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^{51}V NMR Chemical Shift and Anisotropy in Solid Metavanadates

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Synopsis. ^{51}V NMR spectra of alkali and ammonium metavanadates have been measured with and without magic angle spinning (MAS) of the sample at a high static magnetic field (9.40T). The isotropic chemical shifts have been determined accurately from the MAS spectra, while the principal values of the shift tensor have been estimated from the static spectra. Correlations between the NMR parameters and structural factors have been briefly discussed.

In metavanadates, VO_4 tetrahedra form one-dimensional chains, sharing two oxygen atoms with other VO_4 tetrahedra. The ^{51}V NMR spectra of the metavanadates include information on both the quadrupole and chemical shift effects. Baugher et al.[1] and Segel and Creel[2] have estimated the quadrupole coupling constants. The two groups have used low magnetic fields (resonance frequencies less than 25 MHz), which are useful for the estimation of the quadrupole effects, but are disadvantageous for the study of the chemical shift effects. Mastikhin et al.[3] have measured ^{51}V NMR spectra of alkali vanadates at a resonance frequency of 78.86 MHz, and have estimated the principal values of the chemical shift tensor.

Magic angle spinning (MAS) of the sample can narrow the resonance line.[4,5] Oldfield et al.[6] have reported ^{51}V MAS NMR spectra of $NaVO_3$ and NH_4VO_3, and have discussed the contributions of several effects on the line shape. Eckert and Wachs[7,8] have determind the isotropic chemical shifts of some vanadates by means of the MAS technique.

In the present work, ^{51}V isotropic chemical shifts have been determined accurately for alkali and ammonium metavanadates by use of the MAS technique and a high static magnetic field systematically, and principal values of chemical shift tensors have been estimated without using MAS. Correlations between the obtained ^{51}V NMR parameters and structural factors are discussed briefly.

Experimental

Materials were purchased from commercial sources: $LiVO_3$ from Soekawa Chemicals, $NaVO_3$ and KVO_3 from Nacalai Tesque, Inc., $RbVO_3$ and $CsVO_3$ from Cerac Inc. (Milwaukee, U.S.A.), and NH_4VO_3 from Kanto Chemical Co., Inc. The supplied $NaVO_3$ were in the β form, and the α form was obtained by heating at 500 °C for 4 h, according to Lukács and Strusievici.[9]

^{51}V NMR spectra were measured by a Bruker MSL400 pulsed spectrometer at room temperature. The magnetic field was 9.40 T, which corresponds to a resonance frequency (ν_0) of 105.25 MHz. The ordinary single pulse sequence was used with or without ^{1}H dipolar decoupling. The flip angle of the pulse was set at $\pi/12$,[10] and the recycle time was 1 s. The shift values are presented with respect to VO_3Cl neat liquid, with the higher frequency being positive. For routine use, a 0.16 M ($M=\mathrm{mol\,dm^{-3}}$) $NaVO_3$ aqueous solution was used as the second external reference, whose chemical shift is −574.28 ppm.

Results

In the ^{51}V MAS NMR spectra of metavanadates, spinning sidebands spread over a range of more than 8000 ppm (840 kHz), most of which are caused by the satellite transitions. The isotropic peak can be identified by changing the spinning rate of the sample. The full widths at half maximum of the isotropic peak are about 12 ppm (1.2 kHz). The obtained

Table 1. Summary of ^{51}V NMR[a)]

Compound	δ_i	δ_1	δ_2	δ_3	$\Delta\delta$	η	Ref.
	ppm	ppm	ppm	ppm	ppm		
$LiVO_3$	−577.1	−394	−544	−794	−325	0.69	This work
α-$NaVO_3$	−578.2	−364	−524	−824	−380	0.65	This work
	−576	−360	−530	−840	−395	0.66	8
β-$NaVO_3$	−516.4	−264	−264	−1024	−760	0	This work
KVO_3	−557.7	−304	−494	−854	−455	0.64	This work
	−553	—	—	—	—	—	8
$RbVO_3$	−569.1	−314	−524	−864	−445	0.71	This work
$CsVO_3$	−582.6	−344	−524	−874	−440	0.62	This work
NH_4VO_3	−571.5	−374	−524	−814	−365	0.62	This work
	−570	−370	−530	−830	−380	0.63	8

a) The following definitions are used; δ_i: isotropic shift, δ_1, δ_2, and δ_3: principal values of shift tensor, $\Delta\delta$: shift anisotropy, and η: asymmetry factor in shift tensor. $|\delta_3-\delta_i| \geqq |\delta_1-\delta_i| \geqq |\delta_2-\delta_i|$, $\delta_i=(\delta_1+\delta_2+\delta_3)/3$, $\Delta\delta=\delta_3-(\delta_1+\delta_2)/2$, $\eta=(\delta_2-\delta_1)/(\delta_3-\delta_i)$. The experimental errors in this work are ±0.5 ppm for δ_i and ±20 ppm for δ_1 to δ_3.

isotropic chemical shifts are listed in Table 1, together with the values of Eckert and Wachs.[8] Other literature data[1–3,7] are not listed in the table, since the accuracy is not so good as in the present work. The isotropic shifts (δ_i) obtained in the present work are in the following decreasing order; β-$NaVO_3$>KVO_3>$RbVO_3$>NH_4VO_3>$LiVO_3$>α-$NaVO_3$>$CsVO_3$.

The principal values can be estimated from the spectra in the static state, since only one component is present. The obtained parameters are summarized in Table 1. The magnitudes of the shift anisotropy ($|\Delta\delta|$) are in the following decreasing order; β-$NaVO_3$>KVO_3>$RbVO_3$>$CsVO_3$>α-$NaVO_3$>NH_4VO_3>$LiVO_3$. The powder pattern indicates axial symmetry in β-$NaVO_3$, while all other metavanadates show a nonaxial symmetry with asymmetric factors of about 0.7.

It was possible that the β-$NaVO_3$ sample is hydrated. The content of water is about 0.6 wt%, checked by thermogravimetric analysis, and dehydration of the sample has no effect on the spectrum. ^1H dipolar coupling effect might remain in NH_4VO_3. To check it, ^1H dipolar-decoupled spectra have been measured both with MAS and in the static state. However, the decoupling has no effect on the spectra.

Discussion

At first, the origin of the line shape in the static state is briefly discussed. ^1H high-power decoupling has no effect on the line shape in NH_4VO_3, demonstrating that the dipolar interaction with ^1H spins is negligible. Dipolar interaction with alkali nuclei is also negligible, since the γ values of alkali nuclei are much smaller than that of ^1H. Chemical shift anisotropy can contribute to the line shape. Quadrupole effect can also contribute to the line shape, especially in low magnetic fields.[11] The quadrupole coupling constants (e^2Qq/h) in the metavanadates are about 4 MHz.[1,2] The central transition ($m=1/2\leftrightarrow-1/2$) is not affected by the first-order effect, but the second-order effect might broaden the resonance line.[12,13] In the static state, the contribution of the second-order quadrupole effect to the line width is 10~20 ppm in the metavanadates at the present resonance frequency of 105.25 MHz, which is a negligible order of magnitude. On the other hand, in the MAS spectra the contribution reduces to 2~5 ppm, being negligible. Consequently, chemical shift anisotropy is the dominant mechanism to determine the line shape. Chemical shift anisotropy is an inhomogeneous line-broadening mechanism, and thus the signal splits into many lines under MAS.

To obtain the true chemical shifts, the shift values experimentally obtained should be corrected, since the second-order quadrupole interaction causes the frequency shift of the signal.[14] The second-order quadrupole shifts are estimated to be −2~−5 ppm. Since the estimated corrections are small, the obtained shift values are not corrected in the following discussion.

Much efforts have been made to correlate the chemical shift with structural factors, especially in ^{29}Si NMR of silicates and aluminosilicates.[15–22] We also attempt to correlate the isotropic chemical shifts with structural factors.

The crystal structures of the metavanadates have been studied in detail.[23–26] In the metavanadates except for β-$NaVO_3$, the vanadium atom is coordinated by four oxygen atoms. The tetrahedral oxyanions, VO_4^{3-}, are connected linearly by sharing two oxygen atoms, forming VO_3 chains. The adjacent chains are linked by cations. The crystal structures of KVO_3, $RbVO_3$, $CsVO_3$, and NH_4VO_3 are orthorhombic, and the cations are coordinated by eight oxygen atoms. The crystal strutures of $LiVO_3$ and α-$NaVO_3$ are monoclinic, and two types of cations are present, both of which are sixfold-coordinated. The structure of β-$NaVO_3$ is much different, since the vanadium atom is coordinated by five oxygen atoms, although the crystal symmetry is orthorhombic.

There are following trends in the observed chemical shift:

(1) β-$NaVO_3$ has a large downfield shift compared to the other metavanadates. The vanadium atom is fivefold-coordinated in β-$NaVO_3$, while it is fourfold-coordinated in the other metavanadates. As long as the first coordination sphere is concerned, downfield shift takes place with the increase in the coordination number around the vanadium atom.

(2) KVO_3, $RbVO_3$, $CsVO_3$, and NH_4VO_3 have the same crystal structure. The ionic radii are $K^+<Rb^+<Cs^+$,[27] while the chemical shifts are −557.7, −569.1, and −582.6 for KVO_3, $RbVO_3$, and $CsVO_3$, respectively. In conclusion, the chemical shift value decreases as the radius of the cation increases. It is reasonable that NH_4VO_3 and $RbVO_3$ have similar chemical shifts, since the ionic radii of NH_4^+ and Rb^+ are of similar magnitudes. This trend is caused by the second coordination sphere.

(3) Although the ionic radii of Li^+ and Na^+ are shorter than those of K^+ and Rb^+, $LiVO_3$ and α-$NaVO_3$ have upfield shifts compared with KVO_3 and $RbVO_3$. The cation coordination is sixfold in $LiVO_3$ and α-$NaVO_3$, while it is eightfold in KVO_3 and $RbVO_3$. In the crystalline lattice, the number of the cation coordination is equal to the number of cations coordinated to the oxygen. This means that the large coordination number in the second coordination sphere causes downfield shift.

Thus, the contribution of the second coordination sphere should be taken into consideration in addition to the first coordination sphere. In order to facilitate the understanding, we propose a tentative formula which can correlate the chemical shifts with structural factors as follows:

$$\delta_i = CX + D, \tag{1}$$

$$X = \frac{c_v}{r_v{}^n} + p\frac{c_m}{r_m{}^n}, \tag{2}$$

where the two terms in Eq. 2 express the contributions from the first and the second coordination spheres, respectively. C (positive) and D are constants, r_v the average interatomic distance between V and O, r_m the average interatomic distance between the cation and

O, c_v the coordination number of V, and c_m the coordination number of the cation, p a positive constant determining the relative contribution of the second coordination sphere to the first coordination sphere, and n represents the dependence on the distance. Equations 1 and 2 express that a downfield shift takes place with increase in the coordination. This behavior is consistent with the idea of "the overlap integral" introduced by Kondo and Yamashita.[28] It should be noted that the formula is not unique. For example, different n values can be used for the two terms, although the same n value is assumed in the present work.

After trial-and-error calculations, we estimate the coefficients which can be applied to the present results as follows: $n=1.2$, $p=2/3$, $C=172$, and $D=-1770$. In the course of this treatment, the coordination of Li^+ is assumed to be fivefold. One should note that one interatomic distance is markedly long (2.670 Å) compared to the other distances, and also compared to the sum of the ionic radii (2.16 Å).[27] Since two types of Li^+ ions are present in $LiVO_3$, the average fivefold coordination means that half of the Li^+ ions are fourfold-coordinated and the other half are sixfold-coordinated.

Several efforts have been made to correlate the ^{31}P chemical shift anisotropy with some structural factors such as the P–O bond length[29] and the O–P–O angle.[30] We deduce the following conclusions from a detailed inspection of the results and the crystal structure. β-$NaVO_3$ is omitted in the present discussion, since the vanadium coordination is different.

(1) The magnitude of the chemical shift anisotropy is much more dependent on θ(O(3)–V–O(3′)) than on the other O–V–O angles. The O(3)–V–O(3′) bond is the backbone of the VO_3 chain.

(2) The chemical shift anisotropy is smallest for the O(3)–V–O(3′) angle larger than 111 ° rather than for the perfect tetrahedral angle (109.5 °).

(3) The other O–V–O angles play some role in the chemical shift anisotropy. α-$NaVO_3$ and $LiVO_3$ have the larger anisotropies than the values extrapolated from the other four metavanadates which are orthorhombic. This deviation can be explained by the fact that some O–V–O angles in $LiVO_3$ and α-$NaVO_3$ deviate very much from the perfect tetrahedral angle. The O(2)–V–O(3′) angles are 103.23 ° and 105.3 ° in $LiVO_3$ and α-$NaVO_3$, respectively.

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