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# Phase separation of miscible fluids in mesoporous media monitored by q space microscopy and relaxometry

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**Introduction:** The distribution of mixtures of fluids in geometric confinement is affected by the differential interaction of the individual components with the interface. Radial density functions of the molecular distribution reveal that, depending on fluid combinations, density variations occur from between one to several molecular diameters away from the surface. Overall molecular dynamics must therefore become significantly affected if the pore sizes do not exceed dimensions of several nm. Important factors that affect the molecular distribution are firstly polarity of the surface and the molecule, furthermore molecular shape, proticity and charge distribution. In order to experimentally verify the molecular distributions in mesopores, neutron scattering and in particular NMR represent suitable approaches: deviations of molecular locations from their bulk behavior affect both the NMR spectral features and the relaxation properties, whereas translational motion both on a micro- and macroscopic scale enter into the diffusion behavior. Q space studies of transport properties as a function of encoding time are the preferred approach to visualize the equilibrium distribution of liquids in the pore space and to quantify their long-range mobility.

**Methods:** Binary mixtures of liquids were prepared with one component perdeuterated, and were filled into Vycor porous glass as well as several types of silica gels. Samples included acetone/cyclohexane, THF/cyclohexane and acetone/water which are all fully miscible in the bulk. Relaxation times $T_1$ and $T_2$ of $^1H$ as well as $^2H$ were determined for a range of Larmor frequencies between 1 kHz and 300 MHz, employing field-cycling relaxometry for the majority of studies. Diffusion coefficients as a function of encoding time were determined by PFG methods on 1T and 7T scanners. For selected fluid combinations, MD simulations were carried out for equivalent cylindrical silica pores, from which radial density profiles and diffusion coefficients were computed.

**Results and Discussion:** For acetone/cyclohexane, a pronounced reduction of the apparent tortuosity – the ratio of bulk to confined diffusivity – was found in acetone but was absent in cyclohexane [1,2]. Similar observations were made for water and acetone, suggesting a trend of surface affinity in the order water>acetone>cyclohexane. Very long NMR relaxation times confirm that cyclohexane is removed from the silica surface unless it constitutes the only phase present [3]; the effect is apparent but less absolute for water/acetone. MD radial density profiles clearly confirm the preferred adsorption of the more polar liquid. At very low acetone concentration in the mixture with cyclohexane, we found evidence for a reduction of D of 1-2 orders of magnitude, suggesting that the acetone phase close to the surface falls beyond the percolation threshold and forms islands.

**Conclusion:** Interaction of polar molecules with the solid polar silica surface and its hydroxyl groups leads to concentration gradients in confined liquid mixtures, possibly up to semi-stable layering of certain combinations of fluids that are otherwise fully miscible. Q space microscopy in combination with relaxation studies reveals hints towards full demixing, although local molecular exchange on scales of nm still exists. Experiments are in agreement with MD simulations on short time scales below microseconds, whereas longer times are currently only accessible by PFG experiments.

**References:** [1] S. Stapf *et al.,* Magn. Reson. Lett. **3**, 108 (2023), [2] R. Kimmich *et al.*, Magn. Reson. Imaging 14, 793 (1996), [3] J. Ward-Williams *et al.*, Magn. Reson. Imaging 56, 57 (2019),