard deviations):

$$(\nu_1 - \nu_2) = (75.59 \pm 7.18)\,DN + (46.31 \pm 7.45)\,AN + (1\,003 \pm 183) \qquad (6)$$

with a correlation coefficient of $r = 0.969$ and with the *Fisher-Snedecor* test[31] of $F = 56.0$ (Fig. 1), and

$$\varepsilon_1/\varepsilon_2 = (-0.014 \pm 0.002)\,DN - (0.010 \pm 0.002)\,AN + (1.16 \pm 0.05) \qquad (7)$$

with $r = 0.953$ and $F = 36.1$ (Fig. 2).

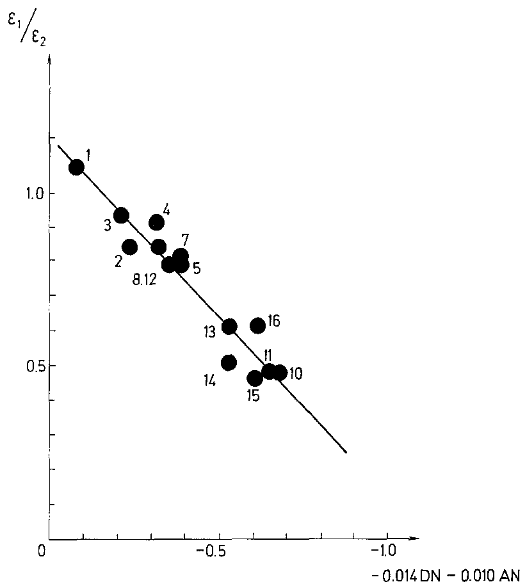

Fig. 2. Dependence of $\varepsilon_1/\varepsilon_2$ values on *DN* and *AN* for 15 solvents according to eqn. (7) (for solvent numbers cf. Table **1**)

Comparison of the correlation coefficients for eqns. (6) and (7) with the r values for corresponding linear relationships shows a very significant improvement in accuracy of the planar regressions. The percentage of the explanation of variance for variation of $(\nu_1 - \nu_2)$ and $\varepsilon_1/\varepsilon_2$ is now 93.9% and 90.8%, respectively. Assuming that experimental errors in the determination of $(\nu_1 - \nu_2)$ and $\varepsilon_1/\varepsilon_2$ as well as of solvent parameters are in the order of 10%, we consider that the correlations expressed by eqns. (6) and (7) satisfy fully our data. Thus, the solvent effect on the $(\nu_1 - \nu_2)$ and $\varepsilon_1/\varepsilon_2$ values of VO *acac*$_2$ depends both on the *Lewis* acidic and basic properties of a solvent.

Taking into account this finding we have reanalysed the solvent effect on the e.s.r. A_{iso} (^{51}V) values reported in Ref.[13] (cf. Table 1). For the set of 14 solvents for which *AN* values are known, we have obtained linear correlation in the form of eqn. (8):

$$A_{\text{iso}}(^{51}\text{V}) = (-0.0948 \pm 0.0131) AN + (106.24 \pm 0.31) \qquad (8)$$

with $r = 0.909$ and $F = 26.2$. It should be mentioned that this equation reflects the solvation of the vanadyl oxygen atom, as it was suggested by *Guzy* et al.[13].

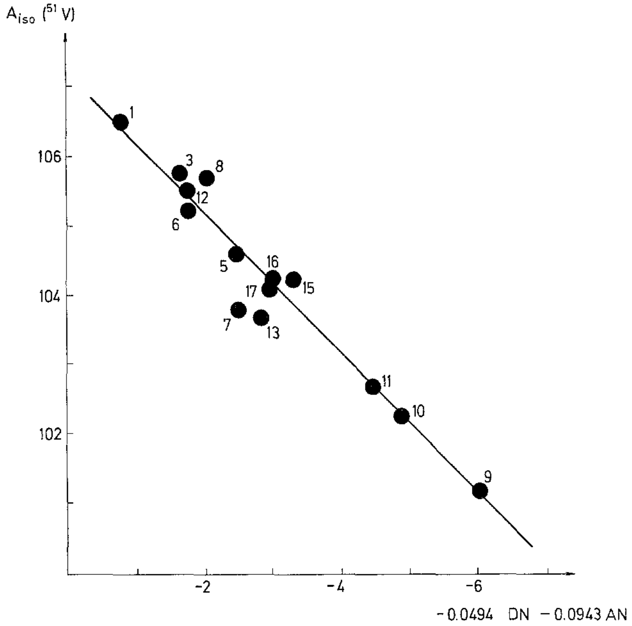

Fig. 3. Plot of the hyperfine splitting constant, A_{iso} (^{51}V), from e.s.r. spectra of vanadyl acetylacetonate versus DN and AN for 14 solvents according to eqn. (9) (for solvent numbers cf. Table 1)

Using the two-parameter model for the same set of solvents one obtaines eqn. (9).

$$A_{\text{iso}}(^{51}\text{V}) = (-0.0495 \pm 0.0099)DN + (0.0944 \pm 0.0073)AN + \\ + (107.18 \pm 0.25) \qquad (9)$$

with $r = 0.974$ and $F = 62.5$. The dependence of $A_{\text{iso}}(^{51}\text{V})$ on DN and AN according to eqn. (9) is graphically presented in Fig. 3.

Thus, the percentage of the explanation of variance for variation of $A_{\text{iso}}(^{51}\text{V})$ is 82.7% when the analysis is performed according to eqn. (8) but it increases up to 95% for the planar regression described by eqn. (9). Moreover, the statistical treatment with the *Fisher-Snedecor* F-value in a way proposed in Ref.[32] indicates strongly that addition of the basicity parameter to eqn. (8) is significant at least at the 0.01 level.

It is then clear that the solvent effects on the optical and e.s.r. spectra of vanadyl acetylacetonate should be interpreted in terms of a two-parameter approach in the general form of eqn. (5). From the formal point of view, two possible explanations exist: i) two solvent molecules are interacting with VO *acac*$_2$ (the first molecule interacts with the vanadyl oxygen, whereas the second one solvates the vanadium atom), and ii) the "secondary" solvent effect, caused by the orientation of solvent molecules in the second coordination sphere, is important. It is premature to discuss quantitatively these problems because this subject is still under investigation. However, independently of possible interpretations, the properties of VO *acac*$_2$ are indeed dependent *both* on the *Lewis* acidity and basicity of a solvent. This is to say that many data in literature should be reinterpreted in terms of the donor—acceptor concept[4] including the donor numbers *and* the acceptor numbers. Let us add, finally, that some indications of the facts described in this work are also manifested in non-aqueous electrochemistry of VO *acac*$_2$. Corresponding results will be discussed in a further communication.

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