Nuclear Quadrupole Perturbations in ^{51}V NMR Spectra of Oxovanadium(+V) Complexes

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Nuclear electric quadrupole coupling constants e^2qQ/h have been obtained by evaluation of quadrupole perturbations in ^{51}V NMR spectra of various vanadyl esters and esterchlorides of the general formula $VOCl_{3-n}(OR)_n$ ($n = 0-3$; R = Me, Pr^n, Pr^i, Bu^n and Bu^i). e^2qQ/h values have been calculated from (i) 2nd. order quadrupole splittings of the ^{51}V NMR signals in pseudo-polycrastalline samples, (ii) 1st. order quadrupole splittings in nematic liquid crystals and (iii) line widths $\Delta\nu_{1/2}$ of the ^{51}V and ^{35}Cl NMR signals in the liquid isotropic state and e^2qQ/h(^{35}Cl) obtained by pure NQR measurements. The influences of the asymmetry parameter η and the orientation of the crystallites in powder spectra are considered, and temperature and concentration effects upon $\Delta\nu_{1/2}$ and ^{51}V shielding (isotropic phases) and the ordering factor S_a (mesophases) are discussed.

Introduction

The ^{51}V nucleus is one of the most suitable transition metal nuclei to carry out NMR experiments (surveyed in [1] to [4]), which is mainly due to its small electric nuclear quadrupole moment eQ and its high sensitivity. Because of the small eQ, line widths $\Delta\nu_{1/2}$ in isotropic media — where quadrupole interactions are restricted to a broadening of the NMR signals — are, in general, small even for complexes of low point symmetry. Under anisotropic conditions quadrupolar nuclei give rise to quadrupole splittings of the NMR signals. The overall situation may be described by the Hamiltonian [5]

$$\hat{H} = -\hbar B_0 \hat{I}_z + \frac{e^2qQ}{4I(2I-1)} \cdot [3\hat{I}_z^2 - I(I+1) + \frac{1}{2}\eta(\hat{I}_+^2 + I_-^2)], \qquad (1\text{a})$$

where the first term is the Zeeman operator and the second term refers to the quadrupole interaction. eq is the electric field gradient (in zz direction), and η is the asymmetry parameter. A perturbation calculation yields the energy eigen values corresponding to $\hat{H}$:

$$E_\mathrm{m} = -\gamma\hbar B_0 m + E_m^{(1)} + E_m^{(2)} + \cdots, \qquad (1\text{b})$$

where $E_m^{(1)}$, $E_m^{(2)}$ etc. are the contributions arising from 1st, 2nd etc. quadrupole interaction. Figure 1 is a graphical presentation for the Zeeman splitting and 1st. order interaction in a single crystal.

In three previous papers [6–8], we have shown that the interaction between eq and eQ, quantified by the quadrupole coupling constant e^2qQ/h, may be correlated to quantities describing the bonding situation in vanadium compounds. Therefore e^2qQ/h proves to be as valuable a parameter as the more "classical" quantities nuclear shielding and nuclear-spin spin coupling. Here, we shall describe the determination of e^2qQ/h for the vanadium nucleus on the bais of evaluations of ^{51}V NMR

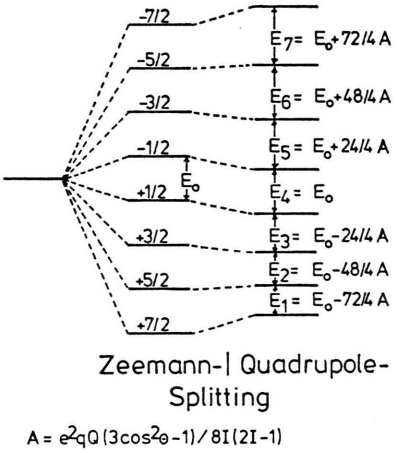

Fig. 1. Zeeman and 1st. order quadrupole splitting for a 7/2 nucleus ($eQ > 0$). θ is the angle between the principal axis of the crystal and the field direction.

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spectra. Due to the low transition frequencies for this nucleus (around 10^{-1} MHz [9]), quadrupole coupling constants cannot be obtained directly, i.e. from pure NQR measurements.

Results and Discussion

1) *Anisotropic Systems: The Pseudo-polycrystalline State*

At room temperature and down to ca. 200 K, vanadyl esters and esterchlorides are colourless to yellow, highly fluid liquids which easily mix with polar and non-polar, dry solvents. Frozen, neat samples show ^{51}V NMR spectra which exhibit a satellite system (Fig. 2a) and a split (Fig. 3a) or asymmetric (Fig. 4a) central line, produced by 2nd. order quadrupole perturbations in (to a first approximation) a powder pattern.

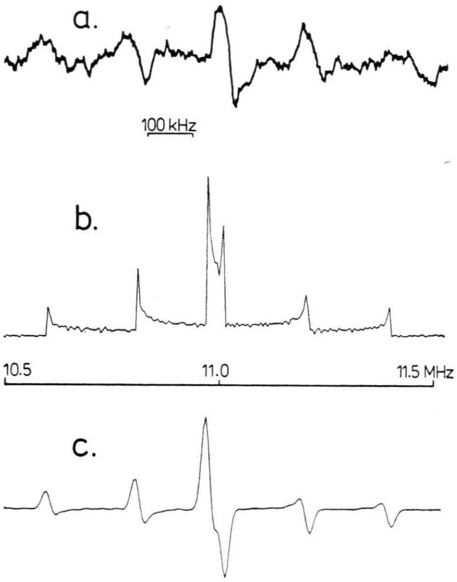

Fig. 2. NMR powder spectrum of $VOCl_3$ at ca. 100 K: a) observed; b) line shape function; c) calculated for $e^2qQ/h = 5.4$ MHz, $\eta = 0.05$ and $\Delta\nu_{1/2} = 10$ kHz.

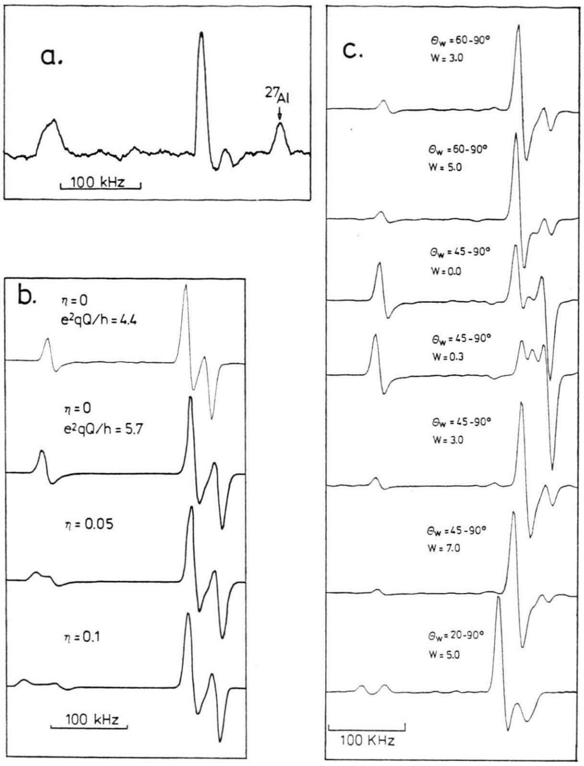

Fig. 3. Expanded section of Fig. 2, showing the central line and the first satellite at reduced modulation amplitude: a) observed; b) calculated ($\Delta\nu_{1/2} = 4$ kHz) for statistical distribution of crystallites; c) weighted orientations (W = weighting factor, θ_W = weighted angle), $e^2qQ/h = 5.7$ and $\eta = 0$. θ describes the orientation of the crystallites relative to B_0. Crystallites with $\theta > \theta_W$ have preferential orientations and therefore contribute to the line shape function to a greater extent, which is considered by a factor W.

The idealized line shape of the NMR signal is described by a function $P_L(\nu)$ as shown in Figure 2b. A realistic line shape (Fig. 2c) is obtained by taking into account relaxation broadening, i.e. by convoluting $P_L(\nu)$ with a Gaussian function $G(\nu)$ [10]. The satellites may be broadened to an extent where the signal-to-noise ratio does no longer allow for their distinction. One is then limited to an analysis of the central line, the line shape function of which is illustrated in Figure 4b. The function exhibits two singularities with a spacing ($\eta = 0$) [11]

$$\Delta p = \frac{25}{9} A, \quad \text{where} \tag{2}$$

$$A = \frac{I(I+1) - 3/4}{16\,\nu_0} \left[\frac{3\,e^2qQ}{2I(2I-1)h} \right]^2 .$$

Provided the half widths of the signals are sufficiently small, e^2qQ/h can be determined from the observed splitting or asymmetry. If $\eta \neq 0$, Δp becomes

$$\Delta p = \frac{25}{9} A \left[1 + \left(\frac{74\,\eta}{135} + \frac{\eta^2}{45} \right) \right]. \tag{3}$$

Although it is possible to estimate e^2qQ/h *and* η from a line shape analysis [12], more exact values

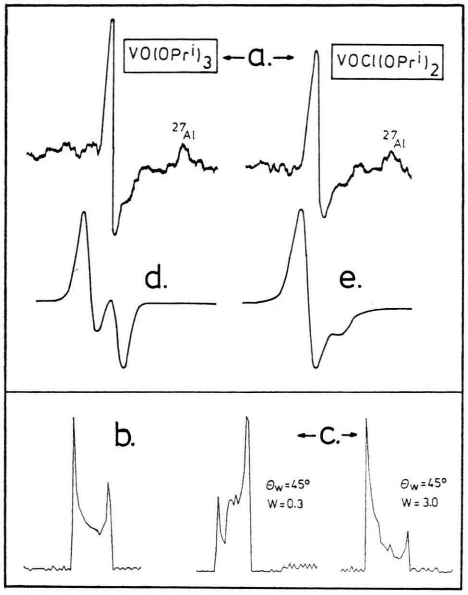

Fig. 4. NMR powder spectra of VO(OPr^i)$_3$ and VOCl(OPr^i)$_2$ at ca. 100 K, showing the central line: a) observed; b) line shape function (2nd. order quadrupole perturbation), statistical distribution of crystallites; c) line shape function ($\eta = 0$), weighted orientations; d) calculated for $e^2qQ/h =$ 5.5 MHz and varied η, statistical distribution of crystallites; e) calculated, weighted orientations.

are obtained if satellites can be included in the evaluation [13]. The distance between two satellites is

$$\Delta\nu_S = \frac{3\,e^2qQ}{4\,I(2I-1)h}\,(1-\eta)\,. \tag{4}$$

Calculations in this paper were — if possible — carried out on the basis of (3) and (4).

Fig. 3b illustrates the influence of variations in e^2qQ/h and η upon the pattern of the spectrum. Figures 3b and 4d show spectra computed with the calculated quadrupole coupling constants and assuming statistically equally distributed orientations of the crystallites. A better agreement for the intensity ratio of the two components of the central line is obtained if partial orientation of the crystallites is taken into account. The influence of weighted orientations is demonstrated in Figs. 3c and 4c. Satisfying correlations between experimental and computed spectra are represented by Figs. 3a/3c (top spectrum), and Figures 4a/4e. The calculated coupling constants are 5.7 (0.2) (VOCl$_3$), 5.1 (0.2) (VOCl(OPr^i)$_2$) and 4.4 (0.2) (VO(OPr^i)$_3$); the asymmetry parameter is < 0.1.

2) *Partially Anisotropic Systems: Liquid Crystal Matrices*

Figure 5 shows a representative spectrum for a nematic system. The pattern originates from first order quadrupole splitting of the ^{51}V NMR signal, and is comparable to first order interaction in polycrystalline powders. Since the mobility of the solute molecules in the liquid crystal lattice is only partially reduced, the splitting, $\Delta\nu_{LC}$, is by several orders of magnitude smaller than in solids. The partially anisotropic nature of the system is taken into consideration by the introduction of an ordering parameter S_a (S_a is not identical with the order parameter of the neat liquid crystal). The first order contribution to the energy eigen value, $E_m^{(1)}$ (compare (1b)), is given by

$$E_m^{(1)} = \frac{3}{4}\,\frac{e^2qQ\,(3\,m^2 - I(I+1))}{I(2I-1)h} \cdot S_a(3\cos^2\theta - 1)\,, \tag{5}$$

where θ is the angle between the director in the liquid crystal and the field B_0. For random angles θ, $(3\cos^2\theta - 1)$ is averaged to 1, and [14]

$$\Delta\nu_{LC} = \frac{3}{4}\,\frac{e^2qQ}{I(2I-1)h}\,S_a \tag{6}$$

for $\eta = 0$, i.e. axial symmetry.

$S_a = 1/2\langle 3\cos^2\varphi - 1\rangle$ (with φ the angle between the director and the molecular axis of the solute molecule) is a measure for the degree of anisotropy in the nematic system, which varies with

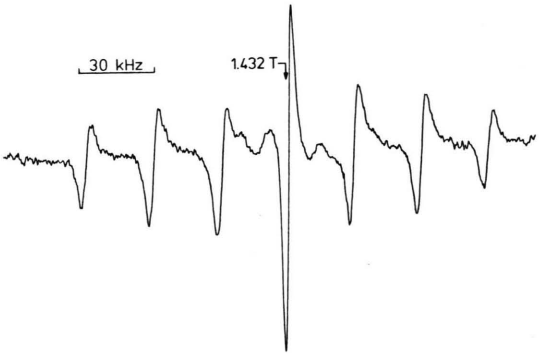

Fig. 5. 16.0001 MHz ^{51}V NMR spectrum of VO(OBu^n)$_3$ in nematic phase 4, $T = 298$ K, concentration 3.3% w/w; modulation amplitude 0.4 mT, RF field max.; Bruker SWL 3-100 with modified Varian V 4230 B (8–16 MHz) probe head; 45 scans. $\Delta\nu_{LC}$ is 26.9 kHz, δ of the central line −582 ppm.

Table 1. Quadrupole splittings $\Delta\nu_{LC}$ and ordering factors S_a in Nematic Phase 4 at 296 K.

Compound	Concentrat. [% w/w]	$\Delta\nu_{LC}$[a] [kHz]	S_a[b]
$VO(OBu^t)_3$	6.0	5.1	
$VO(OPr^i)_3$	6.3	17.4	0.111
	7.8	16.4	0.104
	9.4	15.2	0.097
	10.9	13.5	0.086
	12.5	12.1	0.077
	14.1	10.4	0.066
$VO(OBu^i)_3$	8.3	16.2	
$VO(OPr^n)_3$	8.6	18.4	
$VO(OBu^n)_3$	1.0	32.1	
	1.7	30.5	
	2.5	28.8	
	3.3	26.4	
	5.0	24.5	
	6.7	21.1[c]	
	10.0	15.4	
	13.3	11.8	
$VOCl(OPr^i)_2$	3.3	5.7	0.031
	5.8	4.5	0.025
	6.7[d]	4.3[d]	0.024
	9.3	3.2	0.018
	10.8	2.4	0.013
$VOCl(OPr^i)_2$[e]	3.3	4.9	0.026
	5.8	3.8	0.021
	9.3	2.2	0.012

[a] ± 0.2 kHz;

[b] $S_a = 28\,\Delta\nu_{LC}/(e^2qQ/h)$, $e^2qQ/h = 5.1$ ($VOCl(OPr^i)_2$) and 4.4 MHz ($VO(OPr^i)_3$), respectively;

[c] in Nematic Phase 887: 24.5, in Nematic Phase 1052: 16.3 kHz;

[d] Variations of $\Delta\nu_{LC}$ with the applied magnetic field ($B_0 = 0.9944$ and 2.114 T, respectively) are within the limit of error;

[e] at 305 K.

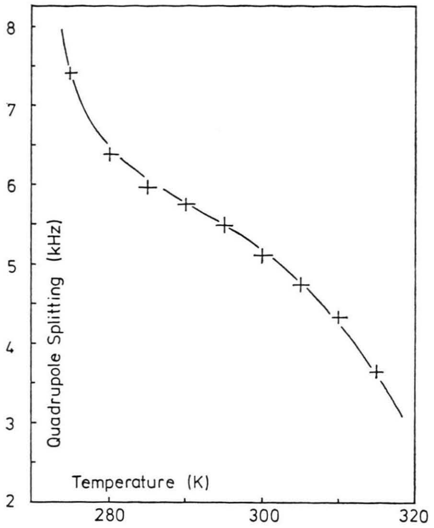

Fig. 6. Temperature dependence of the quadrupole splitting for $VOCl(OPr^i)_2$ in nematic phase 4, 3.3 % w/w.

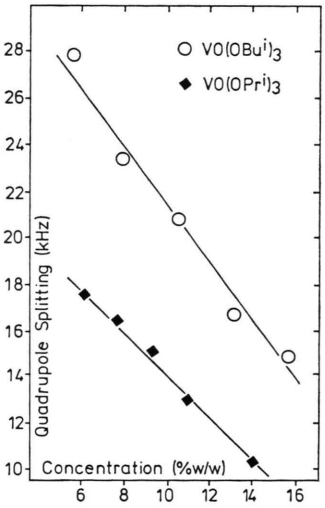

Fig. 7. Concentration dependence of the quadrupole splittings for $VO(OPr^i)_3$ and $VO(OBu^i)_3$ in nematic phase 4.

concentration, temperature and the system (Table 1; Figs. 6 to 8). Since the magnitude of $\Delta\nu_{LC}$ is a function of both S_a *and* e^2qQ/h, it is essential to know S_a values if quadrupole coupling constants are to be calculated from splittings in liquid crystals. The determination of S_a is usually carried out via ^1H or ^2H NMR measurements [15, 16] on the molecule under question, a procedure which, in our (and in comparable) systems cannot be employed, since S_a is related to the preferential molecular axis (V-O or V-Cl), containing the largest component (q_{zz}) of the field gradient at the ^{51}V nucleus. Using the e^2qQ/h values obtained from measurements on the frozen samples, we arrive, however, at the S_a parameters contained in Table 1. $\Delta\nu_{LC}$ and S_a are smaller for $VOCl(OPr^i)_2$ than for $VO(OPr^i)_3$. The order of magnitude of S_a agrees with that found in other systems [17].

The question now arises whether the ordering factors thus obtained can be employed in the determination of e^2qQ/h of other vanadyl esters and esterhalides. Figure 7 demonstrates that comparable vanadyl esters such as $VO(OPr^i)_3$ and $VO(OBu^i)_3$ exhibit similar slopes for the concen-

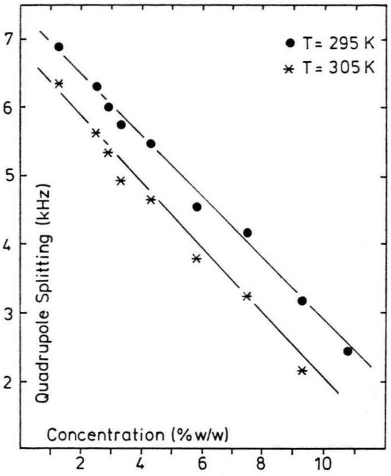

Fig. 8. Temperature and concentration dependencies of the quadrupole splittings for VOCl(OPr^i)$_2$ in nematic phase 4.

tration dependencies of $\Delta\nu_{LC}$ ($\Delta\nu_{LC} = -0.91c + 23.4$ for VO(OPr^i)$_3$; $\Delta\nu_{LC} = -1.02c + 31.7$ for VO(OBu^i)$_3$; c = concentration), while the relation is quite different for VOCl(OPr^i)$_2$ ($\Delta\nu_{LC} = -0.45c + 7.4$ at $T = 295$ K, $\Delta\nu_{LC} = -0.48c + 6.8$ at $T = 305$ K) and VO(OBu^n)$_3$ ($\Delta\nu_{LC} = -1.84c + 34.9$). The order parameter obtained for VO(OPr^i)$_3$ may therefore be employed to estimate the quadrupole coupling constant for VO(OBu^i)$_3$; but the general use of this method to calculate coupling constants of vanadyl esters is limited.

Table 2. ^{51}V Quadrupole coupling constants and ordering factors for vanadyl esters, obtained from the splittings of the NMR signals in liquid crystals.

Compound	Concentrat. [% w/w]	S_a [a]	e^2qQ/h [b] [MHz]
VO(OBu^i)$_3$	5.3	0.118	6.1
	7.9	0.103	6.3
	10.5	0.088	6.6
	13.2	0.072	6.4
VO(OPr^n)$_3$	5.7	0.115	5.6
	8.6	0.099	5.2
VO(OBu^n)$_3$	3.3	0.168	
	6.7	0.134	5.4
	10.0	0.098	4.6

[a] Calculated from $\Delta\nu_{LC}$ (cf. Table 1) and e^2qQ/h of VO(OPr^i)$_3$ = 4.4 MHz; see text for the validity of the values;

[b] calculated with the ordering factor of VO(OPr^i)$_3$ at the respective concentration (Table 1).

3) *Isotropic, Non-viscous Systems*

Since, under isotropic conditions, the field gradient is modulated by the Brownian motion of the solute molecules, quadrupole interactions are confined to a broadening of the NMR signal. A basic treatment of the dependencies of NMR parameters (chemical shift δ and line width $\Delta\nu_{1/2}$) on temperature and solvent effects, and upon the nature of the groups attached to VO^{3+}, is given in three previous reports [6, 18, 19]. Figure 9 is an example of the effects encountered with the temperature dependence of δ and $\Delta\nu_{1/2}$.

The two main factors which are responsible for the line broadening are e^2qQ/h and the molecular correlation time τ_c. The latter is the dominating quantity as the temperature varies. In some cases, a dynamic effect, due to exchange equilibria [n VO(OR)$_3 \rightleftharpoons$ {VO(OR)$_3$}$_n$; $n \geqq 2$] has also to be taken into account [6, 20—23]. This is illustrated in Figure 9: While, at elevated temperatures, the exchange between monomeric and dimeric (or oligomeric) forms is sufficiently fast to equilibrate the signal positions, the two species are represented by distinct signals below ca. 240 K. This effect, which produces inconsistencies in the $\Delta\nu_{1/2}/T$ and δ/T graphs (Fig. 10a, circles) is less pronounced in neat samples, where association to oligomers is more or less completed already at room temperature (Figs. 10b and 10c), or in sufficiently dilute solutions, where association becomes effective at very low temperatures only (Fig. 10a, squares).

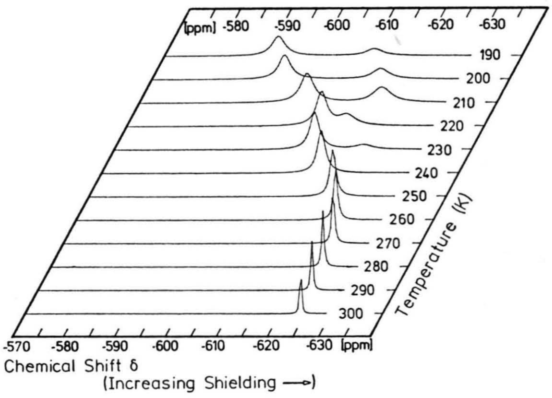

Fig. 9. Temperature dependencies of δ and $\Delta\nu_{1/2}$ for VO(OPr^i)$_3$ dissolved in diethyl ether (1.72 M). For the main component, see also Fig. 10a (circles).

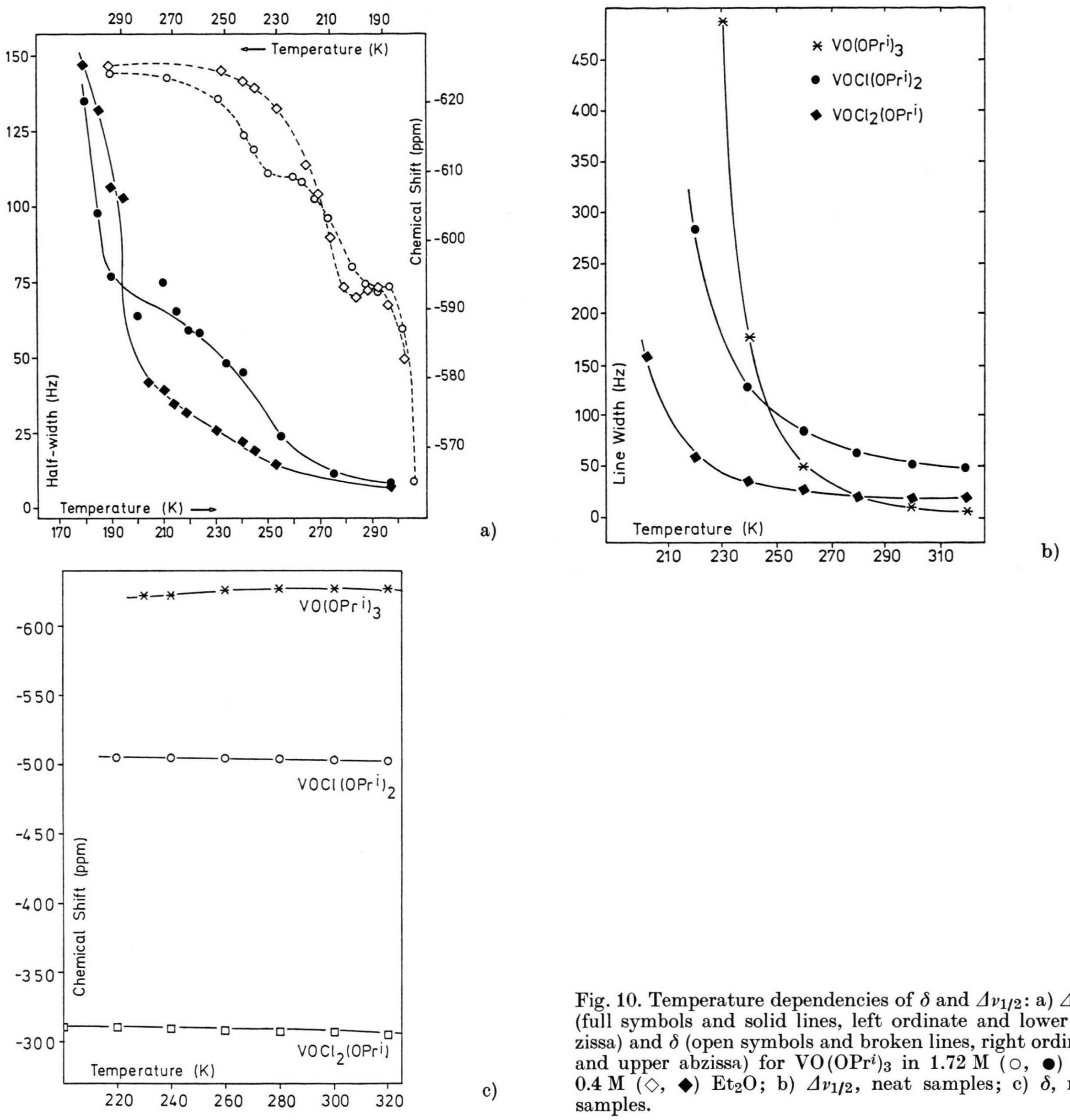

Fig. 10. Temperature dependencies of δ and $\Delta\nu_{1/2}$: a) $\Delta\nu_{1/2}$ (full symbols and solid lines, left ordinate and lower abzissa) and δ (open symbols and broken lines, right ordinate and upper abzissa) for VO(OPr^i)$_3$ in 1.72 M (○, ●) and 0.4 M (◇, ◆) Et$_2$O; b) $\Delta\nu_{1/2}$, neat samples; c) δ, neat samples.

Excluding dynamic effects originating from exchange equilibria, the relaxation is dominated by quadrupolar relaxation, i.e. [24]

$$\Delta\nu_{1/2} = \frac{3\pi}{10}\,\frac{(2I+3)}{I^2(2I-1)}\left(\frac{e^2qQ}{h}\right)^2\left(1+\frac{\eta^2}{3}\right)\tau_c\,. \qquad (7)$$

In Table 3, selected T_1 and T_2 values for VO(OBu^n)$_3$ are listed. Within the range of experimental error, there is satisfying agreement between the two relaxation times; hence, the precondition (extreme narrowing) is fulfilled at least in the case of VO(OBu^n)$_3$, which is the bulkiest compound in our series of esters and should exhibit the largest τ_c. For relaxation measurements on VOCl$_3$ see also [25].

Assuming that τ_c for the directly bonded ^{51}V ($I = 7/2$) and ^{35}Cl ($I = 3/2$) are the same [26], one

Table 3. Selected relaxation data.

Compound	Temperature [K]	T_1 [a] [ms]	T_2 [b] [ms]
$VO(OBu^n)_3$	300	10.5	13.5
	280	7.5	8.8
	260	5.4	5.4
	240	2.5	2.7
	220	1.7	1.3
	200	0.5	0.7
$VO(OPr^i)_3$	280	13.6	12.3
$VOCl(OPr^i)_2$	260	3.4	3.4

[a] ±10%; [b] calculated from the half-widths $\Delta\nu_{1/2}$.

arrives at (8)

$$e^2qQ/h\,(^{51}V) = 3.13\,e^2qQ/h\,(^{35}Cl)\sqrt{\frac{\Delta\nu_{1/2}(^{51}V)}{\Delta\nu_{1/2}(^{35}Cl)}}\,, \tag{8}$$

if η is sufficiently small (see Sect. (1) and Table 6 below). Equation (8) allows to calculate quadrupole coupling constants for the ^{51}V nucleus if the $e^2qQ/h\,(^{35}Cl)$ are known.

We have obtained e^2qQ/h values for the ^{35}Cl nuclei of vanadyl esterchlorides by direct measurements of neat, frozen samples. A representative spectrum is shown in Fig. 11, and the results are summarized in Table 4. The quadrupole coupling constant becomes slightly smaller as the temperature is raised (ca. 2% for an increase of 130°), which is in accord with theory [27]. In two cases (VCl_2OMe and $VOCl(OPr^i)_2$), phase transfer can be observed. The ^{35}Cl quadrupole coupling constant in $VOCl_3$ has already been determined by Dehmelt in 1951 (23.08 MHz) [28]. ^{35}Cl and ^{51}V NMR line widths and ^{51}V quadrupole coupling constants calculated from (8) are collected in Table 5, which also contains τ_c values calculated on the basis of (7). The τ_c for $VOCl_3$ agrees well with that reported by Abragam ($3.2 \cdot 10^{-12}$ s [5]). Recently, Habayeb and Hilman [29] published a τ_c value for this compound ($15 \cdot 10^{-12}$ s), based on calculations employing the Debye-Stokes-Einstein equation. Since application of the hydrodynamic model [30] is restricted to solutions where the solute molecules are large in comparison to the solvent molecules, the deviations from Abramgam's value are not surprising. If, however, we introduce the correction factors given by

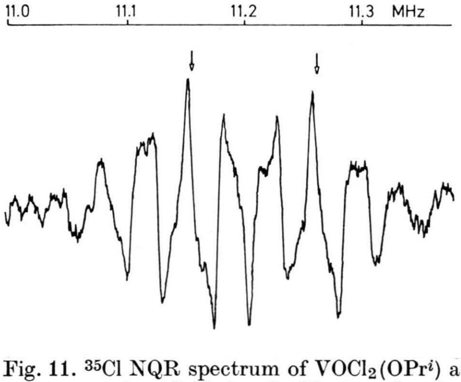

Fig. 11. ^{35}Cl NQR spectrum of $VOCl_2(OPr^i)$ at 77 K without suppression of side bands. The two signals are indicated by arrows.

Table 4. ^{35}Cl NQR transition frequencies and quadrupole coupling constants for vanadyl esterchlorides.

Compound	Temperature [K]	f_1 [a] [MHz]	f_2 [a] [MHz]	e^2qQ/h [MHz]
$VOCl_2(OMe)$	201	11.19	—	22.38
	77	11.35	11.40	22.75
$VOCl_2(OEt)$	77	11.06	11.18	22.24
$VOCl_2(OPr^i)$	77	11.16	11.26	22.42
$VOCl_2(OBu^i)$	77	11.08	11.14	22.22
$VOCl(OPr^i)_2$	195	11.83	—	23.66
	77	12.11	12.19	24.30
$VOCl_3$	77	11.54	11.58	23.12

[a] Transition frequencies ±10 kHz; the two frequencies f_1 and f_2 correspond to crystallographically distinct chlorine species; a mean value was employed to calculate e^2qQ/h.

Table 5. NMR half-widths $\Delta\nu_{1/2}$, ^{51}V quadrupole coupling constants $e^2qQ/h\,(^{51}V)$ calculated from (8), and molecular correlation times τ_c calculated from (7); neat samples.

Compound	$\Delta\nu_{1/2}$ (^{35}Cl) [Hz]	$\Delta\nu_{1/2}$ (^{51}V) [Hz]	e^2qQ/h (^{51}V) [a] [MHz]	τ_c 10^{-12} [s]
$VOCl_3$	1620	17.7	7.5	2.41
$VOCl_2(OMe)$	5150	37.6	6.1	7.92
$VOCl_2(OEt)$ [b]	3990	125.6	[12.4]	6.41
$VOCl_2(OBu^n)$ [c]	5460	63.0	7.5	8.81
$VOCl_2(OBu^i)$	6040	27.8	4.7	9.74
$VOCl_2(OPr^i)$	4160	15.7	4.3	6.58
$VOCl(OBu^n)_2$ [b, c]	11340	360	[13.4]	15.66
$VOCl(OBu^i)_2$ [b, c]	10510	208	[10.5]	14.52
$VOCl(OPr^i)_2$	6490	56.0	7.1	8.75

[a] For values in square brackets see [b];
[b] the large ^{51}V half-widths probably indicate dynamic factors and/or association to larger, less mobile units; the quadrupole coupling constants calculated for these complexes are too large;
[c] calculated from estimated $e^2qQ/h\,(^{35}Cl)$.

Gierer and Wirtz [31], the correct order of magnitude for the correlation time ($2.45 \cdot 10^{-12}$ s) is again obtained.

Conclusions

In Table 6, the e^2qQ/h values derived from procedures I to III are collected. Selected literature values of other vanadium compounds are added. Our data are of the same order of magnitude as those of meta- and orthovanadates, which have extensively been studied by Pletnev and co-workers [3] and, more recently, by Bleaney et al. [41, 42]. $e^2qQ/h(^{51}V)$ values of $VOCl_3$ have previously been estimated by Allerhand [32]. Allerhand investigated the ^{51}V NMR of frozen $VOCl_3$; however, no satellites were observed, which may account for the uncertainty of Allerhand's $\eta (\leqq 0.4)$. η, according to our evaluation, is 0.09.

Vanadium quadrupole coupling constants of vanadylesterchlorides obtained from NMR line widths and $e^2qQ/h(^{35}Cl)$ are larger by about 2 MHz than those derived from powder spectra. Factors responsible for this discrepancy may be (i) the temperature effect (room temperature and 77 K, respectively), (ii) the differing matrix effect, i.e. varying crystal field contributions to $e^2qQ/h(^{51}V)$ and $e^2qQ/h(^{35}Cl)$ due to the differing surroundings of the ^{51}V and the ^{35}Cl nucleus on the one hand, and the crystalline or liquid matrix on the other hand, and (iii) inaccuracies arising from the restrictions induced by the simplifying assumptions introduced into (8). The more reliable data hence should be those obtained by method I. But, if one is interested in correlations between quadrupole coupling constants and other parameters describing the electronic structure of the coordination sphere of vanadium in isotropically mobile molecules, one might rather rely on e^2qQ/h values obtained under isotropic or nearly isotropic conditions as encountered with meso-phases.

An approach to a correlation between quadrupole coupling constants and bonding parameters is given by the theory of Townes and Daily [43]. For the ^{35}Cl nucleus, this theory relates the electric field gradient eq or the quadrupole coupling constant e^2qQ/h to the ionic character i of the Cl-E bond (E = any other element attached to chlorine), the s character of the bonding σ-orbital, and contributions to the Cl-E bond by the π_x and π_y orbitals of

Table 6. Quadrupole coupling constants and asymmetry parameters η.

Compound	Ref.	$e^2qQ/h(^{51}V)$ [a]	[MHz]		η	$e^2qQ/h(^{35}Cl)$ [MHz]
		I	II	III		
VOF_3	[32]	8.9 (0.4)			$\leqq 0.4$	
$VOCl_3$	[32]	5.4 (0.2)			$\leqq 0.4$	
	[28]					23.08
	[29]			2.98		
	b	5.7 (0.2)		7.5	0.09 (0.01)	23.12
$VOCl_2(OMe)$	b			6.0		22.75
$VOCl_2(OBu^i)$	b			4.7		22.22
$VOCl_2(OPr^i)$	b			4.3		22.42
$VOCl(OPr^i)_2$	b	5.1 (0.2)		7.1	$\leqq 0.1$	24.30
$VO(OPr^n)_3$	b		5.3			
$VO(OBu^n)_3$	b		5.0			
$VO(OBu^i)_3$	b		6.3			
$VO(OPr^i)_3$	b	4.4 (0.2)			$\leqq 0.1$	
V_2O_5	[33]	0.805 [c]			0.04	
VO_2	[34]	6.72 (0.14)			0.51 (0.02)	
Na_3VO_4	[35]	1.05 (0.03)				
$LaVO_4$	[36]	5.21 (0.07)			0.69 (0.01)	
$NaVO_3$	[37]	3.65 (0.06)			0.60 (0.10)	
$Mg(VO_3)_2$	[38]	6.79			0.63	
V_3Si	[39]	2.924 (0.015)			≈ 0	
η^7-$C_7H_7V(CO)_3$	[40]			2.4 (0.2)	0	
η^5-$C_5H_5V(CO)_4$	[55]	2.79 (0.1)			0.11 (0.01)	

[a] I Powder spectra, II meso-phases for a concentration of ca. 8% w/w, III relaxation measurements;
[b] this work; [c] single crystal study.

chlorine [44–46]:

$$\frac{e^2qQ/h(\mathrm{Cl_M})}{e^2qQ/h(\mathrm{Cl_A})} = (1-i)(1-s^2) - \frac{\pi_x+\pi_y}{2} \tag{9}$$

$\mathrm{Cl_A}$ refers to the chlorine atom, $\mathrm{Cl_M}$ to chlorine incorporated in a molecule. With a constant s-character ($s^2 = 0.15$ [44]), e^2qQ/h is influenced by i and by the π-character of the Cl-E bond only. i increases with the sum of the electronegativities, $\sum$EN, of the groups Z in a series Cl-EZ [44], and thus $e^2qQ/h(^{35}\mathrm{Cl})$ should decrease in the order $\mathrm{VOCl_3} > \mathrm{VOCl_2(OR)} > \mathrm{VOCl(OR)_2}$. This trend is counteracted by an inverse effect induced by π: As shown by the IR stretching frequencies ν(V-Cl) (Table 7), the V-Cl bond strength (i.e. the double bond character π) decreases in the order $\mathrm{VOCl_3} > \mathrm{VOCl_2(OR)} > \mathrm{VOCl(OR)_2}$. The observed ordering of $e^2qQ/h(^{35}\mathrm{Cl})$ ($\mathrm{VOCl(OPr^i)_2} > \mathrm{VOCl_3} > \mathrm{VOCl_2(OR)}$) reflects the counteracting effects.

For the $e^2qQ/h(^{51}\mathrm{V})$, the ordering is $\mathrm{VOCl_3} > \mathrm{VOCl(OPr^i)_2} > \mathrm{VO(OPr^i)_3}$ (solid state), and $\mathrm{VOCl_3} > \mathrm{VOCl_2(OR)}$ ("isotropic" coupling constants). This is paralleled by a decrease of ν(VO) and ν(VCl) and by an increase of nuclear shielding of the ^{51}V nucleus (Table 7). An appropriate application of (9) to the discussion of $e^2qQ/h(^{51}\mathrm{V})$ cannot be carried out unambiguously, since d-orbital contributions will have to be taken into account. The above ordering, which seems to result from dominating influences of increasing ionic character (increasing $\sum$EN), may therefore be accidental. The correlation with the shielding parameter δ is, however, not unexpected, since increasing $\sum$EN increases the ligand field splitting, which should be the main factor affecting δ [2, 4, 47]. Additionally, the degree of association (which decreases with increasing bulk of R [22], shifts $|\delta|$ into the same direction (i.e. $|\delta|$ increases as R increases; cf. Table 7) [6].

Table 7. IR stretching frequencies ν(VO) and ν(VCl) (nujol mull) and ^{51}V chemical shifts $\delta(^{51}\mathrm{V})$ (neat samples) relative $\mathrm{VOCl_3}$.

Compound	ν(V=O) [cm^{-1}]	ν(V–Cl) [cm^{-1}]	$\delta(^{51}\mathrm{V})$ [ppm]
$\mathrm{VOCl_3}$	1040	510	0
$\mathrm{VOCl_2(OMe)}$	1026	495	– 290
$\mathrm{VOCl_2(OEt)}$	1029	495	– 300
$\mathrm{VOCl_2(OBu^n)}$	1025	490	– 290
$\mathrm{VOCl_2(OBu^i)}$	1028	493	– 288
$\mathrm{VOCl_2(OPr^i)}^a$	1025	499	– 309
$\mathrm{VOCl(OEt)_2}$	1017	465	– 414
$\mathrm{VOCl(OBu^n)_2}$	1015	450	– 470
$\mathrm{VOCl(OBu^i)_2}$	1016	460	– 478
$\mathrm{VOCl(OPr^i)_2}^a$	1014	480	– 506
$\mathrm{VO(OPr^n)_3}$	1005	–	– 555
$\mathrm{VO(OBu^n)_3}$	1005	–	– 548
$\mathrm{VO(OBu^i)_3}$	1008	–	– 538
$\mathrm{VO(OPr^i)_3}^a$	1005	–	– 628

[a] See also Ref. [56] for IR data.

Experimental

Spectra

^{51}V NMR spectra of the neat esters and ester-chlorides were registered on a Bruker WH 90 PFT spectrometer at 23.66 MHz and 300 ± 1 K. Samples were filled into 7.5 mm diameter vials, fitted into 10 mm vials containing acetone-d$_6$ as external lock. Standard was $\mathrm{VOCl_3}$ neat. Pulse widths were 5 µs, usual number of scans ca. 1000.

T_1 measurements were carried out in THF solutions by a fast saturation method ($S \cdot 90° - \tau - 90°$ pulse-sequence, $S = 50$–100) proposed by Clin and Lalanne [48]. τ was varied from 1 to 100 ms.

^{51}V NMR spectra in liquid crystal solutions (296 K, 15 mm diameter vials) and of frozen samples (ca. 100 K, 7.5 mm diameter vials) were scanned on a Varian DP 60 wide line spectrometer at 11.2 MHz and 0.993 T (except of $\mathrm{VO(OBu^n)_3}$ in nematic phase 4; cf. Fig. 5 for specifications). Usual modulation amplitude was 0.5 mT, number of scans 90 (sweep time per scan: 10 min, time constant: 1 s). The powder spectra were run at a minimum setting of the applied RF field (0.5 mT) to avoid saturation. No saturation problems were encountered with samples dissolved in liquid crystals.

^{35}Cl NMR spectra were obtained on the Varian spectrometer at 4 MHz and 0.955 T (neat samples in 15 mm tubes, 300 K). Chemical shifts relative to a saturated aqueous KCl solution are ca. – 700 ppm.

For an exact determination of the shift and line widths, all spectra were digitalized (Bruker BNC-12 computer) and submitted to a least squares fitting procedure by use of the program system NMRFIT [49]. This program allows evaluation of the spectra (0. and 1. derivative) on the basis of a linear combination of a Gaussian and Lorentzian function. Powder spectra were analysed with a modified version of the program system POWPAT [50]. The modification includes weighting of distinct orientations of the crystallites.

^{35}Cl NQR spectra were compiled with a Decca Rador NQR spectrometer which works according to the super regenerative principle. For a detailed description see [51].

IR spectra were obtained on a Perkin Elmer 325 spectrometer in dry nujol suspension (CsI plates).

Preparation of Complexes

The vanadylesters and vanadylesterchlorides were prepared according to literature procedures: $VOCl_2(OR)$ from $VOCl_3$ and ROH (molar ratio 1 : 1) in CCl_4 [52, 53], $VOCl(OR)_2$ from $VO(OR)_3$ and $VOCl_3$ (molar ratio 2 : 1) in toluene [52—54], and $VO(OR)_3$ from $VOCl_3$ and ROH (molar ratio 1 : 3) in n-heptane, followed by treatment with ammonia [52].

The compounds were purified by distillation in vacuo (1 Torr) at elevated temperatures. Since all complexes easily undergo hydrolysis (pronounced for compounds containing chlorine), all operations were carried out under nitrogen and in dried solvents. This applies also to the sample preparation for the NMR measurements. Liquid crystals (Merck) were degassed in vacuo at ca. 370 K and loaded with nitrogen.

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