

Study of interaction of asphalt emulsion with mineral aggregate surfaces by nuclear magnetic resonance

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Abstract

There is a need to enhance the asphalt technology by enabling the production at lower temperatures, with compromising the performance as little as possible compared to the conventional approaches. Bitumen emulsion mixtures used in the cold asphalt technology offer certain advantages over hot bituminous road mixtures in terms of potential cost savings, environmental factors, energy savings and easing of logistical difficulties inherent with hot mix. During the process of mixing of bitumen emulsion with mineral aggregates processes of breaking of the emulsion occur followed by changes in physical and mechanical properties of the asphalt mixture. The purpose of this study was to explore processes occurring in bitumen emulsions – mineral aggregates and interactions near the mineral surfaces. Magnetic susceptibility gradient between solid and liquid generally results in purely NMR effects, which not related with molecular events occurring in liquid layers and in the liquid-solid interface: broadening of NMR resonance lines, accelerated NMR relaxation and NMR diffusion artefacts. One of ways to reduce the effect of the susceptibility gradient (ideally to zero) is to place a liquid between parallel flat surfaces of the studied solid support. We used mineral samples prepared as two pieces with flat polished surfaces and applied a thin layer of bitumen emulsion in-between them. Using this experimental approach we abolished artifacts related to roughness of surfaces of natural minerals, their porosity and distribution of sizes of voids intrinsic to dispersed powder used in practice. This methodology has allowed to study emulsion-aggregate surface interaction using NMR techniques. After the choice of NMR parameters, dynamic properties such as diffusion coefficients of confined bitumen emulsion and its components were measured using appropriate NMR pulse sequences.

1. INTRODUCTION

There is a need to enhance asphalt technology by enabling production at lower temperatures, while not compromising the performance compared to conventional approaches [1-3]. Bitumen emulsion mixtures used in cold asphalt technology offer certain advantages over hot bituminous road mixtures in terms of potential cost savings, environmental factors, energy savings and easing the logistical difficulties inherent with a hot mix [1]. Factors influencing the adsorption of bituminous material with aggregates are: the mineralogical and chemical composition of the mineral aggregate, the roughness of the mineral aggregate surface, the aggregate pore size distribution, viscosity, content, structure and reactivity of a bituminous emulsion, among others. During the process of mixing the bitumen emulsion with mineral aggregates, breaking down of the emulsion occurs, as well as development of physical and mechanical properties of the asphalt mixture [2,3]. These processes are complex in nature and have been described in the literature using different approaches [3]. The purpose of this study is to look at the processes occurring during the bitumen emulsion – mineral aggregate interaction near the mineral surface using nuclear magnetic resonance (NMR) methods.

NMR is a unique technique useful for studies of both structure and dynamics in complex liquid, solid and heterogeneous systems. NMR is applicable for systems containing molecules and ions with nuclei having non-zero spins, such as protons (^1H) with natural abundance (n.a.) of 99.985% and spin $I=1/2$, phosphorus (^{31}P , 100% n.a., $I=1/2$), non-radioactive carbon (^{13}C , 1.108% n.a., $I=1/2$), silicon (^{29}Si , 4.683% n.a., $I=1/2$), etc. [4]. An NMR experiment is performed on a sample placed in a strong static magnetic field, in which spins with different quantum states ($-I, -I+1, \dots, +I-1, +I$; i.e. $-1/2$ and $+1/2$ for spins with $I=1/2$) have different energies and different populations dependent on the gyromagnetic ratio (γ) of spins, the strength of the external magnetic field and temperature of the sample. For example, if a sample with water or an organic material such as bitumen, both having many hydrogen atoms, is placed in an external magnetic field of the strength \mathbf{B}_0 , intrinsic magnetic moments of protons adopt either a parallel or an anti-parallel orientation with respect to the magnetic field direction, known as $|\alpha\rangle$ (low energy) and $|\beta\rangle$ (high energy) states, respectively. Since the population of the $|\alpha\rangle$ state is slightly larger than that of the $|\beta\rangle$ state at moderate magnetic field strengths (9.4 T in the NMR spectrometer used in this study) and at ambient temperatures, the sample will have a macroscopic magnetisation parallel to the direction of the external magnetic field (z-direction). If a radio-frequency pulse with a frequency equal to the Larmor frequency of nuclear spins, $\omega_0 = \gamma \cdot \mathbf{B}_0$, is applied to the sample, the magnetisation vector will be inclined from the z-direction towards the xy-plane and will precess with the Larmor frequency generating electrical currents in the detection coil of the NMR spectrometer. This time dependent electrical signal is called the free induction decay (FID), which after the signal processing (Fourier transformation) gives rise to an NMR signal of the sample under study. The detected NMR signal is actually composed of a set of different resonance frequencies, which depend on the electron density and its distribution around different sets of nuclear spins in different chemical groups (so called the chemical shift) and on the presence of other magnetic nuclei coupled through chemical bonds (so called J-couplings) or through space (the magnetic dipole-dipole interaction). Therefore, NMR spectra contain useful information about the chemical structure of molecules and ions, intra- and intermolecular interactions, the structure of molecular aggregates and also on the local and translational dynamics of molecules and ions in the sample without a need of probe molecules. Therefore, NMR is a non-invasive and non-destructive technique that can be used to study molecular liquids such as oils [5], bitumen [6] and high-concentration emulsions [7-9] in bulk [9,10] as well as in pores of solids [5,9,10]. Since this method does not rely on the transparency of the continuous phase, NMR can produce size distributions in opaque systems such as water-in-crude-oil emulsions. One of the first applications of this method for sizing a water-in-crude-oil emulsion was conducted by Balinov *et al.* [7]. In their study, NMR self-diffusion was used to determine water-in-crude-oil emulsion droplet size, in addition to investigating the effect of aging, volume fraction of the dispersed phase, and the addition of demulsifier on the droplet size. It was shown that their results were in good agreement with parallel studies performed using optical microscopy.

In the current study, to explore processes related to the surface of the aggregates, we applied an approach that used samples specially prepared from two flat, polished aggregate (mineral) surfaces with a thin layer of bitumen emulsion placed between them. Using this experimental approach, we ignored the roughness of the surfaces inherent to real aggregates, porosity of the aggregates, and distribution of the sizes of voids intrinsic to dispersed aggregate powder used in practice. However, this approach has an advantage, because it allows one to focus to some degree on the emulsion-aggregate surface interaction. Actually, it is known that in heterogeneous systems, such as liquid confined in porous media, placed in a permanent magnetic field, a jump in the magnetic susceptibility taking place on the liquid-solid border leads to the appearance of a background gradient [11]:

$$G = \frac{(\mu_1 - \mu_2)B_0}{\mu_0 r} \quad (1)$$

where μ_1 and μ_2 are magnetic susceptibilities of the liquid and the solid, respectively, μ_0 is the magnetic susceptibility of the vacuum, B_0 is the induction of a permanent magnetic field, r is the radius of curvature of the surface.

The presence of background gradients (Eq.(1)) generally results in purely NMR effects, which are not related with molecular events occurring in liquid layers and in the liquid-solid interface: broadened NMR spectra lines, enhanced NMR relaxation, and NMR diffusion artefacts [4]. One way to reduce background gradients (ideally to zero) is to place a liquid of the substance being studied between parallel flat surfaces of the studied solid support. In this case, $r \rightarrow \infty$, therefore the difference in magnetic susceptibility of the liquid and solid substrate will lead to zero background gradient according to Eq.(1). Such an approach has been used earlier in NMR studies of oriented lipid bilayers [12] and ionic liquids [13]. In both cases blocks of dozens of parallel glass plates filled with liquids were used that did not increase the line widths of ^1H NMR spectra characteristic for bulk liquid layers between plates. Another source of background gradients is the presence of ferromagnetic particles in the structure of a solid support, which has happened for some minerals. In this case, even the use of a flat geometry for the liquid-solid interface may not completely remove background gradients.

2. MATERIALS AND METHODS

Slow-breaking bitumen emulsion of the EN-grade: C67B4 -160/220 (according to EN 13808) was provided by Nynas AB.

Glass plates (25 x 25 x 0.1 mm, Thermo Scientific Menzel-Gläser, Menzel GmbH, Germany) were used. Two plates, 25 x 3 mm, were cut off and carefully cleaned.

We have also studied two selected minerals used in cold-mix asphalt pilot tests (kindly provided to us by NCC), namely, aggregates from “Supartallen” and “Ljusberget”. According to the literature, the Supartallen mineral aggregate contains 96.4 wt.% granite and 3.6 % pegmatite [14]. Minerals used in the preparation of cold-mix asphalt usually have a complex composition and, sometimes, ferromagnetic and paramagnetic impurities (iron oxides and iron sulphides). As the NMR method is very sensitive to the presence of ferromagnetic particles, we estimated fractions of ferromagnetic particles in Supartallen and Ljusberget. For this purpose, we used fractions of the minerals with particles in the size range of 0.062-2 mm. The fractions were separated into magnetic and nonmagnetic fractions using a permanent 12 x 4-mm, disk-shaped *Nd*-magnet. Sample weight fractions of magnetic particles were 0.06 and less than 0.005 for Supartallen and Ljusberget, respectively.

2.1. Sample preparation

Bulk emulsion was measured in a standard 5-mm NMR tube, with a volume of approximately 300 ml. The tube was closed with a plastic stopper to avoid water evaporation and contact with air.

To reduce (or even remove) internal gradients, instead of mineral powders we used flat parallel slices of minerals (Figure 1). In this case, according to Eq.(1) $r \rightarrow \infty$, therefore $G \rightarrow 0$.

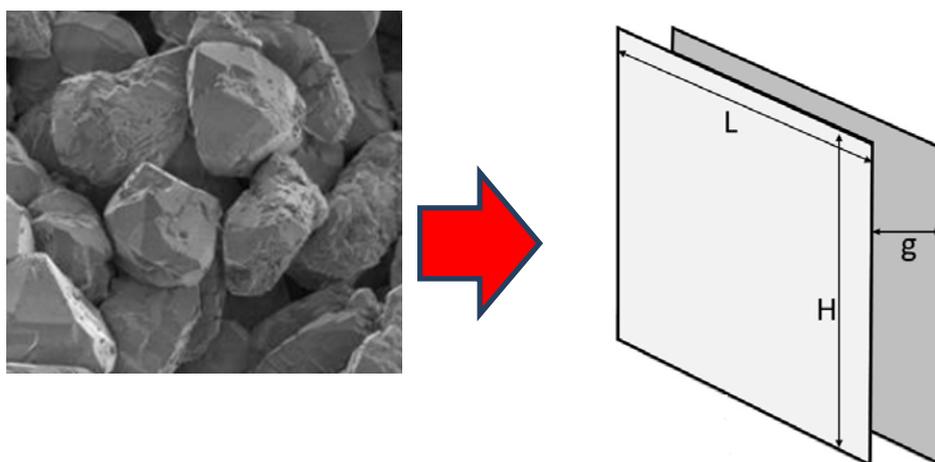


Figure 1: A Sketch illustrating the thin slices of Ljusberget and Supartallen minerals used to decrease the effects of background magnetic field gradients related to the inhomogeneity of magnetic susceptibility of the sample in NMR measurements

We used thin plates of borosilicate glass and of the minerals Supartallen or Ljusberget with thickness ~ 0.5 mm. Plates of Supartallen or Ljusberget were cut using a Struers Minitom cut-off machine (Struers ApS, Denmark) with further polishing (Figure 2). The final prepared plates were of the size 24 x 3 x 0.1 mm for glass and 25 x 3 x 0.5 mm for minerals. A drop of bitumen emulsion was placed between two plates of the same material (glass, Supartallen or Ljusberget) and gently pressed together by hand. Excess emulsion was removed from the edges of the

plates by wiping. The thicknesses of the emulsion layers were estimated by weighing; these were nearly 21 μm in each of samples. Plates with bitumen were adjusted to the internal diameter of the 5-mm NMR sample tubes with the surfaces of the plates oriented along the long axis of the tube (Figure 3). Tubes were closed with plastic stoppers.



Figure 2: Slices of Ljusberget (left) and Supartallen (right) minerals

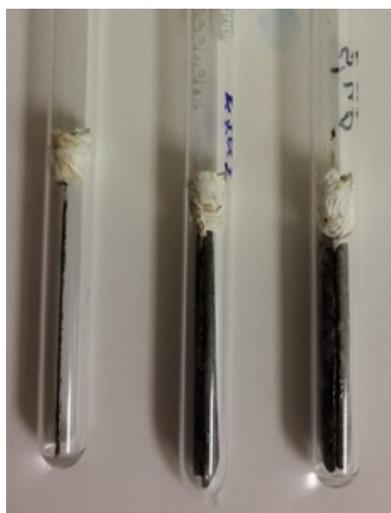


Figure 3: 5-mm NMR tubes with two slices and bitumen emulsion confined between them: glass plates (left), Ljusberget (center) and Supartallen (right). Each tube is closed with a PTFE stopper

2.2. ^1H NMR spectroscopy

NMR measurements were performed on a Bruker Avance III (Bruker BioSpin AG, Fällanden, Switzerland) NMR spectrometer with an Aeon 9.4 T zero-helium boil-off superconducting magnet. The working frequency for ^1H was 400.27 MHz. Data were processed using built-in Bruker Topspin 3.1 software. ^1H NMR self-diffusion measurements on emulsions were performed with a Pulsed-Field-Gradient (PFG) probe Diff50 (Bruker). NMR spectra were obtained by a Fourier transformation of free-induction decays (FID) obtained right after the applied 90° radio-frequency excitation pulse.

The primary information for the diffusion is contained in the diffusion decay (DD) of the NMR-stimulated echo (StE, Figure 4) amplitude A , which in the case of a simple non-associated molecular liquid can be described by the following equation (Eq. 1) [15,16]:

$$A(2\tau, \tau_1, g, \delta) = \frac{I}{2} \exp\left(-\frac{2\tau}{T_2} - \frac{\tau_1}{T_1}\right) \exp\left(-\gamma^2 \delta^2 g^2 D t_d\right) \quad (2)$$

where I is the factor proportional to the proton content in the system; T_1 and T_2 are spin-lattice and spin-spin relaxation times, respectively; τ and τ_1 are time intervals in the pulse sequences; γ is the gyromagnetic ratio for a

used nucleus; g and δ are the amplitude and the duration of the gradient pulse; $t_d = (\Delta - \delta/3)$ is the diffusion time; $\Delta = (\tau + \tau_1)$; and D is the self-diffusion coefficient. In our experiments, the StE pulse sequence was used for ^1H NMR diffusion measurements with the following parameters: $\delta = 2$ ms, $\tau = 5$ ms, $t_d = 10$ -1000 ms. PFG amplitude was varied from 0 to 29.8 T·m $^{-1}$. To check the effect of the background gradient of the magnetic field, we also applied a double-pulsed field gradient NMR [17] in some measurements.

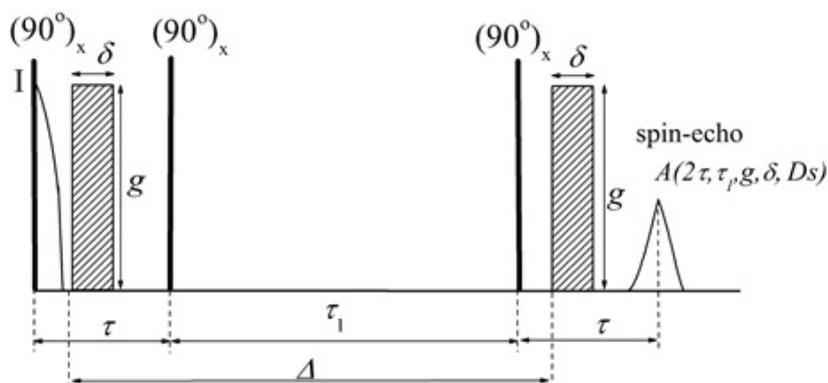


Figure 4: Stimulated spin-echo pulse sequence for self-diffusion measurements. In this figure, 90° radiofrequency (RF) pulses are shown as solid bars. Gradient pulses are shown as hatched rectangles

3. RESULTS AND DISCUSSION

3.1. ^1H NMR spectroscopy and diffusion in bulk bitumen emulsions

The ^1H NMR spectrum of the bulk bitumen emulsion reveals NMR signals from both water and bitumen components (Figure 5). The spectrum contains a resonance line with high intensity at ~ 4.6 ppm, which corresponds to bulk water, and several resonance lines in the range of 2.5 – 3.8 ppm, which correspond to bitumen aliphatic groups. The ^1H NMR line of water in the spectrum is much broader compared with that of the line in bulk water. Lines of bitumen are also poorly resolved. This is a consequence of the restricted rotational mobility of water and bitumen molecules and of the magnetic inhomogeneity of the emulsion. Indeed, the magnetic susceptibilities of water and bitumen are close, but different ($9 \cdot 10^{-6}$ and $9.5 \cdot 10^{-6}$, respectively); this leads to background gradients (Eq.(1)) followed by ^1H NMR line broadening. The ^1H NMR water signal is a factor of ~ 500 larger than that of the bitumen aliphatic signal.

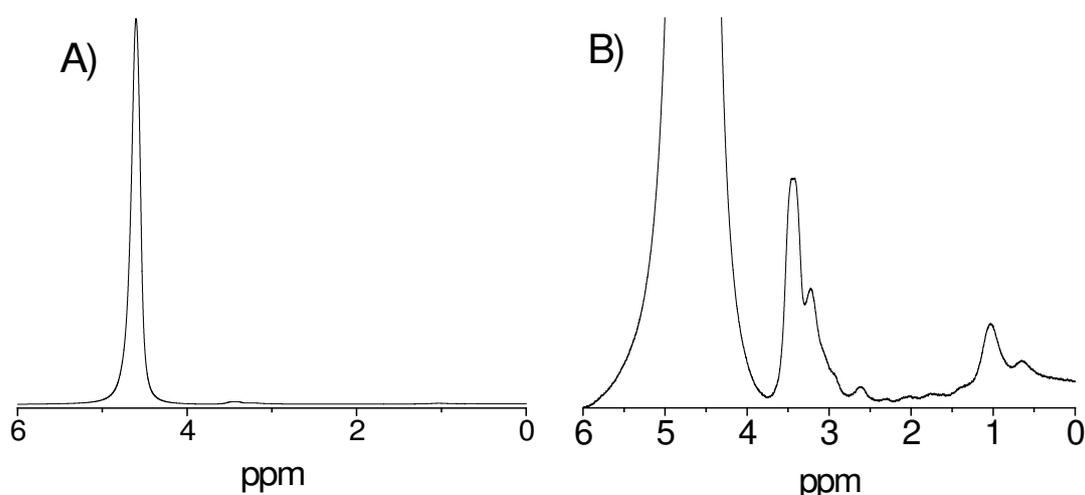


Figure 5: ^1H NMR spectrum of the bulk bitumen emulsion: A) a whole-range spectrum, which demonstrates mainly the water signal at ~ 4.6 ppm, and B) a magnified part (x 50) of the spectrum with the NMR signal at 2.5-3.8 ppm assigned to protons in bitumen

Diffusion decays of the total ^1H NMR signal are of a complicated form (Figure 6).

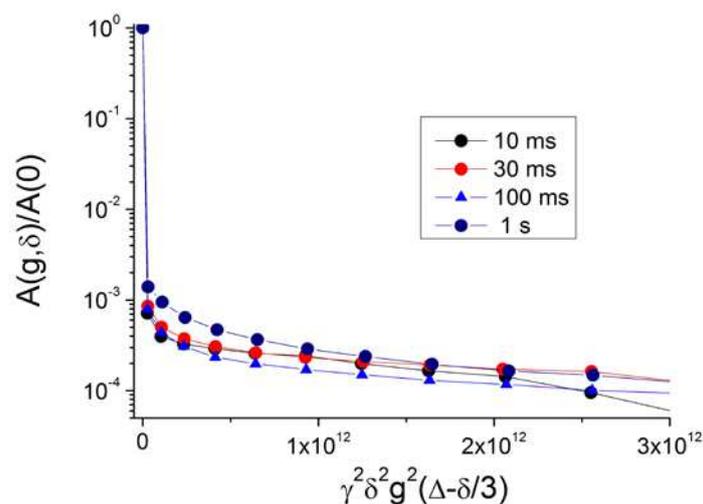


Figure 6: ^1H NMR diffusion decays for the bulk bitumen emulsion obtained at different diffusion times. Temperature is 20°C

An analysis showed that each of the decays can be described by the sum of two components with different diffusion coefficients:

$$A(g, \delta, t_d) = p_1 f_1(g, \delta, t_d D_1) + p_2 f_2(g, \delta, t_d D_2) \quad (3)$$

where p_1 and p_2 are fractions of protons, f_1 and f_2 are diffusion decays of particular components, and D_1 and D_2 ($D_1 > D_2$) are corresponding diffusion coefficients. It is known that the bitumen emulsion contains two main physical components, bitumen and water. To reveal the relationship of the diffusional components in Eq.(3) to the two main substances present in the emulsion, fractional diffusion was measured for ^1H NMR spectral components corresponding in the chemical shift ranges corresponding to water and bitumen NMR signals (Figure 5B). For both chemical shift ranges, diffusion decays demonstrate forms similar to those shown in Figure 6. This means that broadening of the ^1H NMR line, which originated from background gradients of bitumen emulsion, leads to overlapping signals from water and bitumen; fractional diffusion measurements give no advantages compared with diffusion decays of the whole ^1H NMR signal. The fast-diffusing component of decays in Figure 6 is characterised by $D \sim 1 \cdot 10^{-9} \text{ m}^2/\text{s}$, which is of the order of the value of bulk water. Bitumen emulsion is an oil-in-water (o/w) type emulsion stabilised by an emulsifier, where globules of bitumen (dispersed phase) are spread in the continuous water phase [3]. The fast diffusion coefficient related with water is independent of the diffusion time of the experiment. This agrees with the presence of water in the continuous phase of the emulsion.

The slowly-decaying component of diffusion decays in Figure 6 is characterized by $D \sim 3.5 \div 19 \cdot 10^{-12} \text{ m}^2/\text{s}$. This component can be assigned to bitumen globules of the emulsion. The apparent fraction of the protons associated with this slowly-diffusion component is only ~ 0.001 .

3.2. ^1H NMR spectra of bitumen-water emulsion between plates

Bitumen emulsion is a system that contains hydrophilic (polar) as well as hydrophobic (nonpolar) components, while the aggregate surface can contain hydrophobic and hydrophilic sites. Therefore, the interaction of the bitumen emulsion with the aggregate surface can be dependent on properties of the aggregate surface. Because of this, the spectra of single-component polar and nonpolar liquids placed between polar and nonpolar flat plates were studied on model samples. Water and decane were taken as examples of polar and nonpolar liquids, respectively. The surface of glass is highly polar, because it contains $>\text{SiO}$ and $>\text{Si-OH}$ groups. However, a glass surface can be modified by silanization, which makes it hydrophobic. Both, cleaning and silanization procedures are described in the ESI of the paper by Filippov et al. [18]. Contact angles for distilled water in polar and nonpolar plates were 0° and between 91° and 96° , respectively.

3.2.1. Water between polar plates

Figure 7 shows the ^1H NMR spectra of water between clean (polar) glass plates. A spectral width (SW) of 2000 ppm was taken to cover the whole range of chemical shifts. For bulk water, the spectrum presents a single line with ~ 4.6 ppm and line width of ~ 0.1 ppm. For confined water, the line width is ~ 68 ppm. The reason for this difference is not clear, but it was suggested [19] that water may form layers near a solid surface extended up to μm distance from the surface. This suggestion agrees with the strong depression of intensity of the water line in

confinement, which is comparable to that of the background of the spectrum. We tried also to confine water between nonpolar glass plates, but the water was always fully squeezed out from the space between the plates.

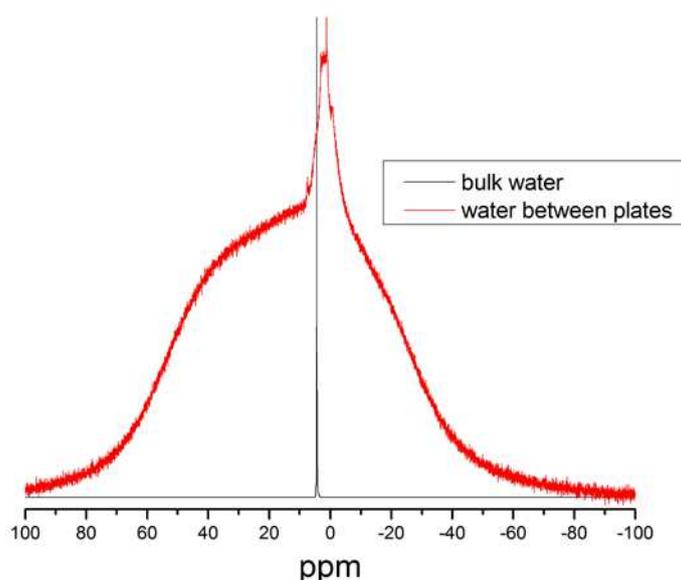


Figure 7: ^1H NMR spectra of water placed between polar (hydrophilic) glass plates (red line). The spectral width (SW) is 2000 ppm. The background of the spectrum is due to the NMR probe. The spectrum for bulk water (black line) is shown for comparison

3.2.2. Decane between polar and nonpolar plates

The ^1H NMR spectra for hydrophobic liquid decane in the layers between polar and nonpolar glass plates are shown in Figure 8. The ^1H NMR spectra of decane in bulk and decane confined between plates are composed of the narrow lines of CH_2 and CH_3 protons (line width ~ 0.1 ppm). The forms and integral intensities of these components are similar for polar and nonpolar surfaces, but intensities of the lines in the case of nonpolar surfaces are much lower, demonstrating a stronger interaction of hydrophobic decane with nonpolar plates. From these spectra, it is seen that the confinement does not change the line widths; the amplitudes of both characteristic lines are equally decreased, to a higher degree in the case of polar surfaces of glass plates compared to nonpolar surfaces.

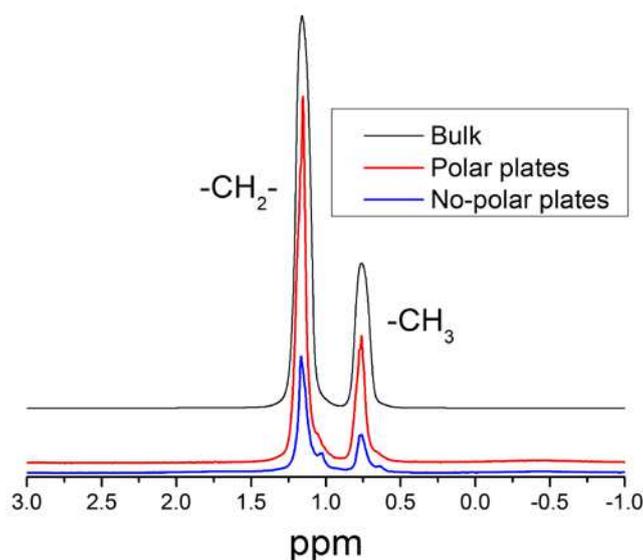


Figure 8: ^1H NMR spectrum of decane and narrow components of ^1H NMR spectra of decane placed between polar (hydrophilic) and nonpolar (hydrophobic) glass plates. Spectral widths in the experiment (SW) are 50 ppm

3.2.3. Bitumen emulsion between plates

The ^1H NMR spectra of bitumen emulsion confined between two plates of polar or nonpolar glass, and also between two plates of minerals are shown in Figures 9 and 10. Resolved spectral lines of water and bitumen chemical groups can be observed in the case of nonpolar glass plates (Figure 9), as well as the signal of bitumen in the case of Ljusberget and Supartallen plates (Figure 10).

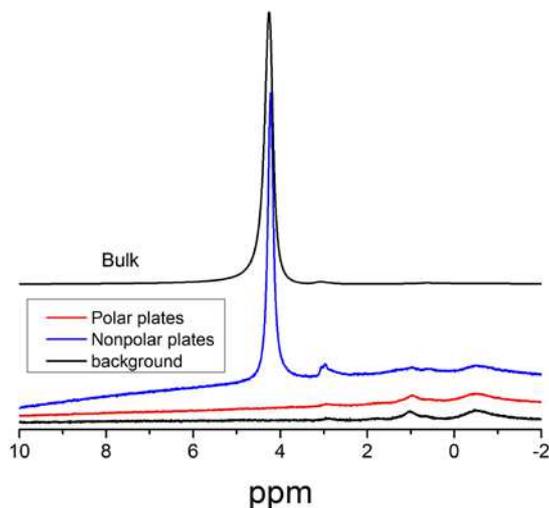


Figure 9: ^1H NMR spectra of a bitumen emulsion in bulk (upper black) and in confinement between two polar (red) and nonpolar (blue) glass plates. The lower black line is the background signal. SW = 50 ppm

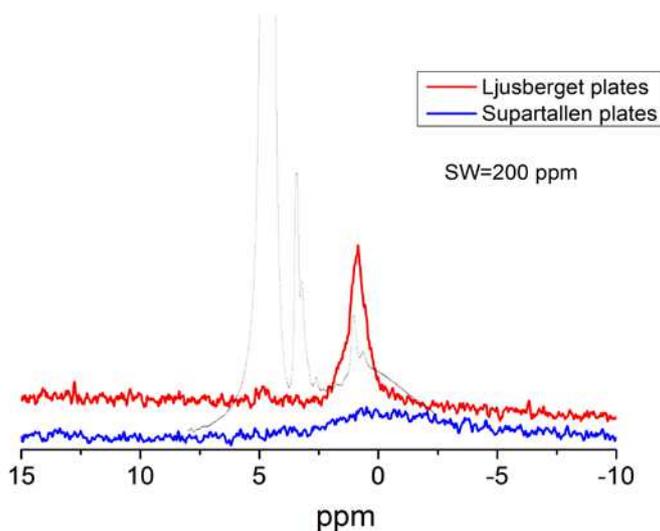


Figure 10: Narrow components of ^1H NMR spectra (SW = 200 ppm) of a bitumen emulsion layered between Ljusberget plates (red) and Supartallen plates (blue) plates. The dashed background line shows the spectrum of bulk bitumen emulsion, which is used as a reference

For water between plates, the line width of the spectra increases by a factor of ~ 46 (Figure 6), which agrees with a very strong interaction of water with the glass surface. This also agrees with earlier findings of water strongly interacting with glass plates and formation of a surface-induced structure of water in the layer [10]. Hydrophobic decane in the layers between polar and nonpolar glass plates shows a different effect (Figure 8). Two lines characteristic of the bulk spectrum were also observed for layers with the same line width, but the intensities of the lines in the case of nonpolar surfaces is much lower, demonstrating stronger interaction of decane in this case. Evidently, no long-range surface-induced structures are formed in systems prepared with decane. We also studied bitumen emulsion Nymix produced by Nynas AB (Sweden), which contains bitumen, water and additives, such as fatty acids, amines and anhydrides. For Nymix bitumen emulsion, the NMR spectra demonstrate a stronger interaction of the water component with the polar glass plates (red line in Figure 9). No characteristic water and bitumen resonance lines are observed, which suggests that the bulk structure of the bitumen emulsion was totally destroyed, because of its strong interaction with the polar surface. For the nonpolar surface, the spectrum (blue line

in Figure 9) does not change much in comparison with bulk, therefore we suggest that there are no strong interactions of the bitumen emulsion with the nonpolar surface. For the bitumen emulsion between mineral plates (Figure 10), no water signal is observed, because the emulsion droplets were destroyed, while signals of the bitumen component are more pronounced for the system with Ljusberget plates, which is less magnetic, and less pronounced for the system with Supartallen plates.

^1H NMR diffusion decays for bitumen emulsion layered between glass plates, and plates of Supartallen and Ljusberget are shown in Figure 11.

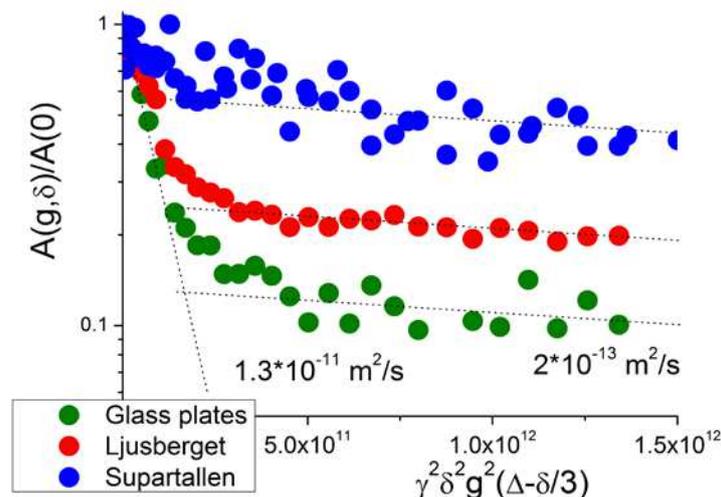


Figure 11: ^1H NMR diffusion decays for the bitumen emulsion confined between plates of glass (green), Supartallen (blue) and Ljusberget (red). $T = 20^\circ\text{C}$

Diffusion decays for the bitumen emulsion between plates demonstrate a two-component form similar to that of the bulk emulsion (Figure 6). Application of the double-pulsed field gradient pulse sequence did not change the results, showing that the diffusion is not affected by the background magnetic field gradient. As stated before (see Figs. 5 and 6), the fast-decaying component of the decay is due to water, while the slowly-decaying one is due to organic (polar) compounds of the emulsion. Despite the composition of the emulsion being the same, the ratios between observed fractions of the components in Figure 11 are different. This difference can be explained by the different emulsion – surface behaviours of the studied systems. In the case of the emulsion - glass system (green circles), the ratio of the diffusion component is closer to that of the undisturbed emulsion. This means that only some of the emulsion droplets were destroyed, while water was adsorbed on the glass surface, which leads to disappearance of the NMR signal from this part of the water. A larger fraction of water disappears in the sample prepared with Ljusberget minerals (red circles). Finally, the water NMR signal almost completely disappears for the sample prepared with Supartallen minerals (blue circles), demonstrating completely destroyed emulsion droplets and adsorption of water on the surface of the mineral aggregate.

4. CONCLUSIONS

In this study, we demonstrated how NMR spectroscopy and NMR diffusometry techniques can be used to study bitumen emulsion-aggregate systems. The most difficult problem in studying asphalt mixtures by NMR is the presence of background gradients due to differences in magnetic susceptibility in the system. This difficulty can be overcome by preparing samples with a flat geometry. After mixing the bitumen emulsion with mineral aggregates and the process of breaking down the emulsion, the emulsion can be studied by NMR. The latter has importance in understanding of breaking mechanisms in cold-mix asphalt blends of bitumen emulsions with different types of minerals and will be in the focus of our future work.

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