

Sodium NMR relaxation in porous materials

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Abstract

The NMR relaxation of hydrogen nuclei of a fluid in a porous material is generally interpreted in terms of the Brownstein–Tarr model, in which the relaxation rate of the signal is inversely proportional to the pore size. We have investigated whether this model can be applied to the relaxation of Na nuclei in a NaCl solution in a porous material. The results indicate that the ion distribution over the pores can be obtained from an analysis of the Na NMR signal decay, if the pore sizes are roughly below 1 μm . This information is very useful for studies of combined moisture and ion transport in porous building materials.

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1. Introduction

Dissolved salts in porous building materials crystallize while drying. Generally this occurs at the surface, causing defacing, or just beneath the surface, where it may cause structural damage. In addition, salts promote corrosion of the reinforcement in concrete. A detailed knowledge of the moisture and salt transport is essential for understanding these deterioration processes. Some of the issues, which still have to be studied experimentally and theoretically are the chemical and physical interactions of ions with the material, the possible supersaturation of ions in a pore system, and the growth of crystals in pores [1–3]. Knowledge of the location of the ions, either in large pores or in small pores, might be essential. Nuclear magnetic resonance (NMR) could be a useful tool for obtaining this information.

It is known that the NMR relaxation of hydrogen nuclei can be used to determine the distribution of water over the various pore sizes. According to the Brownstein–Tarr model [4] the relaxation time of water

depends upon the size of the pore in which it is present. The relaxation time is inversely proportional to the surface to volume ratio S/V and therefore, directly proportional to the pore radius [4,5,7].

The relaxation behavior of sodium is more complex, because it has a quadrupole moment ($I = 3/2$). This can result in quadrupolar splitting. An example of this effect is studied by Delville and co-workers [8]. When a clay suspension is isotropic, no quadrupolar splitting is observed, whereas splitting is observed when the clay particles are ordered.

The central question of this paper is whether or not the Brownstein–Tarr model can be applied to dissolved Na ions in salt solutions confined in porous media.

First, the Brownstein–Tarr model is discussed. Special attention is given to the extra demands needed for the model to be applicable to sodium relaxation. Second, we discuss relaxation measurements in bulk solutions and in model porous materials. The dependencies of the relaxation time on the sodium concentration and the pore radius are investigated. Furthermore, the applicability of the model to porous building materials is discussed. Results for typical building materials, like mortar and calcium silicate brick are presented. We end this paper with some conclusions.

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2. Relaxation model

Because of the Brownian motion of water molecules, the relaxation of a ^1H NMR signal contains information on the size of the pore, which was proposed by Brownstein and Tarr [4]. Three relaxation regimes can be distinguished. For our purpose the so-called *fast diffusion regime* is of interest. In this regime the rate limiting step in the magnetization decay is the relaxation at the pore surface. In this regime the relaxation rate is given by,

$$\frac{1}{T_i} = \frac{1}{T_{i,b}} + \frac{S}{V} \rho_i, \quad (1)$$

where $i = 1$ or 2 , $T_{i,b}$ is the bulk relaxation time, S and V are the area of the surface and volume of a pore, respectively, and ρ is the surface relaxivity. Brownstein–Tarr did not consider the physical nature of the relaxation sources, they considered them as sinks of nuclear magnetization. A possible source of relaxation is the presence of magnetic impurities along the pore wall, which is often the case in building materials [6,7]. This model has proven to be widely applicable [5,9,10].

In principle, one might also apply the model to dissolved ions, as these also move by Brownian motion and therefore probe the pore space in a similar fashion as the water molecules. The Na ion diffusivity in a NaCl solution equals $1.3 \times 10^{-9} \text{ m}^2/\text{s}$ for a diluted solution [11] at 25°C , which is comparable to the self-diffusion of H_2O ($2.3 \times 10^{-9} \text{ m}^2/\text{s}$). So even the time scales for diffusion are of the same order of magnitude.

A complication could be that the Na ions have two regimes of relaxation: the fast modulation regime and the slow modulation regime. In the latter, the magnetization decay is bi-exponential because the central transition and the satellite transitions have different relaxation rates (common notation $1/T_{2,s}$ and $1/T_{2,f}$). The magnetization sink assumption is then inadequate. In order to be able to apply the Brownstein–Tarr model to sodium, the system must be in the fast modulation regime, i.e., the electric field gradients (EFG) experienced by the ion should be uncorrelated while it is probing the pore.

In the case of water the bulk relaxation is commonly neglected, since it is slow (of the order of 3 s) compared to the surface relaxation. For Na ions, however, this assumption does not hold. It is argued by, among others, Woessner [12] and Eisenstadt and Friedman [13], that the fast relaxation of Na ions in the bulk is caused by quadrupolar interactions, whereas for water dipolar interactions are mainly responsible for the relaxation process. In essence, the bulk relaxation of Na ions is driven by the EFG. Woessner concludes that the relevant EFG for the bulk Na ions is the EFG caused by the surrounding hydration water molecules. Therefore, the relaxation rate might vary with concentration change,

which alters the number of surrounding water molecules, or temperature variations, which change the overall density of the solution. Here, only the concentration dependence is discussed.

In applying Eq. (1) to Na, one should bear in mind that $T_{i,b}$ has a concentration dependence, which is likely to show up in the relaxation time for solution in pores. The surface relaxivity $\rho(C)$ may also vary with the concentration. The following equation describes the sodium relaxation,

$$\frac{1}{T_i(C)} = \frac{1}{T_{i,b}(C)} + \frac{S}{V} \rho(C), \quad (2)$$

where C is the concentration of the NaCl solution. By applying this relation to sodium, two basic assumptions are made. First of all, it is assumed that the ions are in the fast modulation regime, which means that the EFG felt by the ions is uncorrelated. This assumption also assures that there is no quadrupole splitting since the nuclei does not experience a net EFG. The criterion for this regime is $\omega_0 a^2/D \ll 1$ in which D is the diffusion coefficient and a the typical distance the ion has to travel to uncorrelate the EFG. Note that this is not necessarily the pore diameter; it also depends on the morphology of the pore surface. Second, the observed relaxation decays are assumed to be mono-exponential, which means that in the pore fast exchange occurs between the surface layer and the bulk. This is only the case when the time needed to probe the pore is much smaller than the time of the experiment ($\sim T_{i,b}$). The time needed to probe the pore is given by $t_D \approx r^2/6D$, where r is the pore radius and D the diffusion coefficient. For a pore of 100 nm, $t_D = 1.3 \mu\text{s}$, which is much smaller than the usual values of the relaxation time (order of 40 ms). We will discuss the validity of these assumptions in the next section.

3. Relaxation measurements

3.1. Solution

To verify the validity of Eq. (2), first information on the bulk relaxation is needed. Both longitudinal (T_1) and transverse (T_2) relaxation times have been determined for several NaCl concentrations at two magnetic fields: 0.78 and 4.7 T. The T_1 measurements are performed by a saturation recovery sequence, which starts with a train of random pulses, of average flip angle 75° , thereby completely destroying the magnetization. This pulse train is followed by a $[\frac{\pi}{2}-\pi$ -acquisition] Hahn sequence. By increasing the delay between the pulse train and the Hahn sequence the longitudinal relaxation can be probed. Fifteen logarithmically spaced delays are used. The saturation recovery sequence is used because it is insensitive to inhomogeneities in the B_1 field. Because our samples are large compared to the selected slice this

sequence yields more accurate results than of the more frequently used inversion recovery sequence. The T_2 was obtained from a Carr-Purcell-Meiboom-Gill (CPMG) sequence, being $(\pi/2)_x[-\pi_y\text{-acquisition}]^n$. Both sequences are applied using a constant magnetic field gradient. In the case of the CPMG sequence, care was taken that the measured signal decay was not affected by diffusion in the applied field gradient. This was checked by varying the inter pulse spacing and the gradient strength. The 4.7 T apparatus is home made with a superconducting magnet (20 cm vertical bore) from Oxford Instruments and equipped with a gradient coil from Doty Scientific (10 cm bore). The Na resonance occurs at 52 MHz. The 0.78 T apparatus consists of an iron-cored electromagnet and is equipped with an Anderson gradient coil set. This scanner is described in detail in [14]. The Na resonance occurs at 9 MHz. The sample temperature during these measurements was $(22 \pm 2)^\circ\text{C}$. Both the T_1 and the T_2 measurements of the NaCl solution show single exponential relaxation and $T_1 \approx T_2$. This is in agreement with the measurements and the theory of Woessner [12], corresponding to the extreme narrowing limit. The obtained relaxation rates $1/T_i$ are presented in Fig. 1. The observed relaxation rate is independent of the magnetic field strength but reveals an evident concentration dependence: $1/T_i = (15.4 \pm 0.9) + (2.3 \pm 0.3) \times C$ (in s^{-1} , C = concentration NaCl in molar). The results are in agreement with those found by Woessner [12] and Eisenstadt and Friedman [13] within experimental accuracy.

3.2. Porous material

Knowing the bulk relaxation times, and their dependence on the concentration, the relaxation times in porous materials can be studied. A dried silica gel was used as model porous material. The silica gel used was

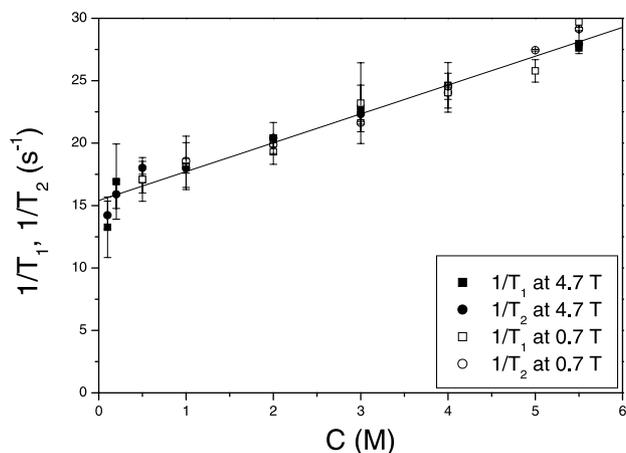


Fig. 1. The transverse and longitudinal relaxation rates of sodium in NaCl solutions at 4.7 and 0.78 T as a function of the concentration. The line represents a least squares fit to the data.

Nucleosil in six pore sizes: 5, 10, 12, 30, 50, and 100 nm. These pore sizes are the nominal values given by the manufacturer. The actual pore size can differ [15], which will be discussed later. A dry sample of Nucleosil was analyzed by NMR MAS spectroscopy at 11.7 T (Bruker AVANCE DMX-500) and revealed no sodium.

As mentioned above, Na ions have a quadrupole moment ($I = 3/2$). Therefore the energy levels can be shifted due to the presence of electric field gradients [17], resulting in a characteristic pattern in, for instance, a powder spectrum [18]. If such a powder spectrum covers a wide range of frequencies, not all ions are excited simultaneously. In order to be sure that all ions are excited in the NMR relaxation experiments, pulses should be used that excite the entire spectrum. To obtain information on this spectrum a series of samples, saturated with a NaCl solution, were analyzed in the 11.7 T Bruker spectrometer. For bulk solution, a single peak was observed, because the ions can tumble freely and by doing so any EFG is averaged out. The linewidth is 0.27 ppm. Also the spectrum of the NaCl solution in a Nucleosil sample revealed one peak with a linewidth of 0.86 ppm. This either means that the signal of the satellite transitions coincides with that of the central transition, because the net EFG is averaged out by ion motion, or that the satellite transitions in the spectrum may be broadened beyond detection. In the latter case, a loss of integrated signal intensity would occur. This hypothesis has been tested by measuring a NMR profile of both H and Na of a set of known samples. The profiles are presented in Fig. 2. Three samples are stacked in the 0.78 T apparatus, which has a tuned LC circuit with a Faraday shield to enable quantitative measurements [14]. The first sample consists of 1.136 g of 4.0 M NaCl solution in sponge. The sponge is used to suppress eddy currents which are likely to be induced in a conducting sample. The second sample is 0.316 g of

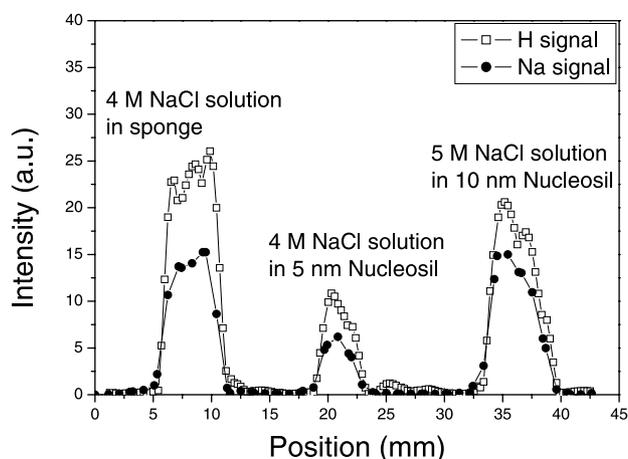


Fig. 2. The measured profiles of H and Na of three different samples.

4.0 M NaCl solution in Nucleosil with a pore size of 5 nm. The third sample is 0.9958 g of 5.0 M NaCl solution in Nucleosil with a pore size of 10 nm. The areas under the profiles were compared with each other. The calculated ratio of the areas Na/H is 0.587, 0.607, and 0.761 for the three samples, respectively. The first two should be the same, which they are within 3%. If we take the bulk sample as a reference, the 5 M NaCl sample Na/H area ratio should be 0.734, which it is within 4%. If the satellite peaks in the spectrum would not contribute to the observed Na profiles, a signal loss of about 60% would occur in the Nucleosil samples [12]. We conclude that the ions in the solution, confined within the pores, have no quadrupole splitting and no signal loss occurs. Hence absolute concentration measurements are possible. We wish to note again that all relaxation measurements presented here reveal mono-exponential behavior. At this point both assumptions underlying Eq. (2), fast modulation and mono-exponential relaxation, have been verified.

Next, we focus on the actual relaxation behavior of Na in pores. Samples with a nominal pore size of 10 nm were saturated with a 1, 2, 3, 4, and 5 M NaCl solution, respectively, and both T_1 and T_2 were determined at 0.78 T. During the experiments the temperature is kept constant at (20.0 ± 0.1) °C. To detect possible deviations from mono-exponential behavior, 100 logarithmically spaced delays were used in the T_1 measurement. No deviations are observed. The resulting relaxation rates ($R_i = 1/T_i$) are plotted in Fig. 3. The solid line represents the bulk relaxation rate (both transverse and longitudinal). The other two lines serve as guide to the eye. From Fig. 3 it is clear that T_1 and T_2 are different. As already outlined above, the magnetization decay is mono-exponential, which implies that the Na ions are in the fast modulation regime. Hence, in our opinion, the difference between T_1 and T_2 is caused by dipolar effects. These

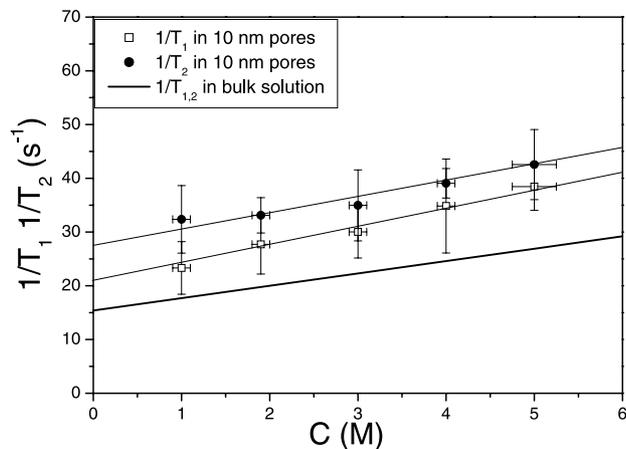


Fig. 3. The longitudinal ($1/T_1$) and transverse ($1/T_2$) relaxation rate of Na in 10 nm pores as a function of the NaCl concentration (C).

effects, caused by magnetic field variations near the pore wall, are known to decrease T_2 much more than T_1 (note that for H in 5 nm Nucleosil samples $T_1 = 0.5$ s; $T_2 = 17$ ms). These field variations are caused by magnetic impurities [6,16], or susceptibility mismatches [19]. The different slopes of the lines plotted in Fig. 3 might suggest a small concentration dependence of the surface relaxation term in Eq. (2). However, such a definite conclusion is not justified, given the limited accuracy of our experiments.

To study the relation between the relaxation rate and the pore size, the ultimate goal of our study, Nucleosils with six different pore sizes were saturated with a 4 M NaCl solution and T_1 and T_2 were determined. The sample temperature was controlled at (20.0 ± 0.1) °C. Again 100 logarithmically spaced delays were used in the T_1 measurements so that multiple exponential decays, if present, would show up in the results. In all cases, mono-exponential relaxation behavior is observed.

In Fig. 4 the sodium relaxation rates, both longitudinal and transverse, have been plotted against the inverse pore size. The pore size is determined by averaging the values obtained with different techniques, among which cryoporometry [15], BET, and mercury intrusion. This was done because earlier studies using these Nucleosils indicated that some of the actual pore sizes differ significantly from the nominal values [15]. As can be seen in Fig. 4 a clear correlation is found between the measured relaxation rates and the pore size. The difference between T_1 and T_2 increases with decreasing pore size. This can be caused by the larger probability of dipolar interaction with a smaller pore since S/V increases as the pore size decreases. The value of $1/T_2$ obtained in the 100 nm pores seems rather high, but the deviation from, e.g., the bulk value is still within experimental inaccuracy. Because also the relaxation times

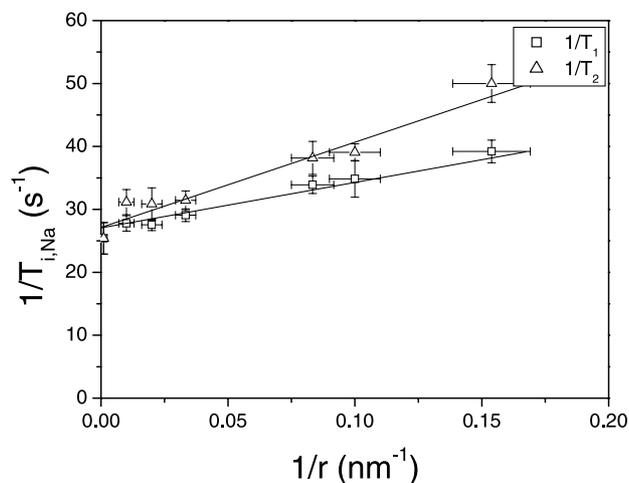


Fig. 4. The longitudinal and transverse relaxation rate for Na ions as a function of $1/r$ (pore size).

of water were measured for the Nucleosils the ratio between the surface relaxivities of H and Na can be determined: $\rho_{2,H} = 2.4\rho_{2,Na}$. From Fig. 4 we can conclude that the Brownstein–Tarr model applies for Na ions in solution.

4. Discussion

The results presented in this paper show that the Brownstein–Tarr model for relaxation in porous materials can be applied to Na ions in solution in porous materials. As already discussed in Section 2, the system has to meet certain requirements to allow for interpretation within this model. First of all, the time needed by the ion to probe the pore space $t_D \approx r^2/6D$ must be smaller than the time scale of the experiment. This is the fast diffusion regime as defined by Brownstein and Tarr [4].

Second, the system should have a fast modulation of the EFG. This criterion is met when $\omega_0 a^2/D \ll 1$ in which a is a typical distance the ion has to travel to uncorrelate the EFG. In isotropic or electrically neutral porous material, such as Nucleosil, this condition is fulfilled. In such a material, a nucleus only needs to travel a small distance over the surface to loose the net EFG. An example of a system in which this conditions are not fulfilled is laponite clay [8], where the Na ions are the counter ion for the clay particles. Therefore a large, non-local EFG exists and the slow modulation regime is observed by a bi-exponential relaxation.

The third criterion states that the surface relaxation must be fast enough to influence the relaxation behavior. It follows from Eq. 2 that $V/S < \rho/T_{2,b}$. When spherical pores are assumed and typical numbers are used, $T_{2,b} = 40$ ms, $\rho_{2,H} = 2.4\rho_{2,Na}$, and $\rho_{2,H} = (1.1 \pm 0.1) \times 10^{-7}$ m/s [20], we arrive at a pore radius of $3.4 \mu\text{m}$ as an upper limit for the pore radius for Nucleosil.

Until now we have only discussed measurements on a model porous material. We have performed T_2 measurements with two typical building materials to show how the model can be applied to less well defined porous media with a broad pore size distribution. According to Eq. 2, a broad range of T_2 relaxation times is expected for such materials. From the magnetization decay, a T_2 distribution was calculated with the CONTIN program [21]. The resulting distributions are presented in Fig. 5. Fig. 5A shows the distributions for H and Na in calcium silicate brick. Clearly three peaks are present in the distribution for H. These peaks correspond to the three pore sizes in calcium silicate brick, (of the order of 10, 1, and $0.01 \mu\text{m}$ [22]). Only two peaks can be seen in the Na distribution, which can be understood as follows. In the larger pores the bulk relaxation $T_{2,b}$ dominates the surface relaxation (Na: $T_{2,b} = 40$ ms, H: $T_{2,b} > 3$ s). As a consequence the method cannot discriminate between

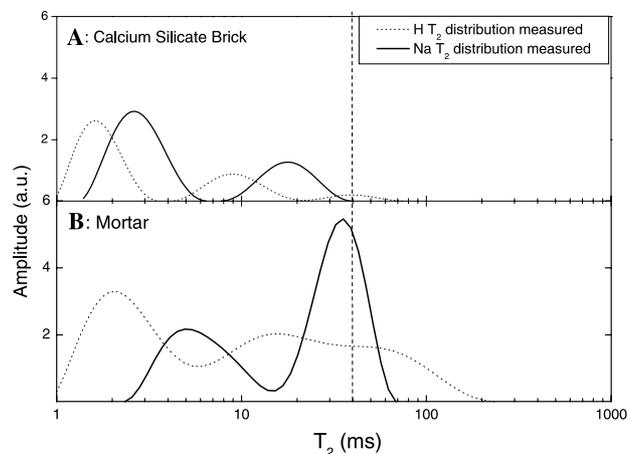


Fig. 5. The T_2 distributions of H (dotted line) and Na (solid line) in two building materials. The dashed line is the bulk T_2 for Na.

the two sets of larger pores (of the order of 10 and $1 \mu\text{m}$). Fig. 5B shows the T_2 distribution for H and Na in a NaCl solution saturated mortar sample. Similar behavior is observed as for the calcium silicate brick. In the Na distribution, the smallest pores can be identified. The other pores cannot be discriminated. Again the criteria, mentioned above, are met for the small pores (order $0.1 \mu\text{m}$) but not for the larger pores (between roughly 1 and $100 \mu\text{m}$ [22]). In order to be sure that the observed bi-exponential behavior is not a consequence of the slow modulation of the quadrupolar interaction, the mortar sample was partially dried after the measurement. When the sample was measured again only the small T_2 peak survived. This is a signature of the drying process. It is well known that in a partially dried medium only the big pores are empty [5]. This proves that the observed bi-exponential behavior has to be attributed to the pore size distribution and is not a slow modulation effect. To analyze the data quantitatively the relaxation curves have been fitted with bi- or tri-exponential functions. For the calcium silicate brick three exponents for water and two exponents for Na have to be used for an accurate fit. The fraction of nuclei in the small pores is 0.70 for H and 0.63 for Na. For mortar these fractions are 0.42 and 0.38 for H and Na, respectively. The fractions for H and Na are in good agreement with each other, which proves that the method enables us to measure Na concentrations in different parts of the pore system of a material.

5. Conclusions

We are able to determine pore size distributions of isotropic porous media by measuring the sodium relaxation and using the Brownstein–Tarr model. We have shown that this method is useful for pore systems with sizes smaller than $1 \mu\text{m}$, due to the fast relaxation of sodium in bulk solution.

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