The Effects of Solute-Solvent Interactions on the Electronic Visible Spectra of Bis(β-diketonato)oxovanadium(IV) Complexes

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Summary. The solvatochromic behaviour of bis(β-diketonato)oxovanadium(IV) complexes is quantitatively correlated by an approach that models specific and non-specific solute-solvent interactions. The applicability of the Selbin-Gutmann relation is discussed. The solvent-induced spectral shifts in VO($acac$)$_2$ are dominated by specific interactions of the donor-acceptor type, whereas for VO(tfa)$_2$, the nonspecific solute-solvent interactions make the dominant contribution.

Keywords. Solvent effects; Electronic spectra; Oxovanadium(IV) β-diketonates.

Der Einfluß von Wechselwirkungen zwischen Lösungsmittel und gelöstem Stoff auf die VIS-Spektren von Bis(β-diketonato)oxovanadium(IV)-Komplexen

Zusammenfassung. Das solvatochrome Verhalten von Bis(β-diketonato)oxovanadium(IV)-Komplexen wird mit einem Modell, das spezifische und nichtspezifische Wechselwirkungen in Lösung berücksichtigt, quantitativ beschrieben. Es wird die Anwendbarkeit der Selbin-Gutmann-Relation diskutiert. Die Solvens-induzierten Verschiebungen in den VIS-Spektren von VO($acac$)$_2$ werden von den spezifischen Wechselwirkungen vom Donor-Acceptor-Typ bestimmt, währenddessen für VO(tfa)$_2$ die nichtspezifischen Wechselwirkungen zwischen Substrat und Lösungsmittel den dominierenden Beitrag liefern.

Introduction

The solvent dependence of the electronic visible spectra of bis(β-diketonato)-oxovanadium(IV) complexes has been the subject of several investigations [1–8]. Attempts [5–8] to account for the observed solvent induced spectral shifts in these systems are usually based on the Selbin-Gutmann (S-G) relation [1, 9] which correlates the energy difference $\Delta v_{1,2}$ (in units of kK = $1\,000\,\mathrm{cm}^{-1}$) of the first two visible bands with the Donor Number (DN) of the solvent as

$$DN = A + B\Delta v_{1,2}. \tag{1}$$

Satisfactory linear correlation has been reported for bis(acetylacetonato)-oxovanadium(IV) [VO($acac$)$_2$] [5, 9] but no linear correlation was found for bis(trifluoroacetylacetonato)oxovanadium(IV) [VO(tfa)$_2$] [6]. The S-G relation

has been employed with different levels of success for VO(*acac-X*)$_2$ (*X* = Cl, Br) [7], VO(*bza*)$_2$ (*bza* = benzoylacetone) [5, 8] and bis(*p*-substituted benzoyl-1,1,1-trifluoroacetonato)oxovanadium(IV) complexes [8].

In the S-G relation, only specific solute-solvent interactions of the donor-acceptor type are included. The neglect of nonspecific solute-solvent interactions is probably responsible for the limited applicability of the S-G relation. The main thrust of the present work was to investigate the effects of specific and nonspecific solute-solvent interactions on the electronic visible spectra of bis(*β*-diketonato)oxovanadium(IV) complexes with a view to examine the applicability of the S-G relation.

Experimental

Acetylacetone (*acac*H) and 1,1,1-trifluoroacetylacetone (*tfa*H) were purchased from Fluka AG Chemische Fabrik (Switzerland) and were used without further purifications. VO(*acac*)$_2$ and VO(*tfa*)$_2$ were prepared by the method of Rowe and Jones [10]. The purity of these well-known complexes was checked by spectroscopic techniques and elemental analyses.

Electronic visible spectra of 0.01 *M* solutions of the complexes in solvents of spectro-quality grade were determined in a 1 cm cell using a Pye Unicam SP8-400 uv-visible spectrophotometer.

Theoretical Methods

In general the solvatochromism of the electronic spectra of molecules are caused by a variety of specific and nonspecific solute-solvent interactions [11]. The latter (largely due to electrostatic interactions) may include contributions from dispersion, dipole-dipole, and dipole-induced dipole interactions. Specific interactions may include contributions from hydrogen bonding, charge transfer, complex formation, etc.

In absence of specific interactions, the frequency shift Δv resulting from a change of medium from vapour to a solution in a given solvent may be represented quantum mechanically by a second order perturbation theory as [12, 13]

$$\Delta v = \text{dispersion term} + \frac{\mu_g^2 - \mu_e^2}{hca^3} \text{f}(n) + \frac{2\mu_g(\mu_g - \mu_e)}{hca^3} \text{f}(D,n)$$

$$+ \frac{6\mu_g^2(\alpha_g - \alpha_e)}{hca^6} \text{f}(D,n)^2, \tag{2}$$

where μ and α are respectively the dipole moment and the polarizability of the solute molecule. The subscripts g and e stand for ground and excited states, respectively; h, c, and a are the Planck's constant, speed of light and Onsager's cavity radius, respectively. f(n) and f(D, n) are functions of the solvent refractive index, n, and the static dielectric constant, D, given by

$$\text{f}(n) = \frac{n^2 - 1}{2n^2 + 1}, \qquad \text{f}(D,n) = \frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2}.$$

An empirical model based on Eq. (2) is represented as

$$v_i^s = v_i^0 + a\,\text{f}(n) + b\,\text{f}(D,n) + c\,\text{f}(D,n)^2, \tag{3}$$

where v_i^s is the frequency of the ith electronic spectral band in a given solvent, s, and a, b, and c are regression coefficients which are related to the constants in Eq. (2).

Remarkable changes in the electronic visible spectra are observed when bis(β-diketonato)oxovanadium(IV) complexes are dissolved in solvents of high donor ability which suggest the presence of specific solute-solvent interaction through axial ligation. This may be accounted for empirically by incorporating an additional term (DN) representing the donor ability of the solvent as

$$v_i^s = v_i^0 + a\,f(n) + b\,f(D,n) + c\,f(D,n)^2 + d\,DN. \qquad (4)$$

There are certain problems associated with the solution of these multi-parameter equations by multiple regression methods. Firstly, it is assumed that all independent variables are exactly known. Secondly, multiple regression methods require almost orthogonal independent variables and finally, the results depend heavily upon the number and spread of points in the data set. To this end, we have re-examined the electronic visible spectra of VO($acac$)$_2$ and VO(tfa)$_2$ in a variety of solvents to determine the band maxima to within $\pm 25\,\text{cm}^{-1}$. Much of the earlier data [1, 2] are less accurately reported.

Results and Discussion

The visible spectra of VO($acac$)$_2$ in non-donor solvent exhibit three distinct bands (labelled v_1, v_2, and v_3) at 15.44, 16.88, and 25.81 kK, respectively. In accord with the Balhausen and Gray MO scheme [14], these bands are assignable [5, 7] to $e_\pi(d_{xz}, d_{yz}) \leftarrow b_2(d_{xy})$, $b_1(d_{x^2-y^2}) \leftarrow b_2$, and $a_1(d_{z^2}) \leftarrow b_2$ transitions, respectively. The band maxima v_i (in units of kK) of VO($acac$)$_2$ and VO(tfa)$_2$ in nine solvents of widely varying polarity and donor ability are listed in Table 1. Values of various solvent parameters are given in Table 2.

The solvent induced spectral shifts in VO($acac$)$_2$ and VO(tfa)$_2$ are quantitatively correlated by an approach that models the various types of nonspecific and specific solute-solvent interactions in these systems. Toward this end, we carried out a large number of multi-parameter correlations using Eq. (4) and its variants. However,

Table 1. Visible spectral data of VO($acac$)$_2$ and VO(tfa)$_2$

Solvent	VO($acac$)$_2$				VO(tfa)$_2$			
	v_1	v_2	v_3	$\Delta v_{1,2}$	v_1	v_2	v_3	$\Delta v_{1,2}$
CCl$_4$	15.337	16.891	25.510	1.554	15.337	16.949	24.271	1.612
Benzene	15.151	16.778	25.510	1.627	15.527	16.891	23.584	1.364
Chloroform	14.750	16.666	25.510	1.916	13.477	16.501	23.148	3.024
Acetonitrile	14.245	16.778	25.380	2.533	13.586	16.722	23.584	3.136
Acetone	14.285	16.778	25.510	2.493	13.477	16.233	23.148	2.756
DMF	12.987	16.891	25.000	3.904	13.123	16.339	22.935	3.216
DMSO	12.820	16.806	24.752	3.986	12.953	15.974	22.522	3.021
Ethanol	12.820	17.123	25.510	4.303	13.157	16.447	23.148	3.290
Methanol	12.886	17.182	25.252	4.296	13.333	16.447	23.255	3.114

Table 2. Values of various solvent parameters

Solvent	n	D	DN[a]	f(n)	f(D, n)
CCl$_4$	1.4601	2.238	0.0	0.2150	0.0182
Benzene	1.5011	2.284	3.4[b]	0.2276	0.00276
Chloroform	1.4459	4.806	10.9[b]	0.2105	0.2926
Acetonitrile	1.3442	37.5	14.1	0.1749	0.7121
Acetone	1.3588	20.7	17.0	0.1804	0.6466
DMF	1.4305	36.71	26.6	0.2055	0.6639
DMSO	1.4770	46.68	29.8	0.2203	0.6558
Ethanol	1.3611	24.33	30.4[b]	0.1812	0.6648
Methanol	1.3288	32.6	33.7[b]	0.1690	0.7100

[a] Donor numbers (DN) are taken from Ref. [15]
[b] Estimated values taken from Refs. [5] and [7]

detailed discussion is limited to statistically significant correlations that have coefficients of multiple regression (R values) of greater than 0.94 with statistically significant F values (F-test). Few cases of less satisfactory correlations are included for comparison purposes.

The results of multi-parameter correlation of the solvent effects on the visible spectra of VO($acac$)$_2$ and VO(tfa)$_2$ using Eqs. (3) and (4) are presented in Tables 3 and 4, respectively. Some interesting features are discussed below.

The use of Eq. (4) to model solute-solvent interactions in these systems provides a satisfactory correlation of the solvent dependence of the spectral parameters in VO($acac$)$_2$ and VO(tfa)$_2$. However, in both complexes, statistical tests of significance (F-test and R values; see Table 4) clearly show that the solvent dependence of the first band (v_1) is more satisfactorily correlated ($R \sim 0.99$). This may reflect the relatively more pronounced solvent dependence of this band in comparison with the second (v_2) and third (v_3) bands in the visible spectra of bis(β-diketonato)-oxovanadium(IV) complexes [5].

Although the calculated regression coefficients are, in principle, related to the constants in Eq. (2), they are numerically non-equivalent due to the presence of the specific interaction term and the approximate nature of the model. Nevertheless, the calculated coefficients may provide an understanding of the solvatochromic behaviour in these systems. Estimates of the contributions to the observed solvent induced spectral shifts arising from specific and nonspecific solute-solvent interactions may be calculated using Eq. (4) and the regression coefficients in Table 4. For v_1 in VO($acac$)$_2$, the regression coefficient of the DN term of $- 0.081$ makes this term dominant. It is of interest to note that the DN term is shown by the t-test to be statistically highly significant with a standard error of 0.0104 and a 95% confidence interval (CI) of ± 0.028. Furthermore, stepwise multiple regression analysis of the v_1 parameter in VO($acac$)$_2$ gave the following final solution,

$$v_1 = 15.46 - 0.0837\,DN,$$

$$R = 0.97, \quad SD = 0.198, \quad F = 216.93.$$

Table 3. The results of multi-Parameter regression analyses according to Eq. (3); degrees of freedom = 5; F values at the α-level of significance $F(\alpha)$: $F(0.05) = 5.41$, $F(0.01) = 12.06$, $F(0.001) = 33.2$

Complex	v_i^0	a	b	c	R	F	SD
VO(*acac*)$_2$							
v_1	19.706	− 20.068	− 1.579	− 3.314	0.767	5.49	0.640
v_2	17.556	− 3.227	− 1.154	1.654	0.405	1.13	0.167
v_3	28.786	− 14.828	0.173	− 1.922	0.859	10.17	0.131
$\Delta v_{1,2}$	− 2.149	16.841	0.426	4.968	0.699	3.876	0.805
VO(*tfa*)$_2$							
v_1	17.104	− 7.105	− 9.864	9.119	0.984	102.08	0.154
v_2	18.934	− 8.290	− 2.765	2.151	0.827	7.97	0.164
v_3	27.757	− 17.121	− 4.459	3.466	0.859	10.17	0.232
$\Delta v_{1,2}$	1.831	− 1.815	7.099	− 6.967	0.940	25.92	0.224

Table 4. The results of multi-parameter regression analyses according to Eq. (4); degrees of freedom = 4; F values at the α-level of significance $F(\alpha)$: $F(0.05) = 6.39$, $F(0.01) = 15.98$, $F(0.001) = 53.4$

Complex	v_i^0	a	b	c	d	R	F	SD
VO(*acac*)$_2$								
v_1	17.297	− 8.687	1.185	− 2.355	− 0.081	0.986	69.19	0.176
v_2	18.164	− 6.096	− 1.851	1.413	0.020	0.931	13.40	0.064
v_3	28.628	− 14.084	0.354	− 1.859	− 0.005	0.872	6.85	0.140
$\Delta v_{1,2}$	0.866	2.590	− 3.036	3.767	0.101	0.980	47.87	0.235
VO(*tfa*)$_2$								
v_1	16.600	− 4.726	− 9.285	9.319	− 0.017	0.995	212.29	0.093
v_2	18.696	− 7.793	− 2.491	2.246	− 0.008	0.851	5.72	0.171
v_3	27.237	− 14.663	− 3.862	3.673	− 0.017	0.906	9.65	0.212
$\Delta v_{1,2}$	2.096	− 3.068	6.794	− 7.073	− 0.009	0.945	17.24	0.238

The DN term has a standard error of 0.0057 and a 95% CI of ± 0.013. Thus, the solvent induced spectral shifts in VO(*acac*)$_2$ are dominated by specific interactions of the donor-acceptor type. It is of interest to note that the $\Delta v_{1,2}$ parameter in VO(*acac*)$_2$ experiences an even heavier dependence on the DN term as a consequence of the cancellation of the nonspecific terms in the regression equations for v_1 and v_2 (see Table 4). These observations provide a rationalization of the well-documented [5, 9] success of the Selbin-Gutmann relation in VO(*acac*)$_2$. The use of the S-G relation [Eq. (1)] in conjunction with the data of Table 1 for VO(*acac*)$_2$ gave a satisfactory linear correlation as

$$DN = - 12.37 + 10.42 \Delta v_{1,2},$$

$$R = 0.96, \qquad SD = 2.62, \qquad F = 170.59.$$

On the other hand, the solvatochromic behaviour of VO(tfa)$_2$ differs significantly. Inspection of the regression coefficients for v_1 in VO(tfa)$_2$ reveals that the solvent induced spectral shifts are dominated by nonspecific solute-solvent interactions consistent with the failure of the S-G relation in VO(tfa)$_2$ [6]. It should be noted, that the use of the S-G relation with the data of Table 1 for VO(tfa)$_2$ gave no satisfactory correlation ($R = 0.8$). These conclusions are consistent with the results of multiple regression calculations using Eq. (3) (see Table 3) where only nonspecific solute-solvent interactions are retained. The use of Eq. (3) for VO($acac$)$_2$ did not provide satisfactory correlation for all the spectral parameters, whereas for VO(tfa)$_2$, the v_1 and $\Delta v_{1,2}$ parameters are satisfactorily correlated.

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