Magnetic Resonance Studies of Adsorption Phenomena

M.L. Johns[1], N. Robinson[1], K, Yang[1]
School of Engineering, University of Western Australia, Perth, WA, Australia

Fluid adsorption using porous media provides a critical underpinning process for numerous separation and reaction operations within Chemical Engineering. Here we will demonstrate the ability of NMR to provide unique, non-invasive insights into adsorption phenomena using the following case studies:

(1) The application of low-field (12.7 MHz) ^{1}H nuclear magnetic resonance (LF-NMR) relaxation measurements to non-invasively characterize ethane dynamics and adsorption within various mesoporous silica materials (exhibiting mean pore diameters between 6 and 50 nm) will be demonstrated [1]. Our measurements provide NMR-based adsorption isotherms within the pressure range 25-50 bar, which incorporates the ethane condensation point (40.7 bar at our experimental temperature of 23.6 °C). The quantitative nature of the acquired data is validated via a direct comparison of NMR-derived excess adsorption capacities with *ex situ* gravimetric ethane adsorption measurements, which are demonstrated to agree to within 0.2 mmol/g of the observed ethane capacity. NMR T_2 relaxation time distributions are further demonstrated as a means to decouple interparticle and mesopore dominated adsorption phenomena, with unexpectedly rapid NMR relaxation values associated with interparticle ethane gas, as confirmed via a direct comparison with NMR self-diffusion analysis.

(2) Quantification of methane content in shales is a critical parameter for estimation of their potential gas production capacity. Traditional gravimetric methods for estimation of this quantity are sensitive only to adsorbed methane and are difficult to apply either to intact shale rock cores or via field measurements. Here non-invasive low-field nuclear magnetic resonance (LF-NMR) is applied to quantify excess methane adsorption capacity in intact shale rock plugs at pressures up to 200 bar; validation is provided against destructive gravimetric methods performed on fragments from the same shale rock plugs [2]. The resultant NMR transverse relaxation time (T_2) distributions contain three distinct peaks (referred to as peaks P1 - P3) which are allocated to adsorbed methane in organic pores, methane constrained to inorganic pores and bulk methane located predominately in fractures respectively. The most accurate estimate of excess methane adsorption capacity is obtained via a combination of an overall system mass balance and the methane located in inorganic pores and fractures (peaks P2 and P3, respectively), where excellent agreement is produced with corresponding destructive gravimetric measurements for the various shale samples studied.

(3) The ability of low-field NMR multi-dimensional relaxometry to distinguish functional group-specific relaxation [3], as a consequence of molecular orientation and binding during adsorption, for a range of alcohols and acids in both mesoporous silica and various metal oxide porous media will be briefly elucidated. Potential applications in adsorption science of this measurement approach will be discussed.

References:

[1] Yang, K. et al. ChemPhysChem, 23(4), (2022). [2] Yang, K. et al. Jnl Natural Gas Sci. and Eng. 108(104847), (2022).
[3] Robinson, N. et al. Magnetic Resonance Letters 3(3), 248 (2023); Dong, S. et al. Langmuir, 40(31), 16160 (2024).