

Solvent and Temperature Dependence of Spin Echo Dephasing for Chromium(V) and Vanadyl Complexes in Glassy Solution

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The solvent and temperature dependence of the rate constant for spin echo dephasing, $1/T_m$, for 0.2 to 1.2 mM glassy solutions of chromyl bis(1-hydroxy-cyclohexanecarboxylic acid), $\text{CrO}(\text{HCA})_2^-$; aquo vanadyl ion, $\text{VO}^{2+}(\text{aq})$, and vanadyl bis(trifluoroacetylacetonate), $\text{VO}(\text{tfac})_2$ were examined. At low temperatures where $1/T_1 \ll 1/T_m$, $1/T_m$ in 1:1 H_2O :glycerol is dominated by solvent protons. At low temperature $1/T_m$ increases in the order 1:1 H_2O :glycerol or 9:1 $\text{CF}_3\text{CH}_2\text{OH}$:ethyleneglycol (no methyl groups) < 9:1 *i*-PrOH:MeOH (hindered methyl groups) < 9:1 *n*-PrOH:MeOH (less hindered methyl groups). This solvent dependence of $1/T_m$ is similar to that observed for nitroxyl radicals, which indicates that the effect of solvent methyl groups on spin-echo dephasing at low temperature is quite general. At higher temperatures the echo dephasing is dominated by spin-lattice relaxation and is concentration dependent. As the glass softens, echo dephasing is dominated by the onset of molecular tumbling. © 1999 Academic Press

Key Words: chromium(V); methyl groups; proton spin diffusion; spin echo dephasing; vanadyl ion.

INTRODUCTION

A wide variety of processes can contribute to dephasing of two-pulse spin echoes in systems that contain a single type of paramagnetic center. An understanding of these processes permits interpretation of the rate constant for spin echo dephasing, $1/T_m$, in terms of the dynamics of a system. It is customary to refer to spins that are excited by the microwave pulses as A spins and all other spins as B spins (1). Echo dephasing results from processes that change the resonance frequency of an A spin such that it is not refocused by the second pulse. Processes that have been demonstrated to contribute to echo dephasing in glassy solutions include instantaneous diffusion (2), dynamic averaging of electron–nuclear coupling to inequivalent protons within the molecule (3–7), low-amplitude molecular motions (librations) (8, 9), onset of molecular tumbling as the glass softens (10), electron spin T_1 (10–12), electron spin T_2 (13), and nuclear spin T_2 -induced dipolar field fluctuations (nuclear spin diffusion) (10, 14–16). Dephasing due to electron spin T_1 - and T_2 -induced dipolar field fluctuations sometimes is called spectral diffusion (2). We have recently shown that spin echo

dephasing for nitroxide spin labels at temperatures below about 60 K depends upon the type of protons in the solvent (14, 15). Echo dephasing occurs more rapidly for solvents that contain methyl groups than for solvents that do not contain methyl groups and depends upon the type of methyl group (14, 15). It is of interest to determine whether comparable solvent dependence is observed for other paramagnetic centers.

Relatively little information is available concerning the mechanism of spin echo dephasing for d^1 transition metals in the concentrations ranges that typically would be considered magnetically dilute. For 1.6 to 100 mM VO^{2+} in glassy sulfuric acid at 77 K, echo dephasing was found to be concentration dependent and attributed to spectral diffusion (2). At 50 K molecular librations cause a dependence of $1/T_m$ on position in the spectrum for a vanadyl porphyrin in glassy organic solvent (17). For 2 and 27 mM Cr(V) doped into CaWO_4 , echo dephasing is due to instantaneous diffusion at low temperature and to spectral diffusion at temperatures above 20 to 30 K (18). For Cr(V) complexes of ligands that contain a methyl group, echo dephasing in 1:1 H_2O :glycerol solution between about 80 and 160 K is dominated by rotation of the methyl groups at a rate comparable to the magnitude of the electron–nuclear coupling to the methyl protons (6).

To determine the relative importance of various dephasing mechanisms as a function of temperature for $3d^1$ transition metal complexes in 0.2 to 1 mM glassy solutions, two-pulse electron spin echo data were obtained for chromyl bis(1-hydroxy-cyclohexanecarboxylic acid), $\text{CrO}(\text{HCA})_2^-$; aquo vanadyl ion, $\text{VO}^{2+}(\text{aq})$, and vanadyl bis(trifluoroacetylacetonate), $\text{VO}(\text{tfac})_2$. The Cr(V) complex was selected because it is relatively stable (6) and the ligand does not contain a methyl group. For the vanadyl complexes the values of $1/T_m$ were measured for the $m_I = -\frac{1}{2}$ transition because this transition has the least anisotropy and therefore is less sensitive to the effects of librations than transitions for other values of m_I . The effects of instantaneous diffusion were minimized by working at concentrations that give small numbers of spins per gauss and by using relatively small microwave magnetic fields, B_1 . This

permits us to examine dephasing by mechanisms other than instantaneous diffusion.

EXPERIMENTAL

Sample Preparation

$\text{CrO}(\text{HCA})_2^-$ (6) and $\text{VO}(\text{tfac})_2$ (19) were prepared by literature methods. Solutions of VO^{2+} (aq) in 1:1 water:glycerol were prepared by dissolving vanadyl sulfate (A. D. Mackay, Inc.) in water, with subsequent addition of an equal volume of glycerol. Solvents were reagent grade and were used without further purification. Solvent mixtures were selected that give good low-temperature glasses to prevent the locally high concentrations that can occur when solvents crystallize. D_2O and glycerol- d_8 (Cambridge Isotope Laboratories) were 99.9% and >98% enriched, respectively. Solutions were freshly prepared with concentrations between 0.2 and 1.2 mM, and 150–200 μl of solution was pipetted into 4 mm OD quartz EPR tubes. Air/oxygen contained in the solvent was removed by three to four freeze–pump–thaw cycles. For experiments at liquid helium temperatures EPR tubes were back-filled with helium and placed directly into the cryostat without thawing.

Electron Spin Echo Experiments

Data were obtained on a Bruker ESP380E spectrometer equipped with a Bruker split-ring resonator and an Oxford CF935 flow cryostat. The microwave frequency was between 9.3 and 9.5 GHz. The Oxford temperature readout was calibrated with a Lakeshore 820 readout connected to a TG-120PL GaAlAs diode immersed in silicone oil in a 4 mm OD quartz EPR tube that replaced the sample tube. For spin echo and inversion recovery experiments the resonator was overcoupled to a Q of about 150, which permitted echo decays to be recorded starting 64 ns after the second pulse. Two-pulse echo decays were obtained with 40 and 80 ns pulses and B_1 was adjusted to give 90°–180° turning angles, or less. The 40, 80 ns low-power pulses were used to reduce excitation of proton modulation relative to that which would be observed with the shorter (ca. 16 and 24 ns) pulses frequently used in ESE experiments.

Spin echo data were fitted to a stretched exponential:

$$Y(\tau) = Y(0)\exp[-(2\tau/T_m)^x], \quad [1]$$

where $Y(\tau)$ is the intensity of the echo as a function of τ , the time between the two pulses. $Y(0)$, echo intensity extrapolated to time zero, and $Y(\tau)$ are in arbitrary units that depend upon the concentration of the sample, resonator Q , and instrument settings. The parameters x and T_m describe the shape of the echo decay and depend upon the dephasing mechanism (10, 14). $1/T_m$ is the rate constant for echo dephasing for the time interval accessible on the Bruker ESP380E. ESE data were fitted to Eq. [1] using a Levenberg–Marquardt algorithm.

For representative samples, echo decays were recorded at a series of turning angles that were obtained by varying the microwave power at constant pulse length. These experiments provide a test for the impact of instantaneous diffusion (2, 10). In protiated solvents, at the concentrations used in these studies, only a minor dependence of echo decay on turning angle was observed, which indicates that the contribution to dephasing from instantaneous diffusion is small, even for 90° and 180° pulses. The echo decays in the figures and parameters reported in the text and tables were obtained at small turning angles, typically 11° or 22° for the first pulse. At these small turning angles the effects of instantaneous diffusion are negligible in protiated solvents, but are significant in deuterated solvents. In protiated solvents the estimated uncertainties at low turning angle are $\pm 0.1 \mu\text{s}$ for T_m and ± 0.1 for the exponent x in Eq. [1].

Inversion recovery data were recorded with a $\pi-T-\pi/2-\tau-\pi-\tau$ -echo sequence in which T was varied. Pulse lengths were 16 and 24 ns and B_1 was adjusted to give maximum intensity of the two-pulse echo. At each magnetic field τ was selected to correspond approximately to a maximum echo intensity in the modulated two-pulse decay. Inversion recovery data were fitted to Eq. [1] with $x = 1$.

Saturation Recovery Measurements

The Bruker ESP380E was modified to permit long-pulse saturation recovery experiments by adding a 2 W amplifier, which permits the use of longer saturating pulses than can be achieved within the duty cycle of the 1 kW TWT. Data were signal-averaged in a Lecroy 9410 digital oscilloscope, transferred to a PC, and fitted to Eq. [1] with $x = 1$. Values of T_1 for VO^{2+} (aq) were obtained by long-pulse saturation recovery and by inversion recovery. Good agreement was observed between inversion recovery and saturation recovery measurements for values of T_1 shorter than about 100 μs . However for longer values of T_1 (observed at temperatures lower than about 40 K), values obtained by inversion recovery were systematically shorter than values obtained by long-pulse saturation recovery. For the longer spin–lattice relaxation times, the longer saturating pulses (100 μs) of the long-pulse saturation recovery method are needed to overcome the effects of spectral diffusion processes. Values of $1/T_1$ for VO^{2+} (aq) in 1:1 D_2O :glycerol- d_8 were indistinguishable from those in 1:1 H_2O :glycerol, which indicates that solvent protons play a negligible role in the spin–lattice relaxation mechanism between 10 and 80 K.

Model of Nuclear Spin Diffusion

Milov *et al.* (20) proposed a model for the effect of nuclear spin diffusion on electron spin echo dephasing, based on equations derived by Zhidomirov and Salikhov (21). The calculation of the change in dipolar coupling to the electron spin that occurs due to a proton flip-flop that is used in the

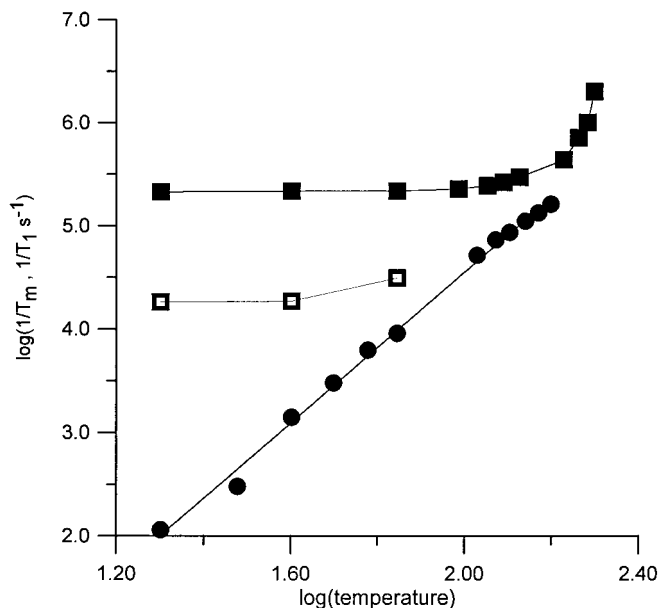


FIG. 1. Temperature dependence of relaxation rates for $\text{CrO}(\text{HCA})_2^-$ at X-band (9.1 to 9.4 GHz): (■) $1/T_m$ for 0.3 mM solution in 1:1 H_2O :glycerol, (□) $1/T_m$ for 0.3 mM solution in D_2O :glycerol- d_8 , (●), $1/T_1$ obtained by long-pulse saturation recovery for 1.0 mM solution in 1:1 H_2O :glycerol. The lines through the data for $1/T_m$ connect the data points. The line through the $1/T_1$ data is a least-squares fit: $\log(1/T_1) = 3.63 \cdot \log(T) - 2.72$. Data were recorded in the center of the spectrum. The data at temperatures above 100 K are taken from Ref. (6).

present paper was modified from that of Ref. 20 to explicitly include the dependence on the orientation of the proton pair with respect to the external magnetic field (15). Calculations of the echo decay curves were performed with Mathcad. For solvents that do not contain methyl groups the proton flip-flop frequency is proportional to proton concentration. In solvents that contain methyl groups the proton flip-flop frequency is independent of methyl proton concentration, but dependent on the type of methyl group. It is proposed that the enhanced echo dephasing by methyl groups in the solvent is due to quantum mechanical tunneling (15). The radius of the spin diffusion barrier (22) was held at 5.8 Å, which is the value determined for nitroxyl radicals by comparison of the spin echo dephasing with that observed for a sterically encumbered trityl radical (15).

RESULTS AND DISCUSSION

The electron spin relaxation rate, $1/T_1$, and the rate constant for echo dephasing, $1/T_m$, for $\text{CrO}(\text{HCA})_2^-$ and VO^{2+} (aq) in 1:1 water:glycerol are summarized in Figs. 1 and 2, respectively. For both metal ions $1/T_1$ is strongly temperature dependent. Throughout the temperature range that was examined (16 to 158 K for $\text{CrO}(\text{HCA})_2^-$ and 11 to 79 K for VO^{2+} (aq)), $1/T_1$ for VO^{2+} (aq) is faster than for $\text{CrO}(\text{HCA})_2^-$. The data for

$1/T_m$ fall in several regimes defined by solvent and by the relationship between $1/T_1$ and $1/T_m$. Different processes dominate the echo dephasing within these different regimes.

$1/T_1 \ll 1/T_m$ in 1:1 H_2O :glycerol. At low temperatures where $1/T_1 \ll 1/T_m$, $1/T_m$ is approximately independent of temperature (Figs. 1 and 2). This regime extends up to about 100 K for $\text{CrO}(\text{HCA})_2^-$ and up to about 40 K for VO^{2+} (aq). In this temperature interval $1/T_m$ in 1:1 H_2O :glycerol is substantially faster than in 1:1 D_2O :glycerol, which indicates that solvent protons play a major role in echo dephasing in the protiated solvent. The fit of the spin echo data to Eq. [1] gave $x = 2.4$ to 2.6 (Table 1), which is in good agreement with the values of x obtained for nitroxyl radicals under conditions where dephasing is dominated by nonmethyl protons (15). At the low concentrations used in these studies and at small B_1 (i.e., negligible impact of instantaneous diffusion), $1/T_m$ is independent of concentration. These observations support assignment of proton spin diffusion as the dominant spin echo dephasing mechanism.

$1/T_1 \ll 1/T_m$ in 1:1 D_2O :glycerol. In 1:1 D_2O :glycerol- d_8 $1/T_m$ was much more strongly dependent on B_1 than in H_2O :glycerol, and fits of the data to Eq. [1] gave $x \sim 1$. The smaller magnetic moment of a deuteron than of a proton predicts a decrease in $1/T_m$ of about a factor of 50 if deuteron flip-flops dominate the dephasing in deuterated solvents. These rates are so much slower than in protiated solvents that instantaneous

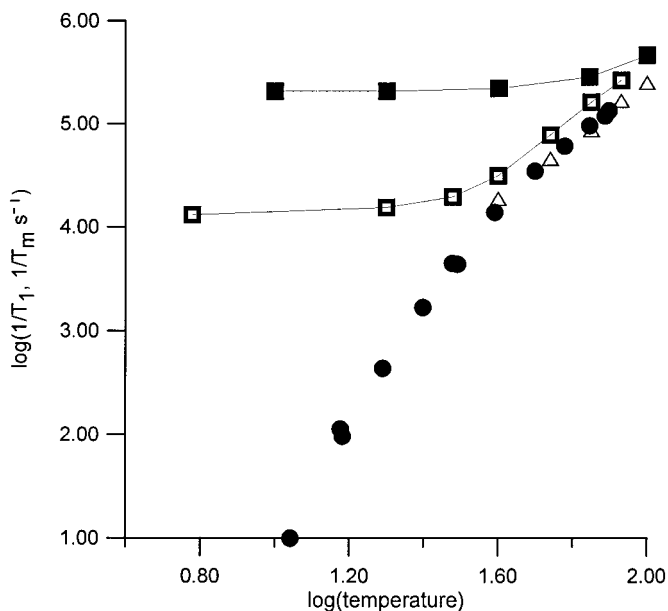


FIG. 2. Temperature dependence of relaxation rates of VO^{2+} (aq) at X-band (9.4 GHz): (■) $1/T_m$ for 1.2 mM solution in 1:1 H_2O :glycerol, (□) $1/T_m$ for 0.3 mM solution in D_2O :glycerol- d_8 , (●), $1/T_1$ obtained by long-pulse saturation recovery for 0.9 mM solution in 1:1 H_2O :glycerol, (△) $1/T_1$ obtained by inversion recovery for 0.3 mM solution in D_2O :glycerol- d_8 . The lines through the data for $1/T_m$ connect the data points. Data were recorded for the $m_I = -\frac{1}{2}$ line.

TABLE 1
Solvent Dependence of Spin Echo Dephasing at 40 K^a

Sample	Solvent		9:1 CF ₃ CH ₂ OH: ethylene glycol		9:1 <i>i</i> -PrOH:MeOH		9:1 <i>n</i> -PrOH:MeOH	
	1:1 H ₂ O:glycerol		T_m	x	T_m	x	T_m	x
Tempone ^b	T_m	x	T_m	x	T_m	x	T_m	x
CrO(HCA) ₂ ^{-c}	4.6	2.3	6.4	2.1	2.1	2.2	0.7	0.8
VO ²⁺ (aq) ^d	4.6	2.4			2.2	2.0	0.7	0.8
VO(tfac) ₂ ^e			5.6	2.0	1.8	1.7	0.7	0.9

^a Values of T_m in μ s.

^b 0.2 to 0.4 mM.

^c 0.2 mM.

^d 0.3 to 1.2 mM.

^e 0.9 to 1.1 mM.

diffusion makes a larger contribution in the deuterated solvent, which is consistent with $x \sim 1$. As B_1 was decreased, $1/T_m$ approached limiting values that were about 20 to 50 times slower than in protonated solvents. Residual protons in the nominally perdeuterated solvents may contribute to faster dephasing than predicted for a proton-free environment. The limiting value of $1/T_m$ was independent of concentration between 0.2 and 1.0 mM.

The previously reported data for Cr(V) in CaWO₄ at low temperature also fall in the regime where $1/T_1 \ll 1/T_m$ (18). In that host there are no protons and the W nuclei have small magnetic moments, so fluctuations of nuclear spins make a negligible contribution to echo dephasing and the dephasing is dominated by instantaneous diffusion (18). Because of the higher concentrations of paramagnetic centers in those experiments (2 and 27 mM), the limiting value of $1/T_m$ at small B_1 for the Cr(V) in CaWO₄ was dominated by electron–electron interaction and was concentration dependent (18).

$1/T_1 \sim 1/T_m$. With increasing temperature $1/T_1$ approaches the value of $1/T_m$ determined by the solvent protons in 1:1 H₂O:glycerol and $1/T_m$ becomes temperature dependent. This occurs above about 100 K for CrO(HCA)₂⁻ and above about 40 K for VO²⁺ (aq). As metal $1/T_1$ begins to play an increasingly important role in echo dephasing, the value of x (Eq. [1]) decreases. For CrO(HCA)₂⁻ x decreased from 2.0 at 113 K to 1.7 at 134 K, and for VO²⁺ (aq) x decreased from 1.9 at 70 K to 1.5 at 100 K. In this regime $1/T_m$ is concentration dependent. Because of the slower rate of low-temperature dephasing in the absence of protons, $1/T_1$ begins to dominate the echo dephasing at lower temperatures in 1:1 D₂O:glycerol-*d*₈ (about 70 K for CrO(HCA)₂⁻ and 30 K for VO²⁺) than in 1:1 H₂O:glycerol.

Short electron spin T_1 affects the echo decay in two ways. The spin–lattice relaxation for an A spin causes a time dependence of magnetization, which is indistinguishable from echo dephasing. This contribution is independent of concentration. In addition, either T_1 or T_2 processes of surrounding electron

spins (B spins) cause changes in the dipolar field of the A spin, which causes echo dephasing. This contribution depends on concentration.

The previously reported results for VO²⁺ at 77 K in glassy sulfuric acid (2) fall in this regime. The high concentrations of paramagnetic centers and the low concentrations of protons in the solvent caused intermolecular electron–electron interaction (denoted as spectral diffusion) to dominate the dephasing. Similarly, the relaxation for Cr(V) in CaWO₄ at higher temperatures falls in this regime (18).

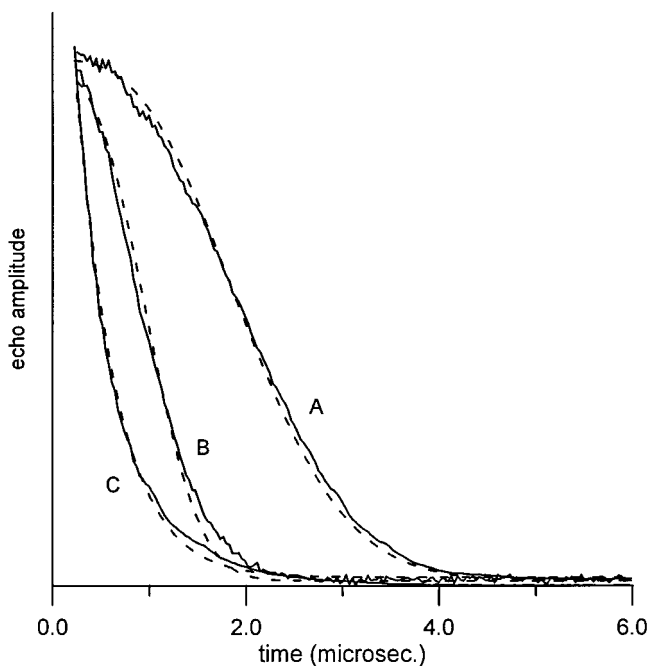


FIG. 3. Electron spin echo decays for 0.20 mM CrO(HCA)₂⁻ at 40 K, 9.44 GHz, and magnetic field = 3405 G in (A) 1:1 H₂O:glycerol, (B) 9:1 *i*-PrOH:MeOH, and (C) 9:1 *n*-PrOH:MeOH. The dashed lines are fits to the proton diffusion model with the same parameters that were used to fit data for the nitroxyl radical tempone in these solvents (15).

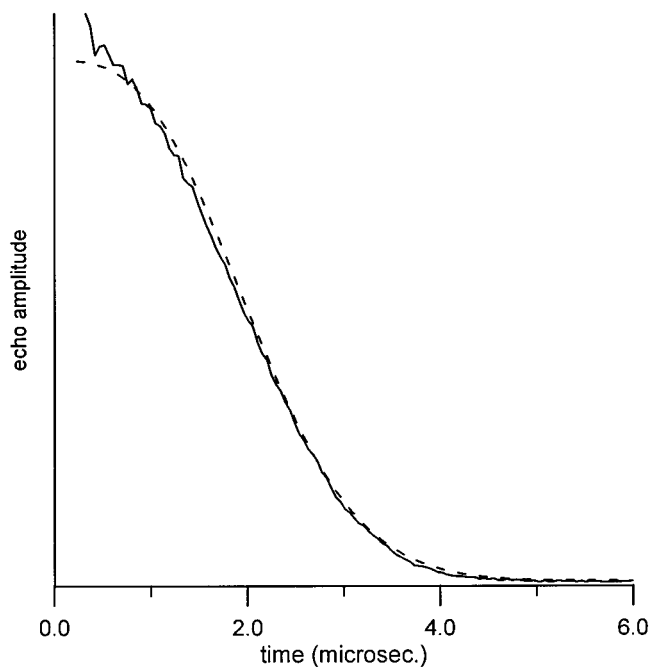


FIG. 4. Electron spin echo decays for 1.2 mM VO^{2+} (aq) in 1:1 H_2O :glycerol at 40 K, 9.422 GHz, and magnetic field = 3341 G (the $m_I = -\frac{1}{2}$ transition). The dashed line is the fit to the proton diffusion model with the same parameters that were used to fit data for the nitroxyl radical tempone in 1:1 H_2O :glycerol (15).

Dephasing dominated by onset of molecular tumbling. Above about 160 K the water:glycerol glass begins to soften, $1/T_m$ for $\text{CrO}(\text{HCA})_2^-$ becomes strongly temperature dependent, and x (Eq. [1]) decreases from 1.4 at 169 K to 1.2 at 192 K.

Solvent dependence of $1/T_m$ in the regime where protons dominate dephasing. Because of the limited solubility of VO^{2+} in solvents other than water, the complex $\text{VO}(\text{tfac})_2$ was used for the studies of solvent dependence of $1/T_m$. The comparisons in the prior paragraphs indicate that in proton-containing solvents, solvent nuclei dominate the echo dephasing at temperatures below about 40 K for both vanadyl ion and $\text{CrO}(\text{HCA})_2^-$. Studies of the solvent dependence of $1/T_m$ for nitroxyl radicals (15) have shown substantial differences between $1/T_m$ in 1:1 H_2O :glycerol or 9:1 $\text{CF}_3\text{CH}_2\text{OH}$:ethylene glycol, which contain no methyl groups, in 9:1 *i*-PrOH:MeOH, which contains relatively hindered aliphatic methyls, and in 9:1 *n*-PrOH:MeOH, which contains less-hindered aliphatic methyls. The values of T_m and x obtained as a function of solvent for the Cr(V) and vanadyl complexes at 40 K are compared in Table 1 with data for the nitroxyl radical tempone (15). These values demonstrate strong similarities in the solvent dependence of T_m and x for the three types of paramagnetic centers.

Examples of the spin echo decay curves for $\text{CrO}(\text{HCA})_2^-$, VO^{2+} (aq), and $\text{VO}(\text{tfac})_2$ at 40 K are shown in Figs. 3–5. To analyze the nitroxyl dephasing data, a model of the nuclear spin diffusion was developed (15). Curves calculated from the parameters that were used to simulate the nitroxyl spin echo decays in

the same solvents are shown as dashed lines superimposed on the decays for the Cr(V) and vanadyl complexes (Figs. 3–5). The agreement between experimental and calculated curves for $\text{CrO}(\text{HCA})_2^-$ (Fig. 3) and VO^{2+} (aq) (Fig. 4) is as good as that obtained for tempone (15). For $\text{VO}(\text{tfac})_2$ (Fig. 5) the experimental echo decayed more quickly than the decay calculated based on the solvent spin diffusion parameters that fit the data for tempone. It is proposed that this discrepancy is due to contributions to $1/T_m$ from librations. Librations have a larger effect on $1/T_m$ for vanadyl than for Cr(V) or nitroxyl radicals because of the much larger anisotropy in g and A values for the vanadyl ion (17). For Cr(V) and nitroxyl radicals $1/T_m$ and x are independent of temperature, within experimental uncertainty, between 20 and 40 K. For the vanadyl complexes, $1/T_m$ increased slightly and x decreased slightly between 20 and 40 K, which is consistent with increasing contributions from librations with increasing temperature. The proposal that librations contribute to $1/T_m$ for $\text{VO}(\text{tfac})_2$ is supported by the observation that $1/T_m$ varies through the spectrum, even at 40 K. However, for the $m_I = -\frac{1}{2}$ transition the effect of librations is small relative to the large effect of changing solvent at 40 K. The effect of librations on the decays for VO^{2+} (aq) in 1:1 H_2O :glycerol is smaller than for $\text{VO}(\text{tfac})_2$ in 9:1 $\text{CF}_3\text{CH}_2\text{OH}$:ethylene glycol because the multiple hydrogen bonds per solvent molecule and hydrogen bonding between water molecules of VO^{2+} (aq) and the solvent make the sample more rigid than for $\text{VO}(\text{tfac})_2$ in the organic alcohol mixture.

The similarity between the values of T_m and x as a function of

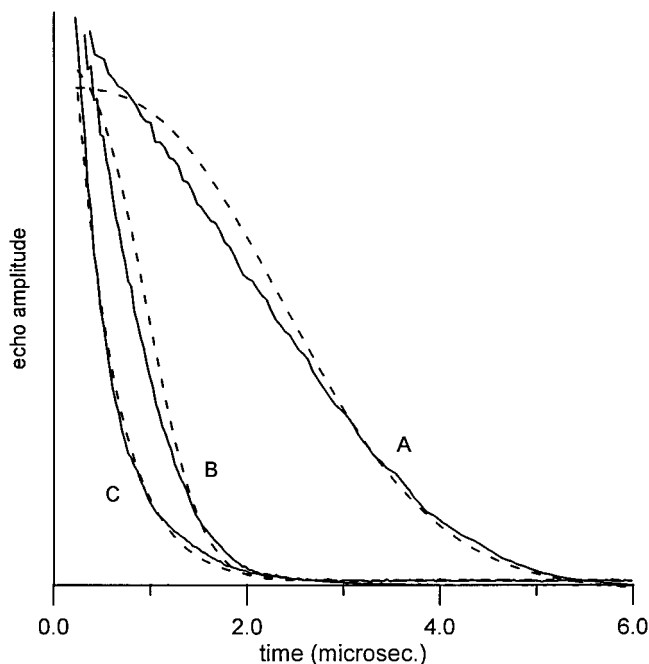


FIG. 5. Electron spin echo decays for 1.1 mM $\text{VO}(\text{tfac})_2$ at 40 K, 9.434 GHz, and magnetic field = 3343 G (the $m_I = -\frac{1}{2}$ transition) in (A) 1:1 H_2O :glycerol, (B) 9:1 *i*-PrOH:MeOH, and (C) 9:1 *n*-PrOH:MeOH. The dashed lines are fits to the proton diffusion model with the same parameters that were used to fit data for the nitroxyl radical tempone in these solvents (15).

solvent (Table 1) and the similarity between experimental and calculated curves in Figs. 3–5 indicate that the solvent effects on T_m observed for nitroxyl radicals also pertain to the Cr(V) and vanadyl complexes. We suggest that this effect of solvent methyl groups on echo dephasing is a general phenomenon that will affect dephasing whenever nuclear spins dominate.

CONCLUSIONS

In the temperature regime where $1/T_1 \ll 1/T_m$ there is substantial similarity between the spin echo dephasing for nitroxyl radicals (14, 15), Cr(V) complexes, and vanadyl complexes. In this regime (1) echo dephasing is dominated by solvent nuclei and is substantially faster in protiated solvents than in deuterated solvents, (2) at the same concentration of paramagnetic solute instantaneous diffusion plays a larger role in deuterated solvents than in protiated solvents, (3) in the absence of the effects of instantaneous diffusion, echo dephasing is independent of solute concentration, and (4) in protiated solvents echo dephasing is enhanced by methyl groups in the solvent, and these effects depend upon both the concentration and types of methyl groups. The upper limit for this temperature regime increases in the order vanadyl complexes < Cr(V) < nitroxyl radicals because of differences between T_1 for the paramagnetic centers. Dephasing for other organic radicals is likely to be similar to that for nitroxyl radicals.

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