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Noble-Gas Relaxation Agents

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Noble gases such as ^{3}He or ^{129}Xe are of current interest because they may be very highly spin polarized by optical pumping methods (*1*). For applications of hyperpolarized systems, very long spin–lattice relaxation times are desirable; however, for studies at thermal equilbrium, practically short T_1 values are an asset to rapid spectral accumulation and quantitative comparisons. For example, we find that the ^{129}Xe T_1 in D_2O is 592 ± 37 s in a 11.75 T magnetic field, and a relaxation agent may facilitate experiments where equilibrium Boltzmann magnetizations are used to follow partitioning, binding, or spectral averaging processes.

Transition-metal complexes of diethylenetriaminepentaacetic acid are good choices of relaxation agents for aqueous solutions because the high-spin manganese(II) or iron(III) complexes are coordinatively saturated and the high metal–ligand association constants minimize other metal ion chemistry or binding interactions. Thus, all spin–lattice relaxation induced by these agents is outersphere. The addition of 10 m*M* $[MnDTPA]^{3-}$ to a D_2O solution in equilibrium with ^{129}Xe at 1 atm reduces the ^{129}Xe T_1 from 592 to 1.7 s in D_2O, and from 66 to 0.8 s in a 20 m*M* solution of α-cyclodextrin. These relaxation times are more practical for routine spectral acquisitions.

A simple application is shown in Fig. 1. The two samples contain a solution of 10 m*M* $[MnDTPA]^{3-}$ in D_2O, and are in equilibrium with 1 atm of xenon gas. In addition, one sample contains 20 m*M* α-cyclodextrin which binds xenon in the central cavity. Both samples were prepared by bubbling research grade xenon gas (BOC gases) through the solution for more than five minutes. Only one ^{129}Xe resonance line is observed for the α-cyclodextrin solution which is consistent with the report that xenon atoms are in rapid chemical exchange between the α-cyclodextrin binding site and the free aqueous environment.

The spectra, undistorted by spin–lattice relaxation effects, were acquired in several minutes and provide direct access to the equilibrium constant for xenon binding. If we assume that the concentration of xenon in the 10 m*M* $[MnDTPA]^{3-}$ solution is equal to that of saturated xenon in water, 4.37 m*M* (*2*), then the relative resonance intensities yield a total concentration of xenon in the α-cyclodextrin solution of 5.7 m*M*. This result implies an association constant for xenon binding to α-cyclodextrin of 16 M^{-1}, which is in reasonable agreement with the value of 20 M^{-1} reported by Bartik and co-workers based on chemical-shift studies (*3*). The xenon resonance line in the 20 m*M* α-cyclodextrin solution is shifted 2.05 ppm to a lower frequency relative to the solution that does not contain α-cyclodextrin. For a similar concentration of α-cyclodextrin, Bartik and co-workers report a chemical-shift difference of approximately 1.6 ppm. This disagreement of the chemical-shift differences may result from the absence of an internal reference and the change in magnetic susceptibility attending the addition of 10 m*M* $[MnDTPA]^{3-}$ to the solution.

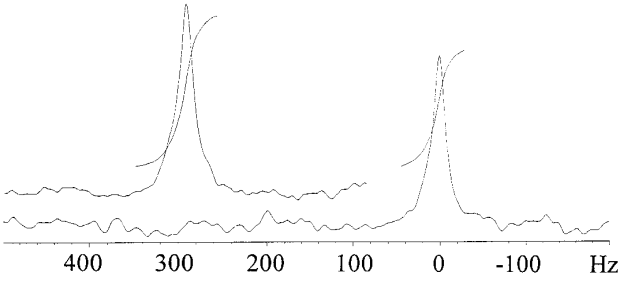

FIG. 1. ^{129}Xe spectra recorded with 64 transients using a Varian 500 MHz Unity*plus* Spectrometer with a 10 mm broadband probe tuned to 138.3 MHz. The deuterium oxide solutions are in equilibrium with 1 atm of xenon gas at 25°C and in both cases 10 m*M* $[MnDTPA]^{3-}$ served as a relaxation agent. The offset spectrum contains 20 m*M* α-cyclodextrin. The ratio of the resonance intensities implies an association constant of 16 M^{-1} for xenon binding to α-cyclodextrin.

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