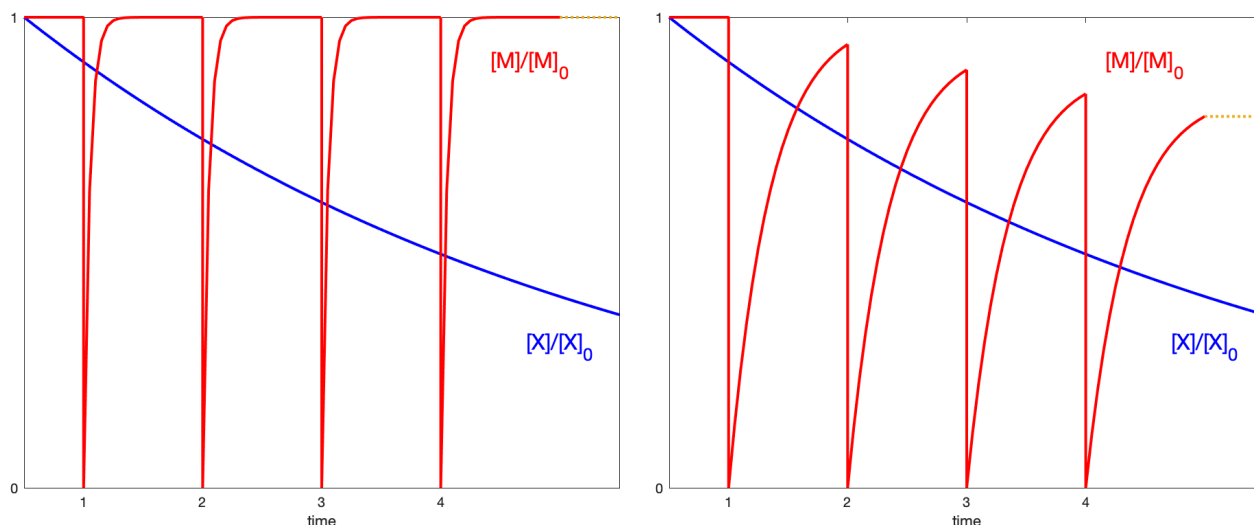


December 2024 NMR Topic of the Month: Kinetics and NMR



Ideally, what is going on here (left figure)?

Suppose you want to monitor a first order reaction by NMR. You are watching some species X with initial concentration $[X]_0$ decay over time. If there is plenty of time between transients ($\Delta t \geq 7T_1$ for a $\frac{\pi}{2}$ -pulse where T_1 is the longitudinal relaxation time) then you can be assured that the decay of the signal (S) depends only on the rate of the reaction (k). In this case, you can acquire the data, then (**properly**) integrate a signal from the target, fit those integrations to a first order kinetics equation ($[X] = [X]_0 \exp[-kt]$), and thereby determine the rate of the reaction.

But what if I do not allow enough time between transients (right figure)?

Now things are more complicated because in addition to the reaction's kinetics the magnetization's relaxation affects the quantity of signal. In other words, the concentration of target ($[X]$) is not the sole contributor to the magnetization ($[M]$) at a given time point. Now the signal at a given time point (S_i) is:

$$S_i \sim \{ [M]_0 \exp[-(t_i - t_1)/T_1] + [M]_{eq} (1 - \exp[-(t_i - t_1)/T_1]) \} \exp[-kt_i]$$

There are two magnetization terms that replace the target's concentration. The first magnetization term is the fully relaxed (true thermal equilibrium) term designated $[M]_0$, and the other is a the pseudo-equilibrium term designated $[M]_{eq}$. This pseudo-equilibrium results from repeatedly pulsing on the sample, and is known to be $[M]_{eq} = [M]_0 \frac{1 - \exp[-\Delta t/T_1]}{1 - \exp[-\Delta t/T_1] \cos\beta} \sin\beta$

where β is the pulse flip angle. Substituting back into the signal above and collecting terms yields:

$$S_i \sim [M]_0 \left\{ \left(1 - \frac{1 - \exp[-\Delta t/T_1]}{1 - \exp[-\Delta t/T_1] \cos\beta} \sin\beta \right) \exp[-(t_i - t_1)/T_1] + \frac{1 - \exp[-\Delta t/T_1]}{1 - \exp[-\Delta t/T_1] \cos\beta} \sin\beta \right\} \exp[-kt_i]$$

Note that $\lim_{\Delta t \rightarrow \infty} S_i \sim [M]_0 (\sin\beta) \exp[-kt_i]$, so $[X]_0 \sim [M]_0 \sin\beta$, which indicates that the amount of signal we had assigned to the concentration of target in the ideal case was proportional to the amount of fully relaxed magnetization multiplied by the sine of the flip angle - and that is correct.

References

1. NMR Topics of the Month from May, June, and July of 2022 and the references therein cited.