Microporous and Mesoporous Materials xxx (2017) 1–4

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Sodium-23 NMR in porous media

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ARTICLE INFO

Article history:
Received 14 September 2016
Accepted 1 February 2017
Available online xxx

Keywords:
Sodium NMR
Quadrupole relaxation
Rotational correlation time
Reservoir rock

ABSTRACT

The enhancement in relaxation of ^{1}H spins adsorbed at pore walls is well known, described by the famous solutions of Brownstein and Tarr to the Bloch-Torrey diffusion equation with a partially absorbing boundary. Sodium-23 is an alternative nucleus that can be readily accessed at low field, providing a robust discriminator of brine from organic phases in petrophysics and a marker for aqueous ingress in construction materials. We examine NaCl brine in a chalk selected for its monodispersed pore size distribution. The ^{1}H T_2 distribution reflects the pore size distribution as expected. In contrast, the ^{23}Na T_2 distribution is broad and multimodal, consistent with relaxation outside the motional narrowing regime. To understand the ^{23}Na results, we determine the quadrupole coupling constant QCC and rotational correlation time τ_c, and show that well-defined single values of QCC and τ_c describe the observed relaxation behavior. Our observations call for a new interpretation for quadrupole relaxation in pores.

1. Introduction

The classic Brownstein and Tarr theory of diffusion in porous materials [1] has been applied successfully to interpret longitudinal T_1 and transverse T_2 relaxation time distributions in a variety of materials, from biological cells [2] to oil field reservoir rocks [3–5]. In the case of nuclear magnetic resonance (NMR) applied to oil field systems, ^{1}H spins are ubiquitous in both the oleic and aqueous fluid-phases. The usual contrast mechanisms of relaxation time and diffusion coefficient available at low-field provide, in favorable circumstances, separation of the NMR signal arising from these components [6]. An alternative robust fluid-phase discriminator is ^{23}Na, a spin-3/2 nucleus found uniquely in the aqueous-phase [7]. Together, quantitative ^{1}H and ^{23}Na NMR signal amplitudes provide robust oil and brine volumetrics, independent of pore geometry or liquid viscosity [8].

The ability to access ^{23}Na is advantageous for many applications. Salt crystallization is known to damage construction materials such as stone and concrete [9], and sodium content is a quality control indicator in the food industry [10]. However, very few articles address interpretation of sodium relaxation at pore surfaces. Rijniers et al. attempted to apply the theory of Brownstein and Tarr to sodium relaxation in order to extract pore size information [11]. The results were unsatisfactory because the "fast diffusion" model for ^{1}H spin relaxation in a pore cannot be extended, unaltered, to ^{23}Na. The sodium nucleus has four Zeeman eigenstates, resulting in two transition probabilities for excited spins. Outside the motional narrowing regime, the probabilities for the inner and satellite transitions differ, leading to biexponential relaxation for this quadrupolar nucleus [12,13].

To explore ^{23}Na in porous media, we consider brine in a chalk (limestone) selected for its monodispersed pore size distribution and low paramagnetic content. The ^{1}H T_2 distribution is narrow and monomodal, reflecting the pore size distribution in agreement with mercury injection porosimetry (MICP). In contrast, the ^{23}Na T_2 distribution spans over an order of magnitude. To interpret ^{23}Na relaxation at pore surfaces it is necessary to explore the fundamental parameters that describe quadrupole relaxation in liquids and soft solids, namely the quadrupole coupling constant QCC and the rotational correlation time τ_c. In this paper we explore these initial observations, possible mechanisms for the relaxation behavior, and call for a new interpretation of ^{23}Na relaxation in porous materials.

2. Theory

There are four Zeeman eigenstates associated with the quadrupole spin-3/2 sodium nucleus, resulting in two different decay probabilities for excited spins [14]. In general, the longitudinal relaxation rates are [12]

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http://dx.doi.org/10.1016/j.micromeso.2017.02.004
1387-1811/© 2017 Published by Elsevier Inc.

Please cite this article in press as: J. Mitchell, E.J. Fordham, Sodium-23 NMR in porous media, Microporous and Mesoporous Materials (2017), http://dx.doi.org/10.1016/j.micromeso.2017.02.004

$$\frac{1}{T_{1\mathrm{a}}} = Aj_1, \quad \frac{1}{T_{1\mathrm{b}}} = Aj_2, \tag{1}$$

and the transverse relaxation rates are [15]

$$\frac{1}{T_{2\mathrm{a}}} = \frac{1}{2}A[j_0 + j_1], \quad \frac{1}{T_{2\mathrm{b}}} = \frac{1}{2}A[j_1 + j_2], \tag{2}$$

where the spectral densities for pure quadrupole relaxation are [14]

$$j_n = \frac{\tau_\mathrm{c}}{1 + (n\omega_0\tau_\mathrm{c})^2}, \tag{3}$$

ω_0 being the Larmor frequency and τ_c the rotational correlation time. The pre-factor is

$$A = \frac{2}{5}\left(1 + \frac{\theta^2}{3}\right)\pi^2 \mathrm{QCC}^2, \tag{4}$$

where θ is the asymmetry parameter, with the quadrupole coupling constant

$$\mathrm{QCC}^2 = \left(\frac{eQ}{\hbar}\right)^2 \left\langle (eq(t))^2 \right\rangle, \tag{5}$$

where $\hbar$ is Planck's constant, eQ is the (constant) nuclear quadrupole moment and $eq(t)$ is the time-dependent electric field gradient at the nucleus. The observed recovery of longitudinal magnetization is

$$\mathscr{M}(t) = 1 - \left[\frac{1}{5}\exp\left\{-\frac{t}{T_{1\mathrm{a}}}\right\} + \frac{4}{5}\exp\left\{-\frac{t}{T_{1\mathrm{b}}}\right\}\right], \tag{6}$$

and the decay of transverse magnetization is

$$\mathscr{M}(t) = \frac{3}{5}\exp\left\{-\frac{t}{T_{2\mathrm{a}}}\right\} + \frac{2}{5}\exp\left\{-\frac{t}{T_{2\mathrm{b}}}\right\}. \tag{7}$$

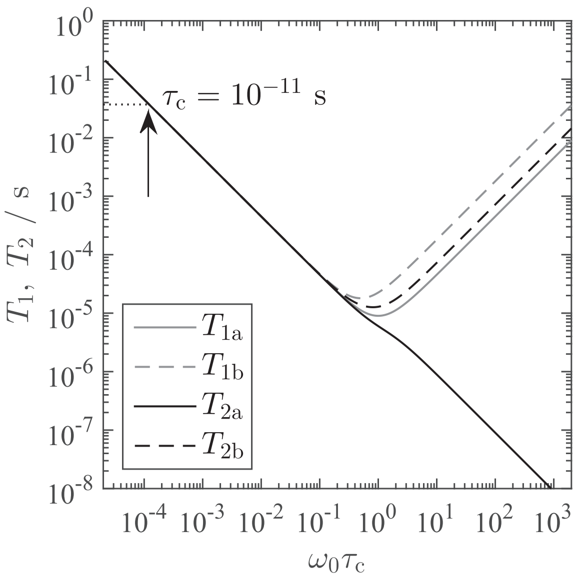

Fig. 1. Variation of ^{23}Na relaxation times with τ_c. The quadrupole coupling constant is fixed at $\mathrm{QCC} = 1.1$ MHz and $\omega_0 = 2.2 \times 10^7$ rad s^{-1} ($\nu_0 = 3.4$ MHz). The arrow indicates the theoretical correlation time for saturated NaCl solution at ambient conditions.

The relaxation behavior as a function of $\omega_0\tau_\mathrm{c}$ is illustrated in Fig. 1. Under the condition of motional narrowing (bulk ionic solutions) the relaxation rates collapse to a single value

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{2}{5}\pi^2\left(1 + \frac{\theta^2}{3}\right)\mathrm{QCC}^2\tau_\mathrm{c}. \tag{8}$$

We assume $\theta = 0$ for the symmetric hydration sphere of a sodium ion [16]. In Eq. (8) the rotational correlation time is defined by the solution viscosity η as

$$\tau_\mathrm{c} = \frac{4\pi\eta r_0^3}{3kT}, \tag{9}$$

where $r_0 = 0.201$ nm [16] is the Stokes radius of the sodium ion and kT is the Boltzmann temperature. Note that the relaxation rates for ^{23}Na in bulk solution are independent of Larmor frequency.

3. Materials and methods

An Oxford Instruments benchtop $B_0 = 0.3$ T permanent magnet ($\nu_0 = 12.9$ MHz for ^{1}H and $\nu_0 = 3.4$ MHz for ^{23}Na) was used in this study. The dual resonance (^{1}H/^{23}Na) solenoid radio frequency (rf) resonator was an active damping probe utilizing a feedback pre-amplifier to maximize signal-to-noise ratio (SNR) and minimize probe dead-time. The probe response was linear with sodium concentration for bulk solutions [17], to saturation, indicating negligible "coil loading" for this pre-amplifier concept.

Longitudinal relaxation times were determined using saturation recovery [18] with recovery times incremented logarithmically between $t_1 = 100$ μs and 300 ms in 32 steps. Transverse relaxation times were determined using the Carr-Purcell-Meiboom-Gill (CPMG) sequence [19–21] with $n = 750$ spin echo amplitudes recorded in each train and an echo time of $t_\mathrm{e} = 200$ μs. 128 repeat scans were summed, with 0.5 s delay between scans. Two-dimensional (2D) $T_1 - T_2$ correlations were obtained using the saturation-recovery-CPMG sequence. Experimental timings were identical to those for the individual T_1 and T_2 acquisitions. The 2D data were inverted to form $T_1 - T_2$ correlations using the method in Ref. [22] for separable kernels.

In general, the saturation-recovery-CPMG data for sodium are described by a kernel function of the form

$$\begin{aligned} k(t_1, nt_\mathrm{e}, \mathrm{QCC}, \tau_\mathrm{c}) = & \left[1 - \left(\frac{1}{5}\exp\{-Aj_1t_1\} + \frac{4}{5}\exp\{-Aj_2t_1\}\right)\right] \\ & \times \left[\frac{3}{5}\exp\left\{-\frac{1}{2}A(j_0 + j_1)nt_\mathrm{e}\right\}\right. \\ & \left. + \frac{2}{5}\exp\left\{-\frac{1}{2}A(j_1 + j_2)nt_\mathrm{e}\right\}\right], \end{aligned} \tag{10}$$

with j_n defined by Eq. (3) and A defined by Eq. (4). The only variables in Eq. (10) are QCC and τ_c. This kernel function is non-separable so a generalized inversion method from Ref. [23] was used to obtain $\mathrm{QCC} - \tau_\mathrm{c}$ correlations.

Stevns Klint chalk was selected as an "ideal" porous media, being a carbonate (modest surface relaxivity and weak internal gradients) with a narrow and monomodal pore size distribution (modal pore size of 1 μm). We expect sodium relaxation at the pore surface to be predominantly quadrupolar with a negligible dipolar contribution. A cylindrical plug of chalk (50 mm × 38 mm, length × diameter) was saturated in brine under vacuum. The brine was prepared with NaCl ionic strength of $I = 5$ mol cm^{-3}.

Please cite this article in press as: J. Mitchell, E.J. Fordham, Sodium-23 NMR in porous media, Microporous and Mesoporous Materials (2017), http://dx.doi.org/10.1016/j.micromeso.2017.02.004