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ESR Spectra of VO^{2+} and Mn^{2+} in Aqueous Solution at L-Band

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L-Band (1.2 GHz) electron spin resonance (ESR) spectra of aqueous solution of vanadyl and manganese sulfate are reported with a comparison to those at X-band (9.4 GHz). ESR spectra of 0.5 mol dm^{-3} VO^{2+} and Mn^{2+} aqueous solution consisted of 3 and 2 resonance lines at L-band, respectively, while those gave 8 and 6 lines at X-band, respectively. The origin of the characteristic ESR spectra will be discussed in terms of frequency dependence of hyperfine coupling constant and line-broadening.

Microwave frequency has large influence on the resonance magnetic field and line width of ESR spectrum of samples having large anisotropy of ESR tensors and zero-field splitting. Metal complexes have been vigorously investigated to clarify such a phenomenum.[1)] Most reports have, however, been carried out with high frequent microwave ESR spectrometer, and have provided informations concerning the anisotropy of ESR parameters.[2)] Low frequent ESR should have large advantage to analyze zero-field splitting and line-broadening, while high frequent ESR measurement is usuful to reveal hyperfine- and g-anisotropy.[3)]

Recently, L-band (1 GHz) ESR apparatus has been developed for *in vivo* ESR measurement, and spin-clearance of nitroxide radicals and their imaging in whole body of animals have been reported from several institutes.[4)] Metal complex seems to be a good candidate as imaging contrast reagent in *in vivo* ESR technique and as spin-labeling reagent for metal binding proteins.[5)] If metal complexes are used for *in vivo* ESR measurement, their spectra at L-band should be exactly clarified. In the present paper, we report ESR spectra of VO^{2+} and Mn^{2+} in aqueous solution at L-band.

Highly purified vanadyl sulfate trihydrate and manganese sulfate tetrahydrate were purchased from Aldorich chemical Co. and Wako Cheimcals Co. Ltd, respectively, and were dissolved in deionized and distilled water. Thirty μl of the solution was transferred to a microcapillary tube (Drummond, 100 μl) for X-band and 1.5 ml were to a quartz sampling tube for L-band, and then ESR spectra were obtained with a X-band spectrometer (JEOL, RE-1X) or L-band one equipped with a Loop-Gap Resonator (JEOL, RE-3L) at room temperature. Calculation of resonance magnetic field of individual hyperfine components was performed with a computor (JEOL, ESPRIT 360) using an equation proposed by Hurd et al.[6)]

Figure 1 shows typical ESR spectra of 0.5 mol dm^{-3} VO^{2+} aqueous solution at L- and X-band. Spectrum at X-band consisted of 8 lines due to the nuclear spin of ^{51}V (I=7/2, natural abundance 99.75%), and its g-value and hyperfine splitting constants coincided with the previous report.[3)] The same solution of VO^{2+}, however, gave only 3 resonance lines in L-band ESR spectrum. The resonance magnetic fields of three lines were 23.0,

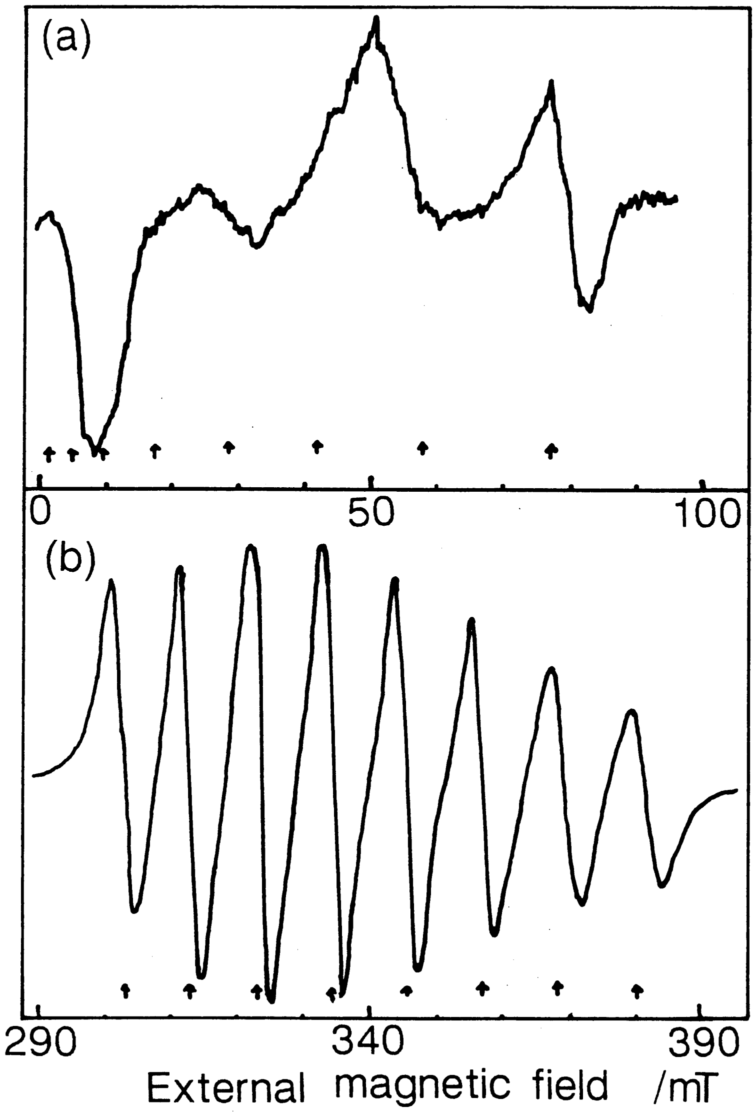

Fig. 1. ESR spectra of VO^{2+} aqueous solution at L- (a) and X-band spectroscopy (b).
0.5 mol dm^{-3} of vanadyl sulfate in aqueous solution was measured with L- and X-band ESR spectroscopy as described in the text. The arrows shown under each spectrum indicate the resonance magnetic fields of the individual hyperfine components which were calculated with the equation of Hurd et al.[6] The parameters used for the calculation were g=1.9624 and hfcc=10.8 mT.[2]

58.5, and 81.0 mT and the line widths (ΔHmsl) of each line were 13.3, 7.8, and 7.1 mT, respectively.

ESR spectra of 0.5 mol dm^{-3} Mn^{2+} aqueous solution at L- and X-band are demonstrated in Fig. 2. The spectrum at L-band consisted of only 2 resonance lines, while the same solution gave 6 lines at X-band. The spectrum at X-band agreed well to the previous one.[3] The resonance magnetic fields at L-band were 21.3 and 61.8 mT and the widths of resonance lines were 12.6 and 13.4 mT, respectively.

Why could only few resonance lines be observed at L-band ESR measurements? There may be the following possibilities for the disappearance of resonance lines at low frequent microwave, 1) invalidity of the high-field approximation to the low frequent ESR spectrum, 2) zero-field splitting due to nuclear spin, 3) convolution of resonance lines, and 4) line-broadening at L-band ESR measurement. The first possibility has been reported by Breit and Rabi.[7] They suggested that hyperfine coupling constants become smaller in the lower frequent ESR spectrum. Thus, we calculated the resonance magnetic fields of individual hyperfine components by the equation of Hurd et al.[6] and indicated them with arrows in Figs. 1 and 2. The resonance magnetic fields calculated at X-band agreed to those observed (Figs. 1b and 2b), indicating that the ESR parameters used for the calculation may be correct. All hyperfine components of Mn^{2+} should appear between 18 - 63 mT at L-band ESR spectrum, while those of VO^{2+} should between 1 - 77 mT. On the other hand, zero-field splitting due to nuclear spin may be calculated with the following equation.

zero-field splitting = hyperfine coupling constant x (nuclear spin number + electron spin number)

Assuming that the electron spin number is 1/2, zero-field splittings due to nuclear spin are estimated to be 26.7 mT for Mn^{2+} and 43.2 mT for VO^{2+}. The calculated values of the resonance magnetic field and the zero-field splitting indicate that most hyperfine components of Mn^{2+} should appear in the L-band ESR spectrum, but that some components of VO^{2+} may be hiding below 0 mT of external magnetic field. If so, the resonance line of VO^{2+} below 0 mT should convolute on those above 0 mT, and such a convolution may contribute the disappearance of resonance lines at L-band ESR measurement.

It is also possible that the line broadening may be larger in L-band ESR spectroscopy than that at X-band and that the extreme line broadening may hide resonance lines. Rogers and Pake²⁾ reported that the line widths of

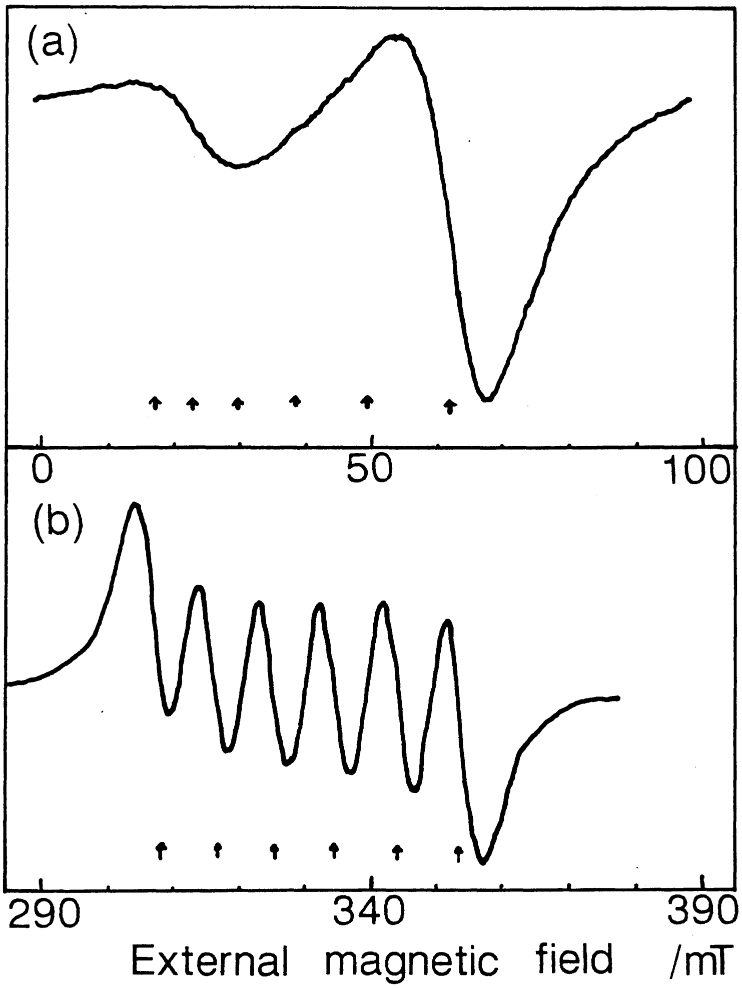

Fig. 2. ESR spectra of Mn^{2+} aqueous solution at L- (a) and X-band spectroscopy (b).
0.5 mol dm^{-3} of managanese sulfate in aqueous solution was measured with L- and X-band ESR spectroscopy as described in the text. The arrows under each spectrum indicate the resonance magnetic fields of the individual hyperfine components which were calculated with the equation of Hurd et al.⁶⁾ The parameters used for the calculation were g=2.023 and hfcc=8.91 mT.

the individual hyperfine components of VO^{2+} depended both on the nuclear spin and on the microwave frequency. In fact, the line width in the spectrum of VO^{2+} powder at L-band was much larger than that at X-band (data not shown). As shown in Figs. 1 and 2, the line widths of observable signals at L-band were also very broad. The line widths of Mn^{2+} (12.6 and 13.4 mT) were larger than the hyperfine coupling constants (8.91 mT) and smaller than the twice (17.8 mT). In that case, only two resonance lines at both ends are known to appear in the differential ESR spectrum and the other are hiding behind the two lines. If so, the other hidden signals should become observable in the lower concentration of VO^{2+} or Mn^{2+}. These facts indicate that the line-broadening may be major factor for disappearance of some hyperfine components of Mn^{2+} at L-band. We are now attempting to measure ESR spectrum with the solution containing the lower concentration of VO^{2+} or Mn^{2+}, although the sensitivity of L-band ESR apparatus is not sufficient.

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