

material, saturated with acetonitrile and sealed. The NMR measurements were carried out at 9.4 T on a Bruker Avance DMX 400 spectrometer. The liquid and solid components were separated, on the basis of the spin-spin relaxation time, by employing a Carr-Purcell spin-echo sequence. The liquid at the interior of a pore solidifies at a temperature reduced according to the Kelvin equation¹ which relates the freezing point to the inverse pore radius, R . The intensity of the liquid component (I), as a function of the inverse temperature, can be expressed in terms of the well-known error function². By differentiating the expression for the intensity with respect to the radius the melting point distribution curve, dI/dR versus R , is obtained. Some representative results are shown in Fig. 1. The smooth increase in the intensity with increasing temperature is due to the gradual melting of the frozen liquid. The evaluated pore size distributions reveal two well-defined peaks as demonstrated in Fig. 2. The high-temperature transition point, giving rise to peak at the larger R -value in Fig. 2, is interpreted as the average depressed melting point of the confined substance. The intensity data indicate that a significant proportion of the liquid remains unfrozen even at 180 K. This low-temperature component is attributed to the non-frozen liquid at the pore walls and in micropores (or pockets).

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Overcoming mechanical and electronic instabilities in diffusion measurements with very high PFG-intensities

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Pulsed field gradient (PFG) NMR permits a most direct access to non-destructive and non-invasive investigation of transport properties of fluids in porous media. In particular, this technique allows direct measurements of the time-dependence of the mean square displacement and self-diffusion coefficient.

To overcome the severe experimental conditions if such studies are performed with adsorbed molecules in meso- and microporous host materials a 400 MHz (¹H) NMR spectrometer FEGRIS 400 NT was developed which combines the high NMR sensitivity of high field NMR spectrometer with our technology to generate stable bipolar pulsed field gradients of very high intensities. By using two TECHRON 8604 amplifiers in a push-pull configuration we are able to switch current pulses of up to ± 100 A with a maximum supply voltage of ± 300 V. This concept of the power supply yields pulsed gradient intensities in an actively screened Anti-Helmholz coil of up to ± 35 T/m over the active sample volume of 7.5 mm diameter and 10 mm length. The measured averaged gradient rise and fall time is 300 T/m per millisecond. 35 T/m are achieved after 150 μ s! This allows the reliable use of PFG NMR pulse sequences under the condition of short transverse relaxation times of adsorbate/adsorbent systems.

By using shaped pulsed field gradients with controlled deviation from rectangular shape, a high electronical and mechanical stability of the system is guaranteed. This is the precondition for the implementation of an automatic routine for the adjustment of the pairs of pulse field gradients, which is based on the determination of the spin echo position in the time domain. The high stability and this automated pulsed field gradient adjustment routine enable very long signal averaging times which now also permit ¹³C PFG NMR measurements on zeolitic adsorbate/adsorbent systems.

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¹H MAS and stray field gradient NMR on guest molecules and surface coatings in mesoporous silica MCM-41 and SBA-15

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After synthesis and characterization by X-ray diffraction and nitrogen adsorption the mesoporous materials MCM-41 ($d_{\text{pore}} \sim 3$ nm) and SBA-15 [$d_{\text{pore}} \sim 8$ nm) were loaded with small guest molecules or rendered hydrophobe by silylation with different silylating agents (HMDS, chlorated alkylsilanes). The mobility of the guest molecules in the pores was measured by stray field gradient NMR and compared with the bulk liquid. The data show significantly higher intensity at longer diffusion times. This can be interpreted either as restricted diffusion due to the pores' geometry or as anisotropic diffusion, which has a different mathematical description. ¹H MAS NMR spectra of non-loaded and loaded SBA-15 exhibit distinct differences, distinguishing surface OH-groups and water clusters. In the loaded silica spectra only one line is present, which renders a biexponential diffusion model improbable. Further MAS spectra on silylated SBA-15 prove the successful coating with hydrophobe functions like HMDS or alkylsilanes. In addition it is shown that water returns into the pores after calcination at 550°C.

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NMR measurements of the stagnant hydrocarbon fraction in two-phase flow through Fontainebleau sandstone

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Quantitative PGSE NMR measurements of the fractions of stationary and flowing dodecane present during two-phase (dodecane and water) flow through a Fontainebleau sandstone core are reported. Data have been obtained over the whole range from residual oil to irreducible water saturations at observation times in the range 0.2–2.0 seconds. The experimentally determined dependence of the static hydrocarbon fraction upon relative saturation is compared with the predictions of percolation models.

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Water dynamics on MCM-41 surface

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The properties of simple liquids in the vicinity of solid surfaces or confined in some specific regions have drawn much attention. For liquids in contact with a single smooth solid surface, layering of the molecules is induced [1–3]. A detailed knowledge of the adsorbate dynamics and diffusion in porous systems is essential in understanding the adsorption and catalytic properties of materials. Recent advances in both theory and experimental techniques have substantially increased the level of information obtainable by NMR characterization of porous materials [4]. The use of double quantum filtered (DQF) NMR spectroscopy as a diagnostic tool for the detection of anisotropy in porous systems has recently been developed [5,6]. It may be utilized as a sensitive tool to determine the residual quadrupolar interaction resulting from adsorption. In particular, for the $I = 1$ spin system, the DQF spectrum vanishes in the isotropic medium, and hence its observation indicates the presence of the adsorbed spin-bearing

molecules. In this work, we report on the use of deuterium NMR relaxation studies to investigate the temperature-dependent water dynamics and exchange process in various D₂O-loading MCM-41 systems. In addition to the usual investigation by T₁ and line shape analysis, DQF NMR with different evolution time was also employed in the analyses. Water-saturated mesoporous material is commonly studied by conventional NMR methods [1]. It is believed that the water molecule interacts specifically with the adsorption sites available on the pore surface. Generation of DQF signal may be helpful in selective excitation of adsorption related spin species [4]. The method is particularly advantageous to the study of molecular adsorption in unsaturated sample in order to decipher the various adsorbate dynamics. We employ a three-sites exchange model and a modified form of the Brainard and Szabo's cone model [7] to calculate the spectral density functions for restricted motion of adsorbed water molecules. We then determine the amount of monolayer water and the liquid mobility on the surface. In terms of the residual quadrupolar interaction, the solid like pattern with ~4 kHz edge splitting reflects the presence of anisotropic interactions upon adsorption on pore surface. e.g., the "slow site." Besides, by increasing loading, it is found two additional sites for water adsorption on MCM-41, namely "fast site I" and "fast site II." The amount of D₂O distributed in each site depends on temperatures and also on loading. The signals of D₂O in slow site dominate the observed DQF NMR. Based on the characteristic motion of D₂O, it is believed that the adsorption of D₂O in slow site is associated with the silanol groups on the MCM-41 surface. Fast site I for D₂O adsorption is adjacent to those adsorbed in slow site, and D₂O are exchangeable in these two sites. D₂O in fast site II is next to fast site I and is only exchangeable with fast site I. The signal of D₂O in fast site I is observed not only in single quantum spectra, but also in DQF spectra through the exchange process. By comparing with the simulation results, it is found that when the loading of D₂O in fast site I is saturated, the wobbling motion of adsorbed D₂O in slow site becomes fast, but it has no influence on the internal rotation. The momentum transfer through collision from D₂O in fast site I may account for the escalation of the wobbling motion of D₂O in slow site. Equivocally, it may induce the translational diffusion of D₂O in this site [8].

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Simulation of two-phase liquid transport in porous media: development and evaluation using MRI

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An understanding of the transport of hydrocarbons and water in a porous medium is key to our ability to optimise oil recovery and soil remediation processes. Previous work has compared model predictions with macroscopic experimental parameters, giving limited insight as to the extent to which the physics of the problem is adequately represented in the model. In this work, predictions of the 3-D distribution of hydrocarbon and water are compared directly with pore-scale MRI visualisations for the infiltration of water into a hydrocarbon-saturated model porous medium (randomly packed spherical ballotini), and the dissolution of the resultant trapped hydrocarbon fragments (ganglia) by a flowing aqueous stream. Hydrocarbon and water are selectively imaged using T₁-contrast.

Infiltration of water into the hydrocarbon-saturated bed is simulated

using an invasion percolation (IP) description. The IP algorithm is applied to a pore network model generated from the initial image of the hydrocarbon-saturated packing. The algorithm determines the next pore(s) located adjacent to the oil-water interface to be invaded, based on consideration of the effects of both capillary pressure and gravity. During infiltration by water, hydrocarbon ganglia will become separated and remain trapped in the pore space by capillary forces. The location and volume of these ganglia are observed using MRI, and compare favourably with the results of the IP simulation. The dissolution of the ganglia is then imaged as water is flushed through the packing. To model dissolution a Cellular Automata (CA) algorithm has been used. The initial 3-D image of the ganglia is used as the lattice to which the CA simulation is applied. Comparison of these MR images with the numerical predictions shows adequate agreement between model and experiment. However, it is clear that the dissolution process is influenced by the aqueous flowrate in the pores adjacent to the entrapped ganglia. When velocity data, obtained directly from the 3-D velocity maps of the system, are included in the CA dissolution model, the agreement between experiment and simulation is significantly improved.

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Long range order of surface water in glass pores

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In this report the effect of temperature and pH on relaxation of water protons confined within porous glass are presented.

In the first part hydration and pore size are analyzed. The long range surface order is derived from the relaxation's dependence on temperature and hydration. The nature of the temperature dependence of 1/T₂ of water protons in porous glass is unexpected since the rate decreases with decreasing temperature.

We will show that silica surface perturbs water over large distances. We will use the terms short range surface water for water that is strongly perturbed by the surface. The range of such strong interactions may be a few molecular layers. In addition there exists long range surface water, which is affected only weakly, but over longer distances of perhaps several hundred molecular layers.

It will be shown that ordered water and the precursors to freezing are in competition, the result of which is a severe suppression of long range surface order with decreasing temperature.

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Diffusion of fluids inside cross-linked elastomeric materials

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Diffusion of fluids inside elastomeric materials and related swelling phenomena are widely applied in polymer science with the purpose to investigate chemical and physical properties, leading to design of highly performing materials [1,2]. These elastomeric materials are widely applied in industrial manufacturing and the preparation could be very critical in order to achieve good performance. A simple and very effective method of characterisation is based on visualisation of solvent penetration by NMR imaging which allows a detailed investigation of chemical and physical equilibria avoiding any significant interference with the occurring phenomena. In this work, we have investigated polybutadiene rubber samples characterised by different cross-link density chemically induced in the network chains. Selected materials were shaped in disks and subjected to