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Rapid and simultaneous relaxometric methods to study paramagnetic ion complexes in solution: An alternative to spectrophotometry

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ABSTRACT

T_1 and T_2 relaxation times, measured with rapid and simultaneous continuous wave free precession (CWFP) and Carr–Purcell-continuous wave free precession (CP-CWFP) pulse sequences were used to study complexes of EDTA with paramagnetic ions in solution. The relaxation times of Cu(II)-EDTA and $[CuEDTA.NH_3]^{-2}$ complexes, from pH 1 to 13, measured in a 0.47 T time-domain nuclear magnetic resonance (TD-NMR) spectrometer show good agreement with the absorbance at approximately 730 nm. These methods were also used to study colorless complexes containing paramagnetic ions, not accessible by electronic spectroscopy, such as Mn(II)-EDTA. Therefore, these sequences can be used in any bench top TD-NMR spectrometers as faster alternative to spectrophotometry in analytical routine analyses.

1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy has been a powerful tool used to study structure and dynamic of organic and inorganic compounds [1–3]. However, most of these applications use expensive and sophisticated high-resolution spectrometers, based on heavy and bulk high field superconducting magnets. Therefore high-resolution NMR is rarely used in routine analyses when compared to ultraviolet–visible and infrared spectroscopies.

In the last decades much cheaper bench top spectrometers, based on permanent magnets, have been developed for medium and low-resolution applications [4]. Recently, medium resolution bench top spectrometers from 40 to 60 MHz (B_0 = 1 to 1.4 T) have been manufactured by several companies and are opening a new era for NMR routine analysis [5]. The medium resolution analyses are normally based in the frequency-domain spectrum, using chemical shift, spin–spin coupling and signal area, similar to high-resolution NMR analysis [6].

Much simpler NMR spectrometers, based on low field, normally from 0.05 to 0.5 T (2 to 20 MHz for ^1H), low homogeneity ($\Delta B_0 > 10$ ppm) and permanent magnets have been applied in quantitative analyses [7,8]. In these spectrometers all samples give a single and broad signal and the analyses are performed in time-domain, using free induction decays (FID) or spin-echoes signals [7,8]. This NMR spectroscopy is known as time-domain NMR (TD-NMR) [9].

TD-NMR measurements are much simpler and straightforward than medium and high-resolution NMR. TD-NMR methods have been used in industrial quality control processes for more than four decades [12], replacing laborious and time-consuming traditional methods in food [13,14], petrochemical [15,16] and cosmetic industries [17].

Additionally to the use of FID and echoes amplitudes, TD-NMR analyses can be performed using diffusion coefficient measurements and longitudinal (T_1) and transverse (T_2) relaxation times [10,11]. However, T_1 is rarely used because the measurement, performed with standard inversion-recovery pulse sequence is a long experiment (tenth of minutes) when compared to rapid (few seconds) T_2 measurement obtained with Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence [18]. Recently we have introduced some rapid methods (few seconds) to measure both relaxation times (T_1 and T_2) in a single experiment based on continuous wave free precession (CWFP) regime [7,8,13].

The CWFP method is a variation of steady state free precession (SSFP) pulse sequence [19,20]. CWFP regime is attained when a train of equally spaced radio frequency pulses with period $T_p < T_2^*$ (Fig. 1a) is applied to a spin system. T_2^* is the FID time constant that depend on T_2 and magnetic field inhomogeneity [8,19–21].

Fig. 2 shows the magnitude of NMR signal submitted to a train of π/2 pulses, $T_p < T_2^*$ and a precession angle $\psi = (2n + 1)\pi$, where n is an integer number [7,8]. After the first pulse, the amplitude is proportional to M_0. After the second pulse, the amplitude of signal between consecutives pulses oscillates and decays to a quasi-stationary state (QSS).

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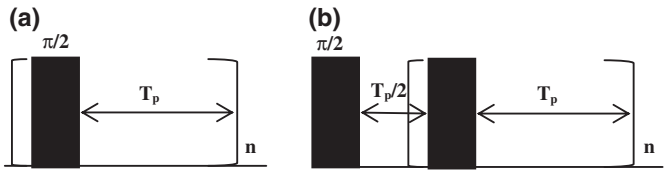

Fig. 1. a) Continuous wave free precession (CWFP) sequence, showing train (n) of π/2 pulses separated by time T_p. b) Carr–Purcell sequence with π/2 refocusing pulses separated by time $T_p/2$ between the first and the second pulse (CP-CWFP).

From QSS to CWFP constant amplitude (M_{ss}), the signal decays with a time constant T*. The M_{ss} amplitude and T* depend on both relaxation times according to Eqs. (1) and (2) [8].

$$M_{SS} = \frac{M_0 \times T_2}{(T_1 + T_2)} \tag{1}$$

$$T^* = \frac{2 \cdot T_1 \cdot T_2}{T_1 + T_2} \tag{2}$$

Rearranging these equations, we obtain the Eqs. (3) and (4):

$$T_1 = \frac{T^*/2}{M_{ss}/M_0} \tag{3}$$

$$T_2 = \frac{T^*/2}{1 - (M_{ss}/M_0)} \tag{4}$$

with M_0, M_{ss} and T* values obtained from the CWFP signal (Fig. 2a), T_1 and T_2 can be obtained using the Eqs. (3) and (4), respectively.

CWFP sequence is not indicated to measure the relaxation times, when T_1–T_2, because the dynamic range between QSS and CWFP state is minimal, which hinders the T* measurement [7]. For this situation, a pulse sequence known as Carr–Purcell continuous wave free precession (CP-CWFP) is applied. This sequence differs from CWFP only by the use of time interval $T_p/2$ between the first and the second pulse (Fig. 1b) [8]. The time interval after the second pulse is equal T_p, as in CWFP pulse sequence. Fig. 2b shows the CP-CWFP signal for a sample with T_1–T_2. Conversely to CWFP, for this type of sample, the dynamic range between QSS and CWFP state is maximum and T* is easily fitted.

In this study we demonstrated that CWFP and CP-CWFP are rapid and precise methods to measure both relaxation times (T_1 and T_2) of color and colorless complexes containing EDTA and paramagnetic ions in aqueous solution. The relaxation results in function of pH, obtained in a bench top TD-NMR spectrometer show similar variation to the absorbance of the electronic spectra. Therefore, TD-NMR relaxometry data obtained with CWFP and CP-CWFP sequences can be a simple and efficient alternative to spectrophotometry to study paramagnetic ion complexes in solution.

2. Experimental section

2.1. Reagents

The analytical grade salts $CuSO_4 \cdot 5H_2O$, $C_{10}H_{12}N_2Na_4O_8 \cdot xH_2O$, $(NH_4)_2SO_4$ and $MnSO_4 \cdot H_2O$ were purchased from SIGMA-ALDRICH and Synth (São Paulo, Brazil). The ion:EDTA complex (1:2 mol/mol ion-EDTA) solutions were prepared in concentration of 3.3×10^{-3} and 6.6×10^{-3} mol L^{-1}, respectively. For the NH_4^+ study, a 1.0 mol L^{-1} solution of $(NH_4)_2SO_4$ was used. These solutions were prepared by dissolving an appropriate amount of correspondent salt and adding a required amount of deionized water to reach the desired concentration.

2.2. Methods

2.2.1. pH

The pH measurements were carried out using a pH instrument, QX 150, Qualxtron. The equipment was calibrated before each measurement. The pH of ion:EDTA complex solutions was adjusted with NaOH and HCl solutions. After that deionized water was added to maintain the concentration and the ion:EDTA ratio, the pH was checked again.

2.2.2. Absorbance measurement

The absorbance measurements were realized with an UV/Vis spectrophotometer, model LAMBDA 25, Perkin Elmer. The measurements were realized in a plastic cuvette of 1 cm of optical length. The samples were scanning from 1000 nm to 500 nm, with a scan speed of 480 nm/min.

2.3. Relaxation times measurements

The relaxometric time measurements (T_1 and T_2) were performed in a bench top time-domain NMR spectrometer, minispec mq 20, Bruker (Germany) equipped with a permanent magnet of 0.47 T (19.9 MHz for ^1H), 10 mm probe at 28.0 ± 0.1 °C.

2.3.1. Standards methods

The longitudinal relaxation time (T_1) values were obtained using inversion-recovery (IR) pulse sequence using π/2 and π pulses with duration of 2.34 μs and 4.68 μs, respectively, recycle time of 5 s and 2 scans. T_1 was calculated using 36 IR experiments, with time between pulses distributed logarithmically from 0.1 ms to 10 s.

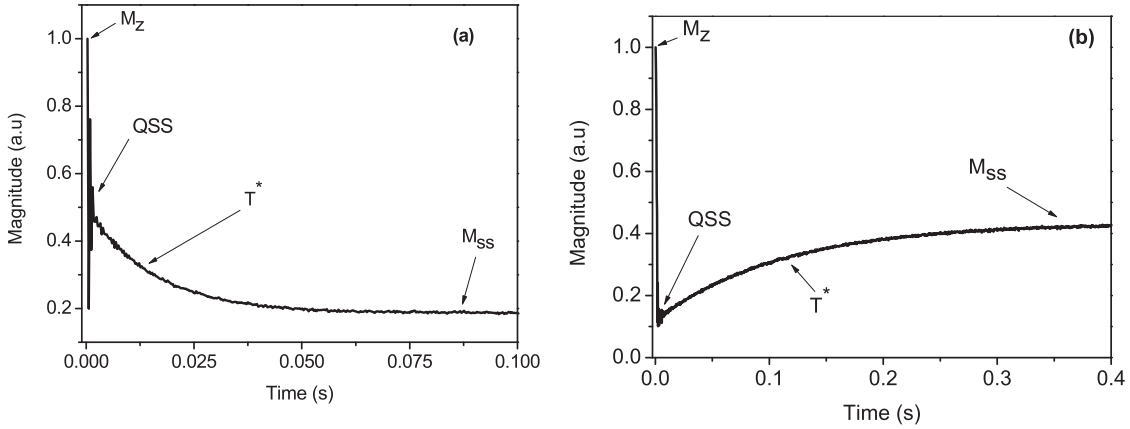

Fig. 2. a) CWFP signal for a sample with T_1/T_2 ~5. b) CP-CWFP signal for same sample with T_1/T_2 ~1.