1-H and 14-N NMR Relaxation Studies on Solutions of Mn(ClO₄)₂ in Acetonitrile

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Proton spin–lattice and spin–spin relaxation times of acetonitrile solutions of Mn(ClO₄)₂ between 298 K < T < 413 K have been measured over a wide frequency range (10 kHz < ν < 90 MHz). From these data and corresponding 14-N NMR line width measurements of acetonitrile at varying temperatures, it is possible to extract structural and dynamical parameters such as the number of complexed acetonitrile molecules, their mean lifetime in the first solvation sphere of the manganese ions, and the rotational diffusion constant of the [Mn(CH₃CN)₆]²⁺ complex.

KEY WORDS: 1-H, 14-N NMR relaxation; frequency dependence; paramagnetic electrolyte; acetonitrile; manganese perchlorate.

1. INTRODUCTION

The use of nuclear magnetic resonance (NMR) in the study of ion solvation has been extensively reviewed in the literature.¹⁻³ This method is particularly suited for solutions of paramagnetic ions, where the magnetic relaxation behavior of the solvent nuclei is dominated by the temporal modulated interactions between the unpaired electron spins and the nuclei in the solvation sphere around the paramagnetic center.⁴⁻⁸ For many relevant cases, on the other hand, the electron spin relaxation of the solvated metal ion itself depends on the fluctuating interactions with the surrounding solvent molecules. Especially for manganese ions, the time modulations of the quadratic zero-field-splitting interaction arising from Brownian motions of the paramagnetic complex and/or from collisions between the solvated ions and the solvent molecules are responsible for the EPR relaxation mechanism. Although the theoretical background describing the relaxation behavior of

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manganese ions is well established, there are still some features of solution spectra which are still unclear in the light of the present theories\(^{9-11}\); their interpretation raises some questions concerning the magnitude of several dynamical parameters such as the correlation time or the mean lifetime for the complexed solvent molecules,\(^{12}\) which are partially in contradiction if compared with corresponding data extracted from NMR relaxation studies.

Here, we report on measurements of the proton spin–lattice \((T_1)\) and spin–spin \((T_2)\) relaxation times in the frequency range between 10 kHz and 90 MHz on diluted solutions of Mn(Clo\(_4\))\(_2\) in acetonitrile between 298 and 413°K. From these data and additional line width measurements of the 14-N NMR absorption on Mn(II)–CH\(_3\)CN, it is possible to extract all micro-dynamical time constants such as the rotational diffusion correlation time and the mean lifetime of the [Mn(CH\(_3\)CN)\(_n\)]\(^{2+}\) complex. These data can also be used for a determination of the solvation number \(n\) of complexed CH\(_3\)CN molecules and the geometry of the complex. It is the aim of the present and previous investigations\(^{13}\) to correlate these data with EPR measurements at different frequencies on the same systems.

2. EXPERIMENTAL

All spin–lattice and spin–spin relaxation times between 4 and 90 MHz were performed in the usual way\(^{14}\) on a commercial spectrometer (Bruker B-KR 322s) equipped with a computer (B-NC 12). The 14-N line widths of Mn(II)–CH\(_3\)CN were determined by FT-NMR at 6.5 MHz (2.114 T). For the low-frequency range between 10 kHz and 2 MHz a home-built “field-frequency pulsed” NMR spectrometer has been used as described elsewhere.\(^{13}\) The standard deviation for both \(T_1\) and \(T_2\) was better than 10%.

Mn(Clo\(_4\))\(_2\)·6H\(_2\)O of analytical grade was carefully dried over P\(_2\)O\(_5\) under reduced pressure at 380°K for about 24 h. CH\(_3\)CN was distilled before use from P\(_2\)O\(_5\). All NMR sample tubes were thoroughly degassed on a high-vacuum line by at least five freeze–pump cycles and sealed before use.

3. RESULTS

Figure 1 presents the measured proton relaxation rates \((1/T_{1,2})\) of CH\(_3\)CN between 10 kHz and 90 MHz at seven different temperatures. For the sake of clarity the spin–spin relaxation rates are plotted only for five temperatures. The data, from which the contribution \((1/T_{1,2})_b\) of bulk-phase acetonitrile has already been subtracted, were obtained from samples differing in their Mn(Clo\(_4\))\(_2\) concentration \(c\), with \(c \ll 1\). Therefore, they are represented as “molar relaxation rates” \((1/cT_{1,2})\). All points are mean values of at least five measurements. Parallel to these proton relaxation times, the 14-N NMR absorption of Mn(II)–CH\(_3\)CN has been measured by FT-NMR.