^{27}Al / ENDOR study of VO^{2+} adsorbed on δ -alumina

Direct evidence for inner sphere coordination with surface functional groups

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Abstract: A ^{27}Al / ENDOR study on the vanadyl aquoion adsorbed on hydrous δ -alumina is reported. The observed aluminium hyperfine interaction of 7.2 MHz is interpreted in terms of an inner-sphere surface coordination model. The magnitude of the coupling is attributed to spin delocalization from the vanadyl moiety to surface bound aluminium centers. It is concluded that equatorial positions of the VO_2^{2+} fragment are occupied by surface functional groups. Proton ENDOR spectra confirm the presence of both axial and equatorial water ligands.

Key words: ^{27}Al / ENDOR, vanadyl, δ -Alumina, inner-sphere surface coordination

Introduction

For many years the role of vanadium in the chemistry of biological systems has been considered as belonging exclusively to a limited number of living species [2]. In 1977 it was established that vanadate is an inhibitor in the sodium pump (Na, K-ATPase), which is an indication for the high toxicity of the element [3]. Since vanadium is an important trace metal in the global cycle whose anthropogenic emissions exceed the total natural emissions by a factor larger than 3 [4] its fate is of vital importance. Under physiological conditions, the element is stable in the oxidation states V(IV) and V(V), which is a unique characteristic. The vanadyl ion shows the features of a typical transition metal forming strong complexes with proteins and porphyrins, whereas the vanadate ion mimics phosphate in many respects.

Chemical reactions in natural waters tend to take place at the sediment/water interface. It is the purpose of this study to get a detailed insight into the type of bonding of the vanadyl ion onto a hydrous oxide for which δ -alumina has been chosen as a representative surface.

Spectroscopic techniques have been widely applied for the investigation of the structure of surface complexes [5]. Among these EPR is a very sensitive probe for paramagnetic compounds. Probably the best studied transition metal system are copper (II) complexes, where rather detailed structural information may be obtained already at EPR stage [6-9], since its magnetic parameters (electron g -tensor, copper hyperfine tensor) depend critically on the environment of the ion. Recently, Motschi [10] has found a striking correlation between the EPR parameter $g_{\parallel}$ and the thermodynamic stability constant of ternary surface complexes, which may readily be rationalized assuming inner-sphere coordination to the surface. The model of the Cu (II) surface complexes has been considerably refined by means of electron-nuclear double resonance (ENDOR), by revealing the type of coordinated ligands as well as the geometrical and electronic structure of the complex [11].

Although the vanadyl ion, VO^{2+} , is equally well suited for EPR studies as copper (II) from the point of view of its d^1 electron configuration, it is not possible to derive similar detailed information, since the vanadyl magnetic parameters are rather insensitive towards changes in the ligand field (different groundstate symmetry). In order to get insight into the structure of the surface complex, ENDOR has been applied.

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Recently, van Willigen and Chandrashekar [12] reported on an ENDOR study of the vanadyl aquoion on *Y*-zeolites. Proton hyperfine couplings of both axially and equatorially coordinated water have been resolved. The spectrum bears close resemblance to that of the same complex in a frozen solution, which led the authors to conclude that the $\text{VO}(\text{OH}_2)_5^{2+}$ entity remains intact in *Y*-zeolites. The absence of the matrix signal due to purely dipolar coupled protons was attributed to the fact that the complex is shielded from the approach of bulk water. From the proton ENDOR data it was deduced that the complex was probably hydrogen bonded to the zeolite structure. In the same study, van Willigen and Chandrashekar were able to detect signals from lattice- Na^+ near the Na free precession frequency, which manifest the close vicinity of the complex to the surface. However, the question about inner-sphere coordination to zeolite functional groups could not be settled.

A method to establish inner-sphere surface complexation in the case of VO^{2+} is to resolve interactions of the unpaired electron on the VO^{2+} moiety with magnetic nuclei of the surface, e. g. with ^{27}Al in δ -alumina. However, it is not sufficient to detect just signals at the corresponding nuclear free precession frequency, since these arise from nuclei within a distance of typically 5–10 Å from the paramagnetic center and provide no insight into the nature of the surface complex. In this sense, the ^{27}Al envelope modulation reported by Ichikawa and Kevan [13] in an electron-spin-echo study (ESE) of Cu^{2+} on *Na-X*-zeolites proves just that the $\text{Cu}(\text{II})$ ion is surrounded by several aluminiums within the distance mentioned above but gives no specification of the complex structure.

Only the measurement of a hyperfine coupling to surface nuclei (^{27}Al), which may be traced back either to a dipolar interaction at a *V-Al* distance of less than about 4 Å or to direct spin delocalization from the VO^{2+} moiety to surface nuclei may be regarded as direct evidence for inner-sphere vanadyl surface complexes.

Experimental section

ENDOR spectrometer

The ENDOR spectrometer consists of a Varian-E line EPR spectrometer equipped with a homebuilt broadband ENDOR accessory [14]. The radio frequency is generated in a hp 8640 B frequency generator, amplified by two power amplifiers (Electronic Navigation Instruments ENI 3100, Trans World Electronic TWE T1000 LA) and fed through a four-wire two turn loop in the ENDOR cavity to the 50 Ω dummy load. The *rf* field at the sample position was typically .05 *mT* in the rotating frame at 400 W inci-

dent power. The ENDOR signal was double-coded using 3 kHz amplitude modulation of the *rf* and 35 Hz magnetic field modulation.

All experiments have been carried out at 6 to 8 K using a helium gascooling system (Helitran) from Air Products and Chemicals Inc.

Sample preparation

For the adsorption experiments "Aluminoxid C" (Degussa, Frankfurt) was used without further treatment (The supply by Degussa is acknowledged). Adsorption was achieved by first suspending 1 g of $\delta\text{-Al}_2\text{O}_3$ in 10 ml of doubly distilled water and acidifying the suspension with 0.1 M HNO_3 to about pH = 2.5, followed by the addition of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (Fluka, purum). Thereafter the pH was slowly increased with 0.1 M NaOH to reach a final value of pH = 5. Equilibration was allowed for 24 h in a closed flask. The final volume was 25 ml with $[\text{VO}^{2+}]_{\text{tot}} = 2 \cdot 10^{-3}$ M and 0.1 M NaNO_3 (= constant ionic strength). The resulting suspension is centrifuged (~ 30 000 g) and separated from the supernatant solution. The gel was equilibrated in a closed system of a H_2O -saturated atmosphere in order to maintain a hydrous medium on the surface of the adsorbent. In fact the ENDOR spectra of a dried powder were identical to those measured in an aqueous suspension.

Results

a) EPR

The principal values of the electron *g* and the vanadium hyperfine tensors of $\text{VO}_{\text{aq}}^{2+}$ in different matrices are little affected by the variation of the environment of the paramagnetic center (table 1). It is therefore difficult to draw any conclusion on the structure of the vanadyl species on the basis of EPR exclusively.

Table 1. EPR parameters of the vanadyl aquoion in different matrices (Hyperfine Couplings in MHz)

	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^V$	$A_{\perp}^V$	Ref.
frozen solution					
($\text{H}_2\text{O}/\text{glycerol}$ 2:1)	1.937(5)	1.998(5)	543(5)	207(5)	
$\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.937	1.988	542	210	[20]
<i>Na Y</i> -Zeolite	1.938	1.986	534	210	[12]
δ -alumina	1.940	1.988	529	190(10)	

b) ENDOR

Figure 1a shows the ENDOR spectrum of $\text{VO}_{\text{aq}}^{2+}$ on δ -alumina in the frequency range 2 to 14 MHz saturating the $g_{\parallel}$ EPR transition with $m_V = 1/2$. With this B_0 setting orientations of B_0 parallel to the *V = O* bond direction are selected from the powder sample (single crystal type ENDOR [15]). The spectrum consists of a dominant proton matrix signal at 13.7 MHz, a broad unstructured spectral feature at 10.7 MHz and the ^{27}Al matrix peak at 3.55 MHz with an underlying structure centered at 3.7 MHz.

Fig. 1. a) Part of the ENDOR spectrum of VO^{2+} adsorbed on δ - Al_2O_3 (EPR observer line $m_V = 1/2$, $g_{\parallel}$). The free proton precession frequency is 13.72 MHz, the corresponding ^{27}Al frequency 3.55 MHz. b) Reference spectrum of VO^{2+} in frozen water/glycerol solution (2 : 1) (same EPR observer). The shoulder from 11 to 13 MHz is due to protons of inner-sphere coordinated water. c) Spectrum of suspension of VO^{2+}/δ - Al_2O_3 in D_2O , equilibrated for 15 hours (same EPR observer). The proton matrix signal is drastically reduced, however, the broad feature centered at 10.7 MHz remains unchanged

Figure 1b shows the reference ENDOR spectrum of the vanadyl pentahydrate complex in a frozen mixture of water and glycerol (2 : 1), saturating the same EPR observer transition. The low frequency shoulder of the proton matrix peak is due to the protons of coordinated water. Below 11 MHz, we did not detect any signal, indicating that the broad signal in spectrum 1a does not arise from inner-sphere water protons.

The ENDOR spectrum of a suspension of VO^{2+}/δ - Al_2O_3 in D_2O (equilibrated for 15 hours) is shown in figure 1c. The signal due to matrix protons is drastically reduced. However, the features of the signals at 10.7 MHz and 3.55 MHz are not affected by the D/H exchange. There remain three possible origins for these signals namely (i) non exchangeable protons, (ii) the vanadium center or (iii) surface aluminiums.

The fact that no corresponding resonance to the 10.7 MHz signal has been observed at 16.7 MHz symmetrical to the proton free precession frequency clearly disfavours the first possibility. It is very unlikely that hyperfine enhancement is responsible for the reduction of the intensity of the high-frequency signals ($A^H m_s < 0$) by more than a factor of 10 with respect to the low-frequency component [15].

The possibility of a signal at 10.7 MHz due to a vanadium ENDOR transition may definitely be ruled

out. The ^{51}V hyperfine coupling is of the order of 530 MHz in the $g_{\parallel}$ direction, hence signals centered at 265 MHz are expected. The quadrupole splitting of ^{51}V ($I = 7/2$) is certainly not as large to account for the line at 10.7 MHz, since the EPR spectrum does not show the features of a strong quadrupolar interaction. In the plane associated with the $g_{\perp}$ -region, where the vanadium hyperfine coupling is considerably smaller (~ 200 MHz), the metal ENDOR transition occurs in the frequency range from 70 to 130 MHz [16]. Although the signal around 3.5 MHz could be due to the matrix peak of ^{23}Na and/or ^{51}V nuclei which are present in the system, this probability is small since virtually the same spectral features are observed for a series of ternary complexes in the same frequency range [16].

We therefore attribute the broad signal at 10.7 MHz to nuclear spin transitions of lattice aluminiums. This assignment is supported by the fact that the shoulder underlying the ^{27}Al matrix signal is separated from the 10.7 MHz resonance by approximately 7 MHz, i. e. twice the nuclear Zeeman frequency of aluminium. The ^{27}Al ENDOR frequencies up to first order perturbation treatment are given by

$$\nu(m_s; m_{\text{Al}} \rightarrow m_{\text{Al}} + 1) = \left| m_s A^{\text{Al}} - \nu_{\text{Al}} + \frac{3}{2} P^{\text{Al}}(m_s)(2m_{\text{Al}} + 1) \right|$$

with $m_{\text{Al}} = -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$. The terms on the right hand side of the equation represent the hyperfine, nuclear Zeeman and quadrupole interaction of the aluminium nuclear spin ($I = \frac{5}{2}$).

Another possibility to interpret the aluminium ENDOR spectrum is that the low frequency signals of the strongly coupled aluminiums are not observable due to a pronounced hyperfine enhancement. Similar effects have been observed in the nitrogen and carbon-13 ENDOR of a Co(II) complex [17]. In this case, the spectral feature at 3.55 MHz is exclusively due to matrix aluminiums. This interpretation would also explain the different saturation behaviour of the signals at 3.5 and 10.7 MHz.

From the experimental spectra, an aluminium hyperfine coupling parallel to the $\text{V}=\text{O}$ bond direction of

$$|A^{\text{Al}}(g_{\parallel})| = 7.2(2) \text{ MHz}$$

has been deduced. The corresponding quadrupole splitting is difficult to estimate, since the individual components are not resolved. An upper limit of

$$|P^{Al}(g_{\parallel})| < 0.3 \text{ MHz}$$

has been assumed.

Discussion

Stumm et al. [18, 19] introduced a thermodynamic model which describes the adsorption of a metal ion on hydrous oxide surfaces assuming inner-sphere coordination with monodentate and/or bidentate surface functional groups of the type $(\equiv Al-O)ML_n^q$, and $(\equiv Al-O)_2ML_m^q$, respectively. Recently, indirect evidence for the proposed inner-sphere surface complexation has been derived from EPR [10] and ENDOR studies [11]. Moreover, it has been suggested that the δ - Al_2O_3 surface acts as a bidentate ligand.

In the case of VO^{2+} , the EPR parameters are not sensitive to small changes in the crystal field. Therefore, the EPR results do not primarily exclude the possibility of outer-sphere complexes. The analysis in terms of a ^{27}Al /ENDOR spectra, however, definitely rules out this model, since the hyperfine coupling of 7.2 MHz is not compatible with the assumption of purely dipolar coupled ^{27}Al nuclei at a V-Al distance larger than 5 Å (minimum distance estimated for one molecule of H_2O between the surface and VO^{2+} moiety). Thus, the ENDOR data provide compelling evidence for the inner-sphere surface coordination model.

In analogy to the structure postulated for the copper(II) surface complex [10, 11], a coordination of bidentate surface functional groups of δ - Al_2O_3 to the vanadyl is suggested. Two possible structural fragments have been considered, namely a 6-membered and a 4-membered chelate ring (fig. 2). A coordination of a surface functional group in axial position may be excluded, since the signals of axially coordinated water protons have still been observed in the proton ENDOR [16].

In the case of a 6-membered chelate ring, a V-Al distance of 3.6 Å has been estimated. Using the point-dipole approximation to compute the corresponding ^{27}Al hyperfine coupling,

$$T^{Al} = \mu_B g_{\parallel} \mu_N g_{Al} R_{V-Al}^{-3} (3 \cos^2 \theta - 1),$$

a coupling of -0.44 MHz has been obtained in the direction parallel to the $V=O$ bond ($\theta = \pi/2$).

Fig. 2. Proposed structures for the surface-adsorbed VO^{2+} . Assumed interatomic distances $d_{V-O} = 2.0$ Å, $d_{Al-O} = 1.8$ Å. Projection along z -coordinate (VO-unit = shaded circle). a) Six-membered chelate ring with two nearest ^{27}Al neighbours at a V-Al distance of approximately 3.6 Å. b) Four-membered chelate ring with one nearest ^{27}Al neighbour with $d_{V-Al} \approx 2.6$ Å.

For the 4-membered ring the V-Al distance is approximately 2.6 Å, the corresponding dipolar coupling then becomes -1.17 MHz.

In both cases the calculated dipolar coupling is considerably smaller than the experimental value of 7.2(2) MHz. Therefore, there has to be some direct spin density on the aluminium lattice nuclei. From the point of view of symmetry, $2p_{x,y}$ - and $2s$ -orbitals of the aluminium may participate in the singly occupied MO.

On the basis of the present ENDOR data, it is not possible to discriminate s and p contribution to the ^{27}Al hyperfine coupling, since this requires knowledge of the full hyperfine tensor. However, the data are sufficient to prove spin delocalization from the vanadyl moiety to the surface aluminium atoms which can only occur through inner-sphere coordination of the VO^{2+} with the surface functional groups $(\equiv Al-O)$.

The experimental ENDOR results do not provide any argument that would allow to discriminate between the structural proposals given in figure 2. In fact it is not even possible to rule out a monodentate complexation to the surface. It should be mentioned that also in this last case spin delocalization onto surface atoms has to be taken into account in order to explain the experimental coupling constant.

Comparing the present results with those of the EPR/ENDOR study of Cu(II) on δ -alumina [9, 10], it becomes evident that although the symmetry of the electronic groundstate is different for copper ($d_{x^2-y^2}$) and vanadyl (d_{xy}), there seems to be no qualitative difference in the adsorption behaviour of the two metal ions. Both Cu(II), which is on the borderline towards B-metal characteristics, and VO^{2+} with its close

resemblance to A-metals form inner-sphere surface complexes, probably with a bidentate functional group ($\equiv \text{Al}-\text{O}$)₂.

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