



# Ionic strength-dependent pre-asymptotic diffusion coefficient distribution in porous media - Determination through the pulsed field gradient technique



Heng Wang<sup>a</sup>, Vladimir Alvarado<sup>b,\*</sup>

<sup>a</sup> Department of Petroleum Engineering, University of Wyoming, Laramie, WY, USA

<sup>b</sup> Department of Chemical Engineering, University of Wyoming, Laramie, WY, USA

## ARTICLE INFO

### Keywords:

PFG-NMR

Diffusion coefficient

Porous media

Ions

## ABSTRACT

<sup>1</sup>H pulsed-field gradient nuclear magnetic resonance was used to study early-time water diffusivity in porous media. The method has also been proven useful to characterize porous media from the standpoint of time-dependent diffusion. In porous media such as zeolite, biological cells or reservoir rocks, water molecular diffusion is time- as well as ionic strength-dependent. Diffusion phenomena are relevant transport mechanisms in low-permeability gas reservoirs and consequently in characterization efforts. Model systems are used here to unveil effects of ionic strength and pore size on the self- and effective-diffusion coefficient distributions. For this purpose, diffusion in aqueous phase in beadpacks made up of different glass bead sizes is analyzed. Ion size, ionic strength and hydration play an important role on the resulting diffusion coefficient. Ion-ion interaction leads to an increase of the diffusion coefficient by distorting water structure (hydrogen bond). While for the diffusion coefficient distribution derived using the regularized Inverse Laplace Transform method, ionic strength has little effect on the dominant peak position. With the increase in pore size, the dominant peak shifts to larger diffusion coefficient.

## 1. Introduction

Nuclear Magnetic Resonance (NMR) measurements of the spin-spin relaxation time ( $T_2$ ) and diffusion coefficient have been widely used to study the molecular motion in electrolyte solutions, emulsions, polymer and gels, and to characterize the structure of porous media and the properties of saturated fluids in a wide variety of systems ranging from biological cells, zeolites to reservoir rocks (Tanner and Stejskal, 1968; Brownstein and Tarr, 1979; Pouxviel et al., 1987; Schmidt-Rohr et al., 1992; Mitra et al., 1993; Morris et al., 1999; Sørland et al., 1999; Sevrugin et al., 2005; Beckert et al., 2013; Garcia-Olvera et al., 2015). In the oil industry, NMR  $T_2$ -distribution experiments have been widely used for rock characterization and fluid typing (Borgia et al., 1996; Kleinberg, 1996; Coates et al., 1999; Song et al., 2000). However, due to limitations that overlapping  $T_2$  distributions of different phases, such as water and gas/oil in the complex pore systems, separating out the different fluids based on  $T_2$  distribution analyses becomes a problem in both the field and the lab. To overcome these limitations, the diffusion-editing, Carr-Purcell-Meiboom-Gill (CPMG) technique, in which the signal is edited or reduced by allowing diffusion during the initial time, and the corresponding 2D-NMR model have been proposed to study fluid content and typing, and wettability alteration in conventional or

unconventional reservoirs. The resulting data can be plotted as a 2D map that shows the relationship between the restricted diffusion coefficient and the transverse relaxation time, named  $D - T_2$  map (Hürlimann and Venkataramanan, 2002; Vinegar et al., 1996; Flaum et al., 2005; Zielinski et al., 2011).

In gas reservoirs, diffusion is relevant in at least three different ways. First, gas diffusion represents a relevant and often complex transport mechanism that affects recovery in both conventional and unconventional reservoirs. For instance, modeling of gas drainage in coalbed methane requires knowledge of the diffusion from the matrix (Liu et al., 2017). Carbon dioxide transport in porous media in cases such as storage (Guo et al., 2016) and enhanced recovery (Kim et al., 2017) is heavily controlled by diffusion processes as well. In both cases, diffusive transport is likely multicomponent as well as multiphase. The complexity of these transport processes demands a clear understanding of what controls diffusivity constants in gas and liquid phases as well as surface transport, as it is commonly found in shale systems. Non-Gaussian diffusion associated with nanoscale and early-time scales couples with adsorption-desorption kinetics (Xia et al., 2017; Song et al., 2017; Liu et al., 2016). Second, transport processes through the aqueous phase, including molecular diffusion, play a role in multiphase flow mechanisms and their characterization in gas reservoirs.

\* Corresponding author.

E-mail address: [valvarad@uwyo.edu](mailto:valvarad@uwyo.edu) (V. Alvarado).

Understanding of water distribution through time-domain or low-field Nuclear Magnetic Resonance provides a means to estimate multiphase transport properties relevant to gas reservoirs (Wu et al., 2017; Yang et al., 2016). Third and tightly connected to the two previous aspects of diffusion, reservoir characterization frequently resorts to techniques such as Nuclear Magnetic Resonance (NMR) both in the field and in the lab with a petrophysical objective (Li et al., 2017b, a; Sun et al., 2016; Aliyev et al., 2016). NMR as characterization tool in porous media responds to diffusion time scales in pores and hence understanding its effect on relaxation mechanisms is vital to establish a connection between the magnetic response and the topology and geometry of the pore space.

Self-diffusion is a random translational (or Brownian) motion of molecules or ions which are driven by internal thermal energy (Stepišnik, 1993). The self-diffusion coefficient,  $D_0$ , is related to the mean squared displacement of a Brownian molecules or ions. The determination of self-diffusion coefficient of water by pulsed field gradient (PFG) NMR method have been widely used to analyze dynamical quantities and structure of water in aqueous solutions (Nilsson et al., 1996; Wagner et al., 2001; Mills and Lobo, 2013; Richardson et al., 2014). Recently, effective diffusion (or restricted diffusion) has also been used to probe structures in porous systems (Latour et al., 1993; Mitra et al., 1993; Morris et al., 1999; Mair et al., 2001) or emulsion droplets such as micellar and microemulsion solutions (Packer and Rees, 1972; Hughes et al., 2013; Bernewitz et al., 2014; Ling et al., 2016). The time dependence of a fluid effective diffusion coefficient in porous media can be used to obtain pore geometry information, such as surface-to-pore volume ratio and tortuosity (Latour et al., 1993; Mitra et al., 1993; Mair et al., 2001). The effective diffusion coefficient reflects the molecule diffusion path restricted by pore surfaces, which depends in turn on the observation time in pulsed field gradient NMR experiments. At early time, the mean squared displacement for free diffusion ( $l_D = \sqrt{6D_0\Delta}$ ) is significantly smaller than the average pore size and the measured diffusion coefficient is time dependent. By assuming piecewise smooth and flat surfaces, only a small fraction of the molecules can reach the restricting surface, Mitra et al. (1993) have shown the effective diffusion coefficient can be calculated as:

$$\frac{D(\Delta)}{D_0} = 1 - \frac{4S}{9V_p\sqrt{\pi}}\sqrt{D_0\Delta} + O(D_0\Delta) \quad (1)$$

where  $\Delta$  is the observation time,  $s$ ,  $D_0$  is the free diffusion coefficient in the bulk solution,  $m^2/s$ ,  $D(\Delta)$  is the effective diffusion coefficient in porous media,  $m^2/s$ , and  $O(D_0\Delta)$  represents higher order terms. For long times, in a sufficiently well-connected pore space, the mean squared displacement of the fluid molecules reaches an asymptotic or long-time limit and the diffusion coefficient becomes independent of time. The constant diffusion coefficient is expected to behave as (Dullien, 2012):

$$\lim_{t \rightarrow \infty} \frac{D(t)}{D_0} = \frac{1}{F\phi} = \frac{1}{\tau} \quad (2)$$

where  $F$ ,  $\phi$  and  $\tau$  are the electrical formation factor, porosity and tortuosity, respectively. A two-point Pade approximant is widely used to interpolate between short and long time limits (Latour et al., 1993):

$$\frac{D(t)}{D_0} = 1 - \left(1 - \frac{1}{\alpha}\right) \frac{c\sqrt{t} + (1 - 1/\alpha)t/\theta}{(1 - 1/\alpha) + c\sqrt{t} + (1 - 1/\alpha)t/\theta} \quad (3)$$

where  $c = (4/9\sqrt{\pi})(S/V)\sqrt{D_0}$ , and  $\theta$  has dimensions of time. The Pade approximate is used to interpolate between short and long time data and to extract  $\alpha$  and  $\theta$ .

As aforementioned, NMR diffusion measurements have been widely used in gas/oil reservoir rock characterization and fluid typing. However, none of the techniques considers the effect of ionic strength and components in the aqueous phase on the water diffusion coefficient in brines saturating gas/oil reservoirs. Since formation water composition and ionic strength varies in different reservoirs or in different

layers for same reservoir, their effects on self-diffusion and effective diffusion should be well studied, especially in NMR well logging (Kwak et al., 2005; Ligthelm et al., 2009). For the water self-diffusion coefficient in electrolytic solutions, when temperature is constant, many factors affect the self-diffusion coefficient. In no particular order, ions obstruct water molecules and decrease water molecules diffusion due to lower mobility (Wang, 1954); as a result of bound water molecules (hydration), consequently moving more slowly and also decreasing water diffusion (Wang, 1954); ion-water interactions may distort water structure (structure breaking effect) and increase diffusion (McCall and Douglass, 1965); ion-ion interaction also affects ions diffusion coefficient (Weiss and Nothnagel, 1971). Some computational studies on the structural and dynamic aspects in a wide range of concentration of the aqueous solution and their effect on self-diffusion of ions and water molecules have been conducted. Molecular dynamics (MD) simulation was performed with the rigid Simple Point Charge (SPC) water model and charged Lennard-Jones partials for ions. Simulation results show that the presence of ions perturbs the water associative structure (Bouazizi et al., 2006; Bouazizi and Nasr, 2011). As NaCl concentration increases, the local water structure is broken down and molecules are forced to occupy interstitial positions. The negative part of the water velocity autocorrelation functions (VACFs) is enhanced and consequently decreases the self-diffusion coefficient of water molecules. However, how the solvent ions change water molecular diffusion behavior in porous media is still unclear.

The use of PFG-NMR to analyze the diffusion coefficient spectra in porous media provides a picture of the pore size distribution or the fraction of large and small molecules in humic and fulvic acid samples by changing gradient strength (Sørland, 2014; Morris et al., 1999). Within short observation time limits, the root of the mean-squared displacement for a fraction of the diffusive water molecules near pore surfaces is reduced compared to the value of the bulk fluid free diffusion. In porous media, spins exist in a variety of different size pores, where the measured signal attenuation is a sum of contributions from all spins. As a result of the gradient increase, a deviation of the logarithm of intensity ratio will occur. If the internal magnetic field gradients are neglected, non-Gaussian behavior of the diffusion propagator is expected because of the complexity of the pore geometry experienced by diffusing water molecules during application of the applied gradient. When the gradient is kept constant by changing observation time within the limit of short observation time, fractions of the water molecules that can reach pore surfaces will change, which also results in a deduction of the magnetic signal.

Many methods, such as Inverse Laplace Transform (ILT) have been developed to interpret the diffusion coefficient distribution by a set of exponentials. The main characteristics of such problem is that it is ill-posed, i.e. multiple solutions might exist, and consequently a small noise level in the input data may cause a large change in the solution. To select a single solution from a set of possible solutions, regularization of the integral equation is widely used. Additionally, existing prior information, such as diffusion coefficient that should be positive and the principle of parsimony, are accommodated. A non-negative least square algorithm is used to fit diffusion coefficient decay curve (Istratov and Vyvenko, 1999).

The purpose of this study is to investigate the effectiveness of the PFG-NMR technique to characterize glass bead packs through short-time diffusion coefficient spectra considering the effect of brine composition, ionic strength and pore size, which provides insight into the NMR diffusion measurement applied on gas/oil reservoir rock characterization and/or fluid typing. First, dynamic properties of water molecules are analyzed by measuring self-diffusion coefficients of two brines, varying ionic strengths. Then, we estimate the effective diffusion coefficient on different size of glass beads saturated various brines. With a deep understanding of the effect of ionic strength on self and effective diffusion coefficient, the ionic strength dependence of the diffusion coefficient distribution is analyzed, which serves rock typing

Download English Version:

<https://daneshyari.com/en/article/8128506>

Download Persian Version:

<https://daneshyari.com/article/8128506>

[Daneshyari.com](https://daneshyari.com)